13 Product Improvement

13.1 INTRODUCTION

As already noted (Chapter 1), petroleum and its derivatives have been used for millennia, and it is perhaps the most important raw material consumed in modern society (Abraham, 1945; Forbes, 1958a,b, 1959; James and Thorpe, 1994). It provides not only raw materials for the ubiquitous plastics and other products, but also fuel for energy, industry, heating, and transportation. Thus, the use of petroleum and the development of related technology are not such a modern subject as we are inclined to believe. However, the petroleum industry is essentially a twentieth-century industry but to understand the evolution of the industry, it is essential to have a brief understanding of the first uses of petroleum.

From a chemical standpoint, petroleum is an extremely complex mixture of hydrocarbon compounds, usually with minor amounts of nitrogen-, oxygen-, and sulfur-containing compounds as well as trace amounts of metal-containing compounds (Chapters 2 and 3; Speight, 2001, 2015). In addition, the properties of refinery feedstocks vary widely (Chapters 1, 3, and 4) and, thus, petroleum is not used in its raw state. A variety of processing steps are required to convert petroleum from its raw state to products that are usable in modern society.

The fuel products that are derived from petroleum supply more than half of the world’s total supply of energy. Gasoline, kerosene, and diesel oil provide fuel for automobiles, tractors, trucks, aircraft, and ships. Fuel oil and natural gas are used to heat homes and commercial buildings, as well as to generate electricity. Petroleum products are the basic materials used for the manufacture of synthetic fibers for clothing and in plastics, paints, fertilizers, insecticides, soaps, and synthetic rubber. The uses of petroleum as a source of raw material in manufacturing are central to the functioning of modern industry.

For the purposes of terminology, it is preferable to subdivide petroleum and related materials into three major classes (Chapter 1): (1) materials that are of a natural origin, (2) materials that are manufactured, and (3) materials that are integral fractions derived from natural or manufactured products. The materials included in categories 1 and 2 are relevant here because of their participation in product streams. Straight-run constituents of petroleum (i.e., constituents distilled without change from petroleum) (Chapter 7) are used in products. Manufactured materials are produced by a variety of processes (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2011, 2014) and are also used in product streams. Category 3 materials are usually those materials that are isolated from petroleum or from a product by the use of a variety of techniques (Chapter 3) and are not included here.

The production of liquid product streams by distillation (Chapter 7) or by thermal cracking processes (Chapter 8) or by catalytic cracking processes (Chapter 9) is only the first of a series of steps that leads to the production of marketable liquid products. Several other unit processes are involved in the production of a final product. Such processes may be generally termed secondary processes or product improvement processes since they are not used directly on the crude petroleum but are used on primary product streams that have been produced from the crude petroleum (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2011, 2014).

In addition, the term “product improvement” as used in this chapter includes processes such as reforming processes in which the molecular structure of the feedstock is reorganized. An example is the conversion (reforming, molecular rearrangement) of n-hexane to cyclohexane or cyclohexane to benzene. These processes reform or rearrange one particular molecular type to another thereby
changing the properties of the product relative to the feedstock. Such processes are conducive to expansion of the utility of petroleum products and to sales.

It is, therefore, the purpose of this chapter to present the concepts behind these secondary processes with specific examples of the processes that have reached commercialization. It must be understood that the process examples presented here are only a selection of the total number available. The choice of a process for inclusion here was made to illustrate the different process types that are available.

13.2 REFORMING

When the demand for higher-octane gasoline developed during the 1930s, attention was directed to ways and means of improving the octane number of fractions within the boiling range of gasoline. Straight-run gasoline, for example, frequently had a low octane number, and any process that would improve the octane number would aid in meeting the demand for higher-quality (higher-octane-number) gasoline. Such a process, called thermal reforming, was developed and used widely but to a much lesser extent than thermal cracking.

Upgrading by reforming is essentially a treatment to improve a gasoline octane number and may be accomplished in part by an increase in the volatility (reduction in molecular size) or chiefly by the conversion of \( n \)-paraffins to \( iso \)-paraffins, olefins, and aromatics and the conversion of naphthenes to aromatics (Table 13.1). The nature of the final product is of course influenced by the source (and composition) of the feedstock. In thermal reforming, the reactions resemble the reactions that occur during gas oil cracking: that is, molecular size is reduced, and olefins and some aromatics are produced.

Gasoline has many specifications that must be satisfied before it can be sold on the market. The most widely recognized gasoline specification is the octane number, which refers to the percentage by volume of \( iso \)-octane in a mixture of \( iso \)-octane and heptane in a reference fuel that, when tested in a laboratory engine, matches the antiknock quality, as measured for the fuel being tested under the same conditions. The octane number posted at the gasoline pump is actually the average of the research octane number (RON) and motor octane number (MON), commonly referred to as \((\text{R} + \text{M})/2\). RON and MON are two different test methods that quantify the antiknock qualities of

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>RON</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )-Hexane</td>
<td>( \text{CH}_3(\text{CH}_2)_4\text{CH}_3 )</td>
<td>25</td>
</tr>
<tr>
<td>( 1 )-Hexane</td>
<td>( \text{CH}_2-\text{CH}(\text{CH}_2)_3\text{CH}_3 )</td>
<td>76</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>( \text{C}<em>8\text{H}</em>{12} )</td>
<td>83</td>
</tr>
<tr>
<td>Benzene</td>
<td>( \text{C}_6\text{H}_6 )</td>
<td>123</td>
</tr>
<tr>
<td>2,2,4-Trimethylpentane</td>
<td>( \text{CH}_3 \text{CH}_3 )</td>
<td>100</td>
</tr>
<tr>
<td>(Isooctane)</td>
<td>( \text{CH}_3 \text{CH}_3 )</td>
<td>105</td>
</tr>
<tr>
<td>( 2,4,4 )-Trimethyl-1-pentene (Isooctene)</td>
<td>( \text{CH}_3 \text{CH}_3 )</td>
<td>72</td>
</tr>
<tr>
<td>( 1,3 )-dimethyl-cyclohexane</td>
<td>( \text{C}<em>8\text{H}</em>{16} )</td>
<td>118</td>
</tr>
<tr>
<td>1,3-Dimethylbenzene</td>
<td>( \text{C}<em>8\text{H}</em>{16} )</td>
<td>118</td>
</tr>
</tbody>
</table>
Product Improvement

TABLE 13.2  
Oxygenates Allowed in Gasoline

<table>
<thead>
<tr>
<th>Oxygenate</th>
<th>Maximum (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>5</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>10</td>
</tr>
<tr>
<td>Isobutyl alcohol</td>
<td>10</td>
</tr>
<tr>
<td>tert-Butyl alcohol</td>
<td>7</td>
</tr>
<tr>
<td>Ether (five or more C atoms)</td>
<td>15</td>
</tr>
<tr>
<td>Other oxygenates</td>
<td>10</td>
</tr>
</tbody>
</table>

Unfortunately, the desulfurized light and heavy naphtha fractions of crude oils have very low octane numbers. The heavy naphtha fraction is approximately \( \frac{50(R + M)}{2} \). Reforming is the refinery process that reforms the molecular structure of the heavy naphtha to increase the percentage of high-octane components while reducing the percentage of low-octane components.

When lead was phased out of gasoline, the only way to produce high-octane-number gasolines is to use inherently high-octane hydrocarbons or to use alcohols (often referred to as oxygenates) (Table 13.2). The ether derivatives are also high-octane oxygenates (Table 13.3) and have been used widely as additives. The ethers may be produced at the refinery by reacting suitable alcohols such as methanol and ethanol with branched olefins from the fluid catalytic cracker, such as iso-butene and iso-pentene, under the influence of acid catalysts. In the mid-1990s methyl-\( t \)-butyl ether (MTBE) (Table 13.3), made by etherification of iso-butene with methanol, became the predominant oxygenate used to meet reformulation requirements for adding oxygen to mitigate emissions from gasoline-powered vehicles.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Structure</th>
<th>Oxygen Content Mass (%)</th>
<th>Blending Research Octane Number (BRON)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol (EtOH)</td>
<td>( \text{C}_2\text{H}_5\text{O} )</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} )</td>
<td>34.73</td>
<td>129</td>
</tr>
<tr>
<td>Methyl tertiary-butyl ether (MTBE)</td>
<td>( \text{C}<em>4\text{H}</em>{10}\text{O} )</td>
<td>( \text{CH}_3 \text{O CH}_3 )</td>
<td>18.15</td>
<td>118</td>
</tr>
<tr>
<td>Ethyl tertiary-butyl ether (ETBE)</td>
<td>( \text{C}<em>6\text{H}</em>{14}\text{O} )</td>
<td>( \text{CH}_3 \text{O C CH}_3 )</td>
<td>15.66</td>
<td>119</td>
</tr>
<tr>
<td>Tertiary-amyl methyl ether (TAME)</td>
<td>( \text{C}<em>7\text{H}</em>{18}\text{O} )</td>
<td>( \text{CH}_3 \text{O C CH}_2\text{CH}_3 )</td>
<td>15.66</td>
<td>112</td>
</tr>
</tbody>
</table>
Environmental issues with methyl-\(t\)-butyl ether have made it more desirable to dimerize isobutane from the catalytic cracking unit rather than etherify it. Fortunately, isobutene dimerization may be achieved with minimal modifications to existing methyl-\(t\)-butyl ether plants and process conditions, using the same acidic catalysts. Where olefin levels are not restricted, the extra blending octane boost of the diisobutylene can be retained. Where olefin levels are restricted, the diisobutylene can be hydrotreated to produce a relatively pure isooctane stream that can supplement alkylate for reducing olefins and aromatics in reformulated gasoline.

13.2.1 **THERMAL REFORMING**

Thermal reforming was a natural development from thermal cracking, since reforming is also a thermal decomposition reaction. Cracking converts heavier oils into gasoline; reforming converts (reforms) gasoline into higher-octane gasoline. The equipment for thermal reforming is essentially the same as for thermal cracking, but higher temperatures are used.

When carrying out thermal reforming, a feedstock, such as a 205°C (400°F) end point naphtha or a straight-run gasoline, is heated to 510°C–595°C (950°F–1100°F) in a furnace much the same as a cracking furnace, with pressures from 400 to 1000 psi. As the heated naphtha leaves the furnace, it is cooled or quenched by the addition of cold naphtha. The quenched, reformed 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 number of the product (reformate) is due primarily to the cracking of longer chain paraffins into higher-octane olefins.

Thermal reforming is in general less effective than catalytic processes and has been largely supplanted. As it was practiced, a single-pass operation was employed at temperatures in the range of 540°C–760°C (1000°F–1400°F) and pressures in the range of 500–1000 psi. Octane number improvement depended on the extent of conversion but was not directly proportional to the extent of cracking per pass.

The amount and quality of reformate is dependent on the temperature. A general rule is the higher the reforming temperature, the higher the octane number of the product, but the yield of reformate is relatively low. For example, a gasoline with an octane number of 35 when reformed at 515°C (950°F) yields 92.4% of 56 octane reformate; when reformed at 555°C (1030°F), the yield is 68.7% of 83 octane reformate (Figure 13.1). However, high conversion is not always effective since coke production and gas production usually increase.

Modifications of the thermal reforming process due to the inclusion of hydrocarbon gases with the feedstock are known as gas reversion and polyforming. Thus, olefinic gases produced by

**FIGURE 13.1** Octane number and reformate yield.
cracking and reforming can be converted into liquids boiling in the gasoline range by heating them under high pressure. Since the resulting liquids (polymers) have high octane numbers, they increase the overall quantity and quality of gasoline produced in a refinery.

The gases most susceptible to conversion to liquid products are olefins with three and four carbon atoms. These are propylene (CH$_2$CH=CH$_2$), which is associated with propane in the C$_3$ fraction, and butylene (CH$_2$CH$_2$CH=CH$_2$) and/or CH$_3$CH=CHCH$_3$ and iso-butylene [(CH$_3$)$_2$C=CH$_2$], which are associated with butane (CH$_3$CH$_2$CH$_2$CH$_3$) and iso-butane [(CH$_3$)$_2$CHCH$_3$] in the C$_4$ fraction. When the C$_3$ and C$_4$ fractions are subjected to the temperature and pressure conditions used in thermal reforming, they undergo chemical reactions that result in a small yield of gasoline. When the C$_3$ and C$_4$ fractions are passed through a thermal reformer in admixture with naphtha, the process is called naphtha-gas reversion or naphtha polyforming.

These processes are essentially the same but differ in the manner in which the gases and naphtha are passed through the heating furnace. In gas reversion, the naphtha and gases flow through separate lines in the furnace and are heated independently of one another. Before leaving the furnace, both lines join to form a common soaking section where the reforming, polymerization, and other reactions take place. In naphtha reforming, the C$_3$ and C$_4$ gases are premixed with the naphtha and pass together through the furnace. Except for the gaseous components in the feedstock, both processes operate in much the same manner as thermal reforming and produce similar products.

13.2.2 Catalytic Reforming

Like thermal reforming, catalytic reforming converts low-octane gasoline into high-octane gasoline (reformate). Although thermal reforming can produce reformate with an research octane number in the range of 65–80 depending on the yield, catalytic reforming produces reformate with octane numbers of the order of 90–95. Catalytic reforming is conducted in the presence of hydrogen over hydrogenation–dehydrogenation catalysts, which may be supported on alumina or silica–alumina. Depending on the catalyst, a definite sequence of reactions takes place, involving structural changes in the charge stock. The catalytic reforming process was commercially nonexistent in the United States before 1940. The process is really a process of the 1950s and showed phenomenal growth in the 1953–1959 time period (Riediger, 1971). As a result, thermal reforming is now somewhat obsolete.

Catalytic reformer feeds are saturated (i.e., not olefinic) materials; in the majority of cases the feed may be a straight-run naphtha, but other by-product low-octane naphtha (e.g., coker naphtha) can be processed after treatment to remove olefins and other contaminants. Hydrocarbon naphtha that contains substantial quantities of naphthenes is also a suitable feed. The process uses a precious metal catalyst (platinum supported by an alumina base) in conjunction with very high temperatures to reform the paraffin and naphthenic constituents into high-octane components. Sulfur is a poison to the reforming catalyst, which requires that virtually all the sulfur must be removed from the heavy naphtha through hydrotreating prior to reforming. Several different types of chemical reactions occur in the reforming reactors: paraffins are isomerized to branched chains and to a lesser extent to naphthenes, and naphthenes are converted to aromatics. Overall, the reforming reactions are endothermic. The resulting product stream (reformate) from catalytic reforming has an RON from 96 to 102 depending on the reactor severity and feedstock quality. The dehydrogenation reactions which convert the saturated naphthenes into unsaturated aromatics produce hydrogen, which is available for distribution to other refinery hydroprocesses.

The catalytic reforming process consists of a series of several reactors (Figure 13.2), which operate at temperatures of approximately 480°C (900°F). The hydrocarbons are reheated by direct-fired furnaces in between the subsequent reforming reactors. As a result of the very high temperatures, the catalyst becomes deactivated by the formation of coke (i.e., essentially pure carbon) on the catalyst, which reduces the surface area available to contact with the hydrocarbons.

Catalytic reforming is usually carried out by feeding a naphtha (after pretreating with hydrogen if necessary) and hydrogen mixture to a furnace where the mixture is heated to the desired
temperatures 450°C–520°C (840°F–965°F) and then passed through fixed-bed catalytic reactors at hydrogen pressures of 100–1000 psi. Normally two (or more than one) reactors are used in series, and reheaters are located between adjoining reactors to compensate for the endothermic reactions taking place. Sometimes as many as four or five are kept onstream in series while one or more is being regenerated. The onstream cycle of any one reactor may vary from several hours to many days, depending on the feedstock and reaction conditions.

The product issuing from the last catalytic reactor is cooled and sent to a high-pressure separator where the hydrogen-rich gas (Table 13.4) is split into two streams: one stream goes to recycle, and the remaining portion represents excess hydrogen available for other uses. The excess hydrogen is vented from the unit and used in hydrotreating, as a fuel, or for manufacture of chemicals (e.g., ammonia). The liquid product (reformate) is stabilized (by removal of light ends) and used directly in gasoline or extracted for aromatic blending stocks for aviation gasoline.

The commercial processes available for use can be broadly classified as the moving-bed, fluid-bed, and fixed-bed types. The fluid-bed and moving-bed processes use mixed nonprecious

---

**TABLE 13.4**

Composition of Catalytic Reformer Product Gas

<table>
<thead>
<tr>
<th>Constituent</th>
<th>% by Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>75–85</td>
</tr>
<tr>
<td>Methane</td>
<td>5–10</td>
</tr>
<tr>
<td>Ethane</td>
<td>5–10</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0</td>
</tr>
<tr>
<td>Propane</td>
<td>5–10</td>
</tr>
<tr>
<td>Propylene</td>
<td>0</td>
</tr>
<tr>
<td>Butane</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Butylenes</td>
<td>0</td>
</tr>
<tr>
<td>Pentane plus</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>
metal oxide catalysts in units equipped with separate regeneration facilities. Fixed-bed processes use predominantly platinum-containing catalysts in units equipped for cycle, occasional, or no regeneration.

There are several types of catalytic reforming process configurations that differ in the manner that they accommodate the regeneration of the reforming catalyst. Catalyst regeneration involves burning off the coke with oxygen. The semiregenerative process is the simplest configuration but does require that the unit be shut down for catalyst regeneration in which all reactors (typically four) are regenerated. The cyclic configuration utilizes an additional swing reactor that enables one reactor at a time to be taken offline for regeneration while the other four remain in service. The continuous catalyst regeneration (CCR) configuration is the most complex configuration and enables the catalyst to be continuously removed for regeneration and replaced after regeneration. The benefits to the more complex configurations are that operating severity may be increased as a result of higher catalyst activity but this does come at an increased capital cost for the process.

Although subsequent olefin reactions occur in thermal reforming, the product contains appreciable amounts of unstable unsaturated compounds. In the presence of catalysts and of hydrogen (available from dehydrogenation reactions), hydrocracking of paraffins to yield two lower paraffins occurs. Olefins that do not undergo dehydrocyclization are also produced. The olefins are hydrogenated with or without isomerization, so that the end product contains only traces of olefins.

The addition of a hydrogenation–dehydrogenation catalyst to the system yields a dual-function catalyst complex. Hydrogen reactions—hydrogenation, dehydrogenation, dehydrocyclization, and hydrocracking—take place on the acid catalyst sites.

Under the high-hydrogen partial pressure conditions used in catalytic reforming, sulfur compounds are readily converted into hydrogen sulfide, which, unless removed, builds up to a high concentration in the recycle gas. Hydrogen sulfide is a reversible poison for platinum and causes a decrease in the catalyst dehydrogenation and dehydrocyclization activities. In the first catalytic reformers the hydrogen sulfide was removed from the gas cycle stream by absorption in, for example, diethanolamine. Sulfur is generally removed from the feedstock by use of a conventional desulfurization over cobalt–molybdenum catalyst. An additional benefit of desulfurization of the feed to a level of <5 ppm sulfur is the elimination of hydrogen sulfide (H₂S) corrosion problems in the heaters and reactors.

Organic nitrogen compounds are converted into ammonia under reforming conditions, and this neutralizes acid sites on the catalyst and thus represses the activity for isomerization, hydrocracking, and dehydrocyclization reactions. Straight-run materials do not usually present serious problems with regard to nitrogen, but feeds such as coker naphtha may contain around 50 ppm nitrogen and removal of this quantity may require high-pressure hydrogenation (800–1000 psi) over nickel–cobalt–molybdenum on an alumina catalyst.

The yield of naphtha of a given octane number and at given operating conditions depends on the hydrocarbon types in the feed. For example, high-naphthene stocks, which readily give aromatic gasoline, are the easiest to reform and give the highest gasoline yields. Paraffinic stocks, however, that depend on the more difficult isomerization, dehydrocyclization, and hydrocracking reactions, require more severe conditions and give lower gasoline yields than the naphthenic stocks. The end point of the feed is usually limited to approximately 190°C (375°F), partially because of increased coke deposition on the catalyst as the end point during processing at approximately 15°C (27°F). Limiting the feed end point avoids redistillation of the product to meet the gasoline end point specification of 205°C (400°F), maximum.

In a semiregenerative unit, desulfurized naphtha is mixed with hydrogen, heated to temperatures in excess of 480°C (>900°F) and passed through a series of fixed-bed reactors. The major chemical reactions—dehydrogenation and dehydrocyclization—are endothermic and the reactors are operated under adiabatic conditions insofar as heat cannot enter or leave except by the cooling or heating of reaction fluids. Consequently, the temperature drops as reactants flow through
a reactor. Between reactors, fired heaters bring the process fluids back to desired reactor inlet temperatures.

Because of the dehydrogenation–dehydrocyclization reactions, hydrogen is generated in the reformer and is produced in substantial (but not in sufficient) quantities. The hydrogen is recycled through the reactors where the reforming takes place to provide the atmosphere necessary for the chemical reactions and also prevents the carbon from being deposited on the catalyst, thus extending its operating life. An excess of hydrogen above whatever is consumed in the process is produced, and as a result, catalytic reforming processes are unique in that they are the only petroleum refinery processes to produce hydrogen as a by-product.

13.2.2.1 Fixed-Bed Processes

Fixed-bed, continuous catalytic reforming can be classified by catalyst type: (1) cyclical regenerative with nonprecious metal oxide catalysts and (2) cyclic regenerative with platinum–alumina catalysts. Both types use swing reactors to regenerate a portion of the catalyst while the remainder stays onstream.

The cyclic-regenerative fixed-bed operation using a platinum catalyst is basically a low-pressure process (250–350 psi), which gives higher gasoline yields because of fewer hydrocracking reactions, as well as higher-octane products from a given naphtha charge and better hydrogen yields because of more dehydrogenation and fewer hydrocracking reactions. The coke yield, with attendant catalyst deactivation, increases rapidly at low pressures.

13.2.2.1.1 Hydroforming

The hydroforming process made use of molybdena–alumina (MoO$_2$–Al$_2$O$_3$) catalyst pellets arranged in fixed beds; hence, the process is known as fixed-bed hydroforming. The hydroformer had four reaction vessels or catalyst cases, two of which were regenerated; the other two were on the process cycle. Naphtha feed is preheated to 400°C–540°C (900°F–1000°F) and passed in series through the two catalyst cases under a pressure of 150–300 psi. Gas containing 70% hydrogen produced by the process was passed through the catalyst cases with the naphtha. The material leaving the final catalyst case entered a four-tower system where fractional distillation separated hydrogen-rich gas, a product (reformate) suitable for motor gasoline and an aromatic polymer boiling above 205°C (400°F).

After 4–16 hours on process cycle, the catalyst was regenerated. This was done by burning carbon deposits from the catalyst at a temperature of 565°C (1050°F) by blowing air diluted with flue gas through the catalyst. The air also reoxidized the reduced catalyst (9% molybdenum oxide on activated alumina pellets) and removed sulfur from the catalyst.

13.2.2.1.2 Iso-Plus Houdriforming

This is a combination process using a conventional Houdriformer operated at moderate severity for product production (Table 13.5), in conjunction with one of three possible alternatives: (1) conventional catalytic reforming plus aromatic extraction and separate catalytic reforming of the aromatic raffinate, (2) conventional catalytic reforming plus aromatic extraction and recycling of the aromatic raffinate aligned to the reforming state, and (3) conventional catalytic reforming followed by thermal reforming of the Houdriformer product and catalytic polymerization of the C$_3$ and C$_4$ olefins from thermal reforming.

A typical feedstock for this type of unit is naphtha, and the use of a Houdry guard bed permits charging stocks of relatively high sulfur content.

13.2.2.1.3 Platforming

The first step in the Platforming process (Figure 13.3) is preparation of the naphtha feed. For motor gasoline manufacture, the naphtha feed is distilled to separate a fraction boiling in the 120°C–205°C (250°F–400°F) range. Since sulfur adversely affects the platinum catalyst, the naphtha fraction may
be treated to remove sulfur compounds. Otherwise, the hydrogen-rich gas produced by the process, which is cycled through the catalyst cases, must be scrubbed free of its hydrogen sulfide content.

The prepared naphtha feed is heated to 455°C–540°C (850°F–1000°F) and passed into a series of three catalyst cases under a pressure of 200–1000 psi. Further heat is added to the naphtha between each of the catalyst cases in the series. The material from the final catalyst case is fractionated into a hydrogen-rich gas stream and a reformate stream (Table 13.6). The catalyst is composed of 1/8-inch

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### TABLE 13.5
**Feedstock and Product Data for the Houdriforming Process**

<table>
<thead>
<tr>
<th>Feedstock</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>52.6</td>
</tr>
<tr>
<td>Boiling range</td>
<td></td>
</tr>
<tr>
<td>°C</td>
<td>92–192</td>
</tr>
<tr>
<td>°F</td>
<td>197–377</td>
</tr>
<tr>
<td>Composition (% v/v)</td>
<td></td>
</tr>
<tr>
<td>Paraffins</td>
<td>53</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>38</td>
</tr>
<tr>
<td>Aromatics</td>
<td>9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Product</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Research octane number</td>
<td>100</td>
</tr>
<tr>
<td>Composition (% v/v)</td>
<td></td>
</tr>
<tr>
<td>Paraffins</td>
<td>21</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>2</td>
</tr>
<tr>
<td>Aromatics</td>
<td>77</td>
</tr>
</tbody>
</table>

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![FIGURE 13.3 The Platforming process.](image-url)
pellets of alumina containing chlorine and approximately 0.5% platinum. Each pound of catalyst reforms up to 100 bbl of naphtha before losing its activity. It is possible to regenerate the catalyst, but it is more usual to replace the spent catalyst with new catalyst.

Other fixed-bed processes include Catforming, in which the catalyst is platinum (Pt), alumina (Al₂O₃), and silica-alumina (SiO₂–Al₂O₃) composition, which permits relatively high space velocities and results in very high hydrogen purity. Regeneration to prolong catalyst life is practiced on a block-out basis with a dilute air in-stream mixture. In addition, Houdriforming is a process in which the catalyst may be regenerated, if necessary, on a block-out basis. A guard bed catalytic hydrogenation pretreating stage using the same Houdry catalyst as the Houdriformer reactors is available for high-sulfur feedstocks. Lead and copper salts are also removed under mild conditions of the guard bed operation.

13.2.2.1.4 Powerforming

The cyclic powerforming process is based on frequent regeneration (carbon burn-off) and permits continuous operation. Reforming takes place in several (usually four or five) reactors and regeneration is carried out in the last (or swing) reactor. Thus, the plant need not be shut down to regenerate a catalyst reactor. The cyclic process assures a continuous supply of hydrogen gas for hydrorefining operations and tends to produce a greater yield of higher-octane reformate (Table 13.7). The choice between the semiregenerative process and the cyclic process depends on the size of plant required, the types of feedstocks available, and the octane number needed in the product.

13.2.2.1.5 Rexforming

Rexforming is a combination process using Platforming and aromatic extraction processes in which low-octane raffinate is recycled to the platformer. Operating temperatures may be as much as 27°C (50°F) lower than conventional Platforming, and higher space velocities are used. A balance is struck between hydrocyclization and hydrocracking, excessive coke and gas formation thus being
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13.2.2.1.6 Selectoforming

The selectoforming process uses a fixed-bed reactor operating under a hydrogen partial pressure. Typical operating conditions depend on the process configuration but are in the ranges of 200–600 psi and 315°C–450°C (600°F–900°F). The catalyst used in the selectoforming process is nonnoble metal with low potassium content. As with the large-pore hydrocracking catalysts, the cracking activity increases with decreasing alkali metal content.

There are two configurations of the selectoforming process that are being used commercially. The first selectoformer was designed as a separate system and integrated with the reformer only to the extent of having a common hydrogen system. The reformer naphtha is mixed with hydrogen and passed into the reactor containing the shape-selective catalyst. The reactor effluent is cooled and separated into hydrogen, liquid petroleum, gas, and high-octane gasoline. The removal of n-paraffins reduces the vapor pressure of the reformate since these paraffins are in higher concentration in the front end of the feed. The separate selectoforming system has the additional flexibility of being able to process other refinery streams.

The second process modification is the terminal reactor system. In this system, the shape-selective catalysts replace all or part of the reforming catalyst in the last reforming reactor. Although this configuration is more flexible, the high reforming operating temperature causes butane and propane cracking and consequently decreases the liquid petroleum gas yield and generates higher ethane and methane production. The life of a selectoforming catalyst used in a terminal system is between 2 and 3 years, and regeneration only partially restores fresh catalytic activity.

13.2.2.2 Moving-Bed Processes

13.2.2.2.1 Hyperforming

Hyperforming is a moving-bed reforming process that uses catalyst pellets of cobalt molybdate with a silica-stabilized alumina base. In operation, the catalyst moves downward through the reactor by gravity flow and is returned to the top by means of a solids-conveying technique (hyperflow), which moves the catalyst at low velocities and with minimum attrition loss. Feedstock (naphtha vapor) and

<table>
<thead>
<tr>
<th>TABLE 13.7 Feedstock and Product Data for the Powerforming Process</th>
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<td>Feedstock</td>
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<td>Process operation</td>
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<td>Research octane number</td>
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<tr>
<td>Composition (% v/v)</td>
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<tr>
<td>C1–C4 13 11</td>
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<tr>
<td>C5+ 79 79</td>
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<tr>
<td>Hydrogen (% w/w)</td>
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</tbody>
</table>

avoided. The glycol solvent in the aromatic extraction section is designed to extract low-boiling high-octane iso-paraffins as well as aromatics.
recycle gas flow upward, countercurrent to the catalyst, and regeneration of catalyst is accomplished in either an external vertical lift line or a separate vessel.

Hyperforming naphtha (65°C–230°C, 150°F–450°F) can result in improvement of the motor fuel component; in addition, sulfur and nitrogen removal is accomplished. Light gas oil stocks can also be charged to remove sulfur and nitrogen under mild hydrogenation conditions for the production of premium diesel fuels and middle distillates. Operating conditions in the reactor are 400 psi and 425°C–480°C (800°F–900°F), the higher temperature being employed for a straight-run naphtha feedstock; catalyst regeneration takes place at 510°C (950°F) and 415 psi.

13.2.2.2 Thermofor Catalytic Reforming
The Thermofor catalytic reforming (TCR) process is also a moving-bed process that uses a synthetic bead coprecipitated chromia (CrO₂) and alumina (Al₂O₃) catalyst (Figure 13.4). Catalyst–naphtha ratios have little effect on product yield or quality when varied over a wide range. The catalyst flow downward through the reactor and the naphtha-recycle gas feed enters the center of the reactor. The catalyst is transported from the base of the reactor to the top of the regenerator by bucket-type elevators.

13.2.3 Fluid-Bed Processes
In catalytic reforming processes using a fluidized solids catalyst bed continuous regeneration with a separate or integrated reactor is practiced to maintain catalyst activity by coke and sulfur removal. Cracked or virgin naphtha is charged with hydrogen-rich recycle gas to the reactor. A molybdena (Mo₂O₃, 10.0%) on alumina catalyst, not materially affected by normal amounts of arsenic, iron, nitrogen, or sulfur, is used. Operating conditions in the reactor are approximately 200–300 psi and 480°C–950°C (900°F–950°F).

Fluidized-bed operation with its attendant excellent temperature control prevents over- and under-reforming operations, resulting in more selectivity in the conditions needed for optimum yield of the desired product.

FIGURE 13.4 Thermofor catalytic reforming process.
13.3 ISOMERIZATION

Catalytic reforming processes provide high-octane constituents in the heavier gasoline fraction, but the \( n \)-paraffin components of the lighter gasoline fraction, especially butane (\( C_4 \)) to hexane (\( C_6 \)), have poor octane ratings. The conversion of these \( n \)-paraffins to their isomers (isomerization) yields gasoline components of high octane rating in this lower boiling range. Conversion is obtained in the presence of a catalyst (aluminum chloride activated with hydrochloric acid), and it is essential to inhibit side reactions, such as cracking and olefin formation.

Various companies have developed and operated isomerization processes that increase the octane numbers of light naphtha from say, 70 or less to more than 80. In thermal catalytic alkylation ethylene or propylene is combined with iso-butane at 50°C–280°C (125°F–450°F) and 300–1000 psi in the presence of metal halide catalysts, such as aluminum chloride. Conditions are less stringent in catalytic alkylation; olefins (\( C_3 \), \( C_4 \), and \( C_5 \)) are combined with iso-butane in the presence of an acid catalyst (sulfuric or hydrofluoric) at low temperatures (1–40, 30°F–105°F) and pressures from atmospheric to 150 psi. In a typical process, naphtha is passed over an aluminum chloride catalyst at 120°C (250°F) and at a pressure of approximately 800 psi to produce the Isomerate (Figure 13.5).

Isomerization, another innovation specific to recent times, found initial commercial applications during World War II for making high-octane aviation gasoline components and additional feed for alkylation units. The lowered alkylate demands in the post–World War II period caused a shutdown of the majority of the butane isomerization units. In recent years, the greater demand for high-octane motor fuel has resulted in the installation of new butane isomerization units. The earliest important process was the formation of iso-butane, which is required as an alkylation feed; the isomerization may take place in the vapor phase, with the activated catalyst supported on a solid phase, or in the liquid phase with a dissolved catalyst. Thus, a pure butane feed is mixed with hydrogen (to inhibit olefin formation) and passed to the reactor at 110°C–170°C (230°F–340°F) and 200–300 psi. The product is cooled and the hydrogen separated; the cracked gases are then removed in a stabilizer column. The stabilizer bottom product is passed to a superfractionator, and the \( n \)-butane and iso-butane are separated. With pentanes, the equilibrium is favorable at higher temperatures, and operating conditions of 300–1000 psi and 240°C–500°C (465°F–930°F) may be used.

Present isomerization applications are to provide additional feedstock for alkylation units or high-octane fractions for blending to produce sales gasoline. Straight-chain paraffins (\( n \)-butane) (Figure 13.6) and mixtures of \( n \)-pentane and \( n \)-hexane (Figure 13.7) are converted to respective

![Figure 13.5 Isomerization using an aluminum chloride catalyst.](image-url)

iso-compounds by continuous catalytic (aluminum chloride and noble metals) processes. Natural gasoline or light straight-run gasoline can provide feed by first fractionating as a preparatory step. High volumetric yields (>95%) and 40%–60% conversion per pass are characteristic of the isomerization reaction.

Nonregenerable aluminum chloride catalyst is employed with various carriers in a fixed-bed or liquid contactor. Platinum or other metal catalyst processes utilize a fixed-bed operation and can be regenerable or nonregenerable. The reaction conditions vary widely depending on the particular process and feedstock, 40°C–480°C (100°F–900°F) and 150–1000 psi; residence time in the reactor is 10–40 minutes.

13.3.1 Butamer Process

The Butamer process is designed to convert n-butane to iso-butane under mild operating conditions (Figure 13.8). A platinum catalyst on a support is used in a fixed-bed reactor system. Using reformer off-gas can readily satisfy the low hydrogen requirement. The operation can be designed for once-through or recycle operation and is normally tied in with alkylation unit de-iso-butane operations to provide additional feed.

Butane feed is mixed with hydrogen, heated, and charged to the reactor at moderate pressure. The effluent is cooled before light gas separation and stabilization. The resultant butane mixture is then charged to a de-iso-butane to separate a recycle stream from the iso-butane product.

13.3.2 Butomerate Process

The Butomerate process is specially designed to isomerize n-butane to produce additional alkylation feedstock. The catalyst contains a small amount of nonnoble hydrogenation metal on a high-surface-area support. The process operates with hydrogen recycle to eliminate coke deposition on the catalyst, but the isomerization reaction can continue for extended periods in the absence of hydrogen.

FIGURE 13.8 Butamer process.
The feedstock should be dry and comparatively free of sulfur and water; the feed is heated, mixed with hydrogen, and conveyed to the reactor. Operating conditions range from 150°C to 260°C (300°F to 500°F) and 150 to 450 psi. The effluent is cooled and flashed, and the liquid product is stripped of light material.

13.3.3 **Hysomer Process**

The *Hysomer process* uses hydrotreated feedstocks containing pentane(s) and hexane(s) without further pretreatment. Operating conditions are 400–450 psi hydrogen and ca. 290°C (550°F); it appears that the catalyst (zeolite) life is approximately 2 years.

The influence of sulfur on catalyst activity is minimal, and the catalyst can tolerate a permanent sulfur level of 10 ppm in the feedstock, but concentrations up to 35 ppm are not harmful. The process can operate at a water level of 50 ppm, and feedstocks having saturated water contents can be processed without a deleterious effect on either catalyst stability or conversion. A minimum quantity of water is essential to the activity of zeolite catalysts in this application.

13.3.4 **Iso-Kel Process**

The *Iso-Kel process* is a fixed-bed, vapor-phase isomerization process that employs a precious metal catalyst and hydrogen. A wide variety of feedstocks, including natural gasoline, pentane, and/or hexane cuts, can be processed. Operating conditions include reactor temperatures and pressures from 345°C to 455°C (650°F to 550°F) and 350 to 600 psi.

13.3.5 **Isomate Process**

The *Isomate process* is a nonregenerative pentane and hexane or naphtha (C₆) isomerization process using an aluminum chloride–hydrocarbon complex catalyst with anhydrous hydrochloric acid as a promoter. Hydrogen partial pressure is maintained to suppress undesirable reactions (cracking and disproportionation) and retain catalyst activity. The feed is saturated with anhydrous hydrogen chloride in an absorber, then heated and combined with hydrogen and charged to the reactor (115°C, 240°F, and 700 psi). Catalyst is added to the reactor separately, and the reaction takes place in the liquid phase. The product is washed (caustic and water), acid stripped, and stabilized before going to storage.

13.3.6 **Isomerate Process**

The *Isomerate process* is a continuous isomerization process designed to convert pentanes and hexanes into highly branched isomers; a dual-function catalyst is used in a fixed-bed reactor system.

Operating conditions are mild, less than 750 psi and 400°C (750°F). Hydrogen is added to the feed along with recycle gas, and the usual operation includes fractionation facilities to allow the recycling of *n*-paraffins almost to extinction.

13.3.7 **Penex Process**

The *Penex process* is a nonregenerative pentane(s) and/or hexane(s) isomerization process. The reaction takes place in the presence of hydrogen with a platinum catalyst, and the reactor conditions are selected so that catalyst life is long and regeneration is not required. The reactor temperatures range from 260°C to 480°C (500°F to 900°F) and pressures from 300 to 1000 psi.

The *Penex process* may be applied to many feedstocks by varying the fractionating system. Mixed feeds may be split into pentane and hexane fractions and respective *iso*-fractions...
separated from each. The system can also be operated in conjunction with reforming of the naphtha (>C_7) fraction.

### 13.3.8 Pentafining Process

The *Pentafining process* is a regenerable pentane isomerization process using platinum catalyst on a silica–alumina support. A number of process combinations are possible. For example, with natural gasoline and hydrogen as starting materials, pentanes are removed from the feedstock and the pentane fraction is passed to a low-pressure reformer. The pentane stream is split, and the *n*-pentane fraction is combined with a recycle stream and makeup hydrogen, and charged to the reactor (approximately 300 to 500 psi and 425°C–480°C, 800°F–900°F) where isomerization occurs:

\[
\text{CH}_3\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow (\text{CH}_3)_2\text{CHCH}_2\text{CH}_3
\]

Hydrogen is removed from the effluent, which is degassed and fractionated to separate *n*-pentane and *iso*-pentane (95% purity) fractions. The catalyst is regenerated at 260°C–540°C (500°F–1000°F) using a steam–air mixture.

### 13.4 Hydroisomerization

Hydroisomerization involves catalytic isomerization of hydrocarbons in presence of hydrogen. This process is used for the production of isomers of various low-boiling and high-boiling hydrocarbons. Isomers of normal paraffinic hydrocarbons are found to be more reactive and have higher octane number than the original constituents (Giannetto et al., 1986; Guisnet et al., 1987).

In the traditional Platforming of naphtha, a substantial amount of benzene and higher aromatics are generated leading to high-octane-number reformate. Hydroisomerization processes convert normal paraffin hydrocarbons to isomers which are also high-octane constituents. In another application, hydroisomerization of higher-boiling normal paraffins is being exploited to dewax vacuum oils. This enables refiners to abolish traditional solvent dewaxing technique which is costly and less productive as compared to catalytic dewaxing method.

Typically, isomerization is carried out over aluminum chloride catalyst (in the absence of hydrogen) to convert butane to *iso*-butane, pentane to *iso*-pentane, and hexane to *iso*-hexane commercially. Since isomers have higher octane numbers than the normal or straight-chain hydrocarbons, the process is suitable for the production of gasoline components in refineries. The isomerization of butane to *iso*-butane is also important for the production of butyl rubber where *iso*-butane is alkylated with olefins like ethylene to produce the necessary monomer for polymerization into rubber. In the isomerization of normal hydrocarbons in straight-run naphtha or raffinate from reformate during extraction of benzene, toluene, and xylenes (BTX), using aluminum chloride as the catalyst, the research octane number is increased from approximately 65 to approximately 80.

Because of corrosive damage of the equipment, aluminum chloride process is often replaced by noble metal impregnated on alumina or alumina–silica catalysts. This process uses a higher temperature of operation and a hydrogen pressure sufficient to suppress coking on catalyst surface. Isomerization processes are also applicable for separation of *iso*-butene and 1-butene from steam-cracked naphtha in the olefin production plant by converting 1-butene to 2-butene followed by distillation.

Hydroisomerization of 1-butene to 2-butene is also valuable for petrochemicals production and for high-octane alkylated gasoline production. In the production of benzene-free gasoline, hydroisomerization process is used in the refineries. The C_5 and C_6 fractions are separated from the feed naphtha and isomerized to high-octane isomers and later blended with reformate to produce
benzene-free gasoline. Another important use of hydroisomerization process is to convert paraffinic wax into low pour point components. This process is, in fact, a low-cost process as compared to traditional solvent dewaxing method practiced in refineries.

Isomerization reactions are usually reversible reactions and attain equilibrium at lower temperature with highest concentration of isomer products. The role of catalyst in isomerization is, therefore, extremely important. The intensity of unwanted side reactions diminishes at lower temperatures as higher temperature favors unwanted cracking, hydrogenation, and polymerization reactions. For that reason, isomerizing catalysts must ensure the optimal rate of reactions at as low temperature as possible. To prevent coke deposition, isomerization is carried out at an elevated pressure in a hydrogen atmosphere. Industrial processes are carried out at a temperature of 400°C–480°C (750°F–895°F).

The mechanism of reaction involves generation of \( n \)-carbenium ion in the Lewis acid site as the initiation reaction which propagates to isomer of the carbenium ion and finally converts the \( n \)-hydrocarbon feed molecule to isomer. In the dual-site catalyst, the metal and the acid sites, \( n \rightarrow p \) molecule is dehydrogenated on the metal site, which after diffusing to the acid site initiates the \( n \)-carbenium ion formation. This is followed by isomerization to \( i \)-carbenium ion and propagation to \( i \)-olefin molecule which is then hydrogenated by metal site to \( i \)-paraffin molecule. Cracking reaction also takes place within the acid sites.

Metal sites are responsible for hydrogenation and dehydrogenation reaction, this is influenced by the presence of hydrogen and its partial pressure. Pretreatment of the feedstock is essential to avoid poisoning of the catalyst. Usually desulfurizing the feedstock is essential to reduce sulfur, nitrogen, oxygen, and metal constituents simultaneously and dehydrated to remove moisture.

### 13.5 ALKYLATION

Alkylation is the refinery process that provides an economically feasible outlet for several of the very light olefins produced from the catalytic cracking unit. Propylene, butylene, and pentylene (also known as amylene) products are available for alkylation. Propylene alkylation is the normal disposition for cat cracker product although some butylenes from a fluid catalytic cracking unit could be blended into gasoline. The high vapor pressure of butylenes prevents low-cost butane blending stock from being blended into gasoline, thereby carrying a very high opportunity cost for this option.

In the alkylation process, the propylene, butylene, and pentylene are combined with \( iso \)-butane in the catalyzed alkylation reaction to produce branched, saturated seven, eight, or nine carbon molecules, respectively. The product (alkylate) consists of \( iso \)-heptane, \( iso \)-octane, and \( iso \)-nonane and is a low vapor pressure (relative to the feedstocks), very high-octane gasoline blending stock. The high-octane value makes alkylate an excellent blending stock for premium grades of gasolines. Furthermore, since alkylate contains no olefins, no aromatics, and no sulfur, it is also an excellent blending stock for use in reformulated gasoline. The alkylation reaction is catalyzed by the presence of very strong acid, either sulfuric acid or hydrofluoric acid.

In the sulfuric acid-based alkylation process, the acid is continually cycled through the process; but as it cycles, it becomes diluted and contaminated from impurities in the hydrocarbon feeds. The alkylation reactors typically operate at temperatures of 2°C–21°C (35°F–70°F, maximum) to minimize polymerization of the olefins to form undesirable hydrocarbons for the sulfuric acid process. The concentration of the sulfuric acid catalyst is important to the efficiency of the alkylation reaction, when the concentration of the acid decreases to approximately 88%, a portion of the contaminated acid is withdrawn and replaced with fresh acid. The contaminated, dilute sulfuric acid is then regenerated to its original purity and concentration.

Hydrofluoric acid exists in a vapor state at ambient conditions and this dictates that extreme precaution is necessary to ensure that this toxic substance is contained inside the process equipment. The hydrofluoric acid process, which is less sensitive to polymerization at warmer temperatures,
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typically operates at reactor temperatures of 21°C–38°C (70°F–100°F). Iso-butane concentrations are maintained very high (i.e., at ratios of 4:1 or more above the reaction requirements) in the reactor vessels to ensure that all of the olefins are reacted. The reactor effluent is distilled to separate the propane, iso-butane, and alkylate boiling fractions. The propane is routed to propane product treating, the iso-butane is recycled back to the alkylation reactors, and the alkylate is routed to gasoline blending, or in some cases to additional solvent refinery processing.

The chemistry of the combination of olefins with paraffins to form higher iso-paraffins is simple:

\[(\text{CH}_3)_3\text{CH} + \text{CH}_2=\text{CH}_2 \rightarrow (\text{CH}_3)_3\text{CHCH}_2\text{CH}_3\]

Since olefins are reactive (hence unstable) and are responsible for exhaust pollutants, their conversion to high-octane iso-paraffins is desirable when possible. In refinery practice, only iso-butane is alkylated by reaction with iso- or n-butene and iso-octane is the product. Although alkylation is possible without catalysts, commercial processes use sulfuric acid or hydrogen fluoride as catalysts when the reactions can take place at low temperatures, minimizing undesirable side reactions, such as polymerization of olefins.

Alkylate is composed of a mixture of iso-paraffins that have octane numbers that vary with the olefins from which they were made. Butylenes produce the highest octane numbers, propylene the lowest, and pentylenes the intermediate. All alkylates, however, have high octane numbers (>87) and are particularly valuable because of these high octane numbers.

Alkylation developments in petroleum processing in the late 1930s and during World War II were directed toward production of high-octane blending stock for aviation gasoline. The sulfuric acid process was introduced in 1938, and hydrogen fluoride alkylation was introduced in 1942. Rapid commercialization took place during the war to supply military needs, but many of these plants were shut down at the end of the war.

In the mid-1950s aviation gasoline demand started to decline, and motor gasoline quality requirements rose sharply. Whenever practical, refiners shifted the use of alkylate to premium motor fuel. Alkylate end point was increased for this service, and total alkylate was often used without rerunning. To help improve the economics of the alkylation process and also the sensitivity of the premium gasoline pool, additional olefins were gradually added to alkylation feed. New plants were built to alkylate propylene and the butylenes (butanes) produced in the refinery rather than the butane–butylene stream formerly used. More recently, n-butane isomerization has been utilized to produce additional iso-butane for alkylation feed.

The alkylation reaction as practiced in petroleum refining is the union, through the agency of a catalyst, of an olefin (ethylene, CH2=CH2, propylene, CH3CH=CH2, butene also called butylene, CH2=CH2CH=CH2, and amylene, CH3CH2CH2CH=CH2) with iso-butane [(CH3)3CH] to yield high-octane branched-chain hydrocarbons in the gasoline boiling range. Olefin feedstock is derived from the gas make of a catalytic cracker; iso-butane is recovered from refinery gases or produced by catalytic butane isomerization.

Zeolite catalysts are also used for alkylation processes. For example, cumene (iso-propylbenzene) is produced by the alkylation of benzene by propylene. The cumene can then be used for the production of phenol and acetone by means of oxidation processes.

13.5.1 Sulfuric Acid Alkylation

This is a low-temperature process (Figure 13.9) employing concentrated sulfuric acid catalyst to react olefins with iso-butane to produce high-octane aviation or motor fuel blending stock. The olefin feed is split into equal streams and charged to the individual reaction zones of the cascade reactor. Iso-butane-rich recycle and refrigerant streams are introduced in the front of the reactor and pass through the reaction zones. The olefin is contacted with the iso-butane and acid in the reaction zones, which operate at 2°C–7°C (35°F–45°F) and 5–15 psi, after which vapors are withdrawn from
the top of the reactor, compressed, and condensed. Part of this stream is sent to a depropanizer to control propane concentration in the unit. Depropanizer bottoms and the remainder of the stream are combined and returned to the reactor. Spent acid is withdrawn from the bottom of the settling zone; hydrocarbons spill over a baffle into a special withdrawal section and are hot water washed with caustic addition for pH control before being successively depropanized, de-iso-butanized, and debutanized. Alkylate can then be taken directly to motor fuel blending or be rerun to produce aviation-grade blending stock.

13.5.2 Hydrogen Fluoride Alkylation

The hydrogen fluoride alkylation process (Figure 13.10) uses regenerable hydrofluoric acid as a catalyst to unite olefins with iso-butane to produce high-octane blending stock. The dried charge is intimately contacted in the reactor with acid at 20°C–140°C (70°F–100°F) and a high (15:1) iso-butane–olefin ratio. The mixture is separated in a settler and acid is returned to the reactor, but an acid side stream must be continuously regenerated to 88% purity by fractionation to remove acid-soluble oils. The hydrocarbon fraction from the settler is de-iso-butanized, and alkylate is run to storage.
13.6 POLYMERIZATION

Polymerization (more correctly, oligomerization) as practiced in the petroleum industry, is a process that can claim to be the earliest to employ catalysts on a commercial scale. Catalytic polymerization came into use in the 1930s and was one of the first catalytic processes to be used in the petroleum industry. In the usual industrial sense, polymerization is a process in which a substance of low molecular weight is transformed into one of the same composition but of higher molecular weight while maintaining the atomic arrangement present in the basic molecule. It has also been described as the successive addition of one molecule to another by means of a functional group, such as that present in an aliphatic olefin. In the petroleum industry, polymerization is the controlled process by which olefin gases are converted to liquid condensation products that may be suitable for gasoline (hence polymer gasoline, polymerate) or other liquid fuels.

The feedstock for the process (Figure 13.11) usually consists of propylene (propene, CH₃CH=CH₂) and butylenes (butenes, various isomers of C₄H₈) from cracking processes or might even be selective olefins for dimer, trimer, or tetramer production:

\[ n\text{CH}_2=\text{CH}_2\text{H–(CH}_2\text{CH}_2)_n\text{–H} \]

In this process, \( n \) is usually 2 (dimer), 3 (trimer), or 4 (tetramer); the molecular size of the product is limited to give products boiling in the gasoline range constituents. This is in contrast to polymerization that is carried out in the polymer industry where \( n \) may be on the order of several hundred. Thus, polymerization in the true sense of the word is usually prevented, and all attempts are made to terminate the reaction at the dimer or trimer (three monomers joined together) stage. The 4-carbon to 12-carbon compounds that are required as the constituents of liquid fuels are the prime products. However, in the petrochemical section of a refinery, polymerization, which results in the production of (for example) polyethylene, is allowed to proceed until the products having the required high molecular weight have been produced.

Polymerization may be accomplished thermally or in the presence of a catalyst at lower temperatures. Thermal polymerization is regarded 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 essentially of vapor-phase cracking of, say, propane and butane.

followed by prolonged periods at high temperature (510°C–590°C, 950°F–1100°F) for the reactions to proceed to near completion.

On the other hand, olefins can be conveniently polymerized by means of an acid catalyst. Thus, the treated olefin-rich feed stream is contacted with a catalyst (sulfuric acid, copper pyrophosphate, or phosphoric acid) at 150°C–220°C (300°F–425°F) and 150–1200 psi, depending on feedstock and product requirement. The reaction is exothermic, and the temperature is usually controlled by heat exchange. Stabilization and/or fractionation systems separate saturated and unreacted gases from the product. In both thermal and catalytic polymerization processes, the feedstock is usually pretreated to remove sulfur and nitrogen compounds.

13.6.1 Thermal Polymerization

Thermal polymerization converts butanes and lighter gases into liquid condensation products. Olefins are produced by thermal decomposition and polymerized by heat and pressure. Thus, liquid feed under a pressure of 1200–2000 psi is pumped to a furnace heated to 510°C–595°C (950°F–1100°F), from which the various streams are separated by fractionation.

Thermal polymerization is regarded 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 essentially of vapor-phase cracking of, say, propane and butane followed by prolonged periods at high temperature (510°C–595°C; 950°F–1100°F) for the reactions to proceed to near completion.

13.6.2 Solid Phosphoric Acid Polymerization

Olefins can be conveniently polymerized by means of an acid catalyst. Thus, the treated olefin-rich feed stream is contacted with a catalyst (sulfuric acid, copper pyrophosphate, or phosphoric acid) at 150°C–220°C (300°F–425°F) and 150–1200 psi, depending on the feedstock and the desired product(s). The reaction is exothermic, and temperature is usually controlled by heat exchange. Stabilization and/or fractionation systems separate saturated and unreacted gases from the product. In both thermal and catalytic polymerization processes, the feedstock is usually pretreated to remove sulfur and nitrogen compounds.

This process converts propylene and/or butylene to high-octane gasoline or petrochemical polymers. The catalyst, pelleted kieselguhr (diatomaceous earth) impregnated with phosphoric acid, is used in either a chamber or tubular reactor. The exothermic reaction temperature is controlled by using saturates (separated from the effluent as recycle to the feed) as a quench liquid between the catalyst chamber beds. Tubular reactors are temperature-controlled by water or oil circulation around the catalyst tubes.

Reaction temperatures and pressures are 175°C–225°C (350°F–435°F) and 400–1200 psi. Olefins and aromatics may be united by alkylation for special applications at 205°C–315°C (400°F–600°F) and 400–900 psi, and a rerun column is required in addition to the usual fractionating.

13.6.3 Bulk Acid Polymerization

This process is used to produce high-octane polymer gasoline from all types of light olefin feed—the olefin concentration can be as high as 95% v/v. Liquid phosphoric acid is used as the catalyst.

The olefin feed is washed (caustic and water) and then contacted thoroughly by liquid phosphoric acid in a small reactor. The effluent stream and the acid are separated in a settler, and acid is returned to the reactor through a cooler. Gasoline is first stabilized and washed with caustic before storage. The heat of reaction is removed by circulation through an exchanger before contact with the olefin feed, and catalyst activity is maintained by continuous addition of fresh acid and withdrawal of spent acid.
13.7 CATALYSTS

The various catalysts used in product improvement processes have already been mentioned in the context of a particular reaction or reactor. However, for convenience it is worth mentioning the salient facts about these catalysts under one particular heading.

13.7.1 Reforming Processes

The composition of a reforming catalyst is dictated by the composition of the reformer feedstock and the desired reformate. Reforming consists of two types of chemical reactions that are catalyzed by two different types of catalysts: (1) isomerization of straight-chain paraffins and isomerization (simultaneously with hydrogenation) of olefins to produce branched-chain paraffins and (2) dehydrogenation–hydrogenation of paraffins to produce aromatics and olefins to produce paraffins.

The composition of a reforming catalyst is dictated by the composition of the feedstock and the desired reformate. The catalysts used are principally molybdena–alumina (MoO$_2$–Al$_2$O$_3$), chromia–alumina (Cr$_2$O$_3$–Al$_2$O$_3$), or platinum (Pt) on a silica–alumina (SiO$_2$–Al$_2$O$_3$) or alumina (Al$_2$O$_3$) base. The nonplatinum catalysts are widely used in regenerative process for feeds containing, for example, sulfur, which poisons platinum catalysts, although pretreatment processes (e.g., hydodesulfurization) may permit platinum catalysts to be employed.

The purpose of platinum on the catalyst is to promote dehydrogenation and hydrogenation reactions, that is, the production of aromatics, participation in hydrocracking, and rapid hydrogenation of carbon-forming precursors. For the catalyst to have an activity for isomerization of both paraffins and naphthenes—the initial cracking step of hydrocracking—and to participate in paraffin dehydrocyclization, it must have an acid activity. The balance between these two activities is most important in a reforming catalyst.

In the production of aromatics from cyclic saturated materials (naphthenes), it is important that hydrocracking be minimized to avoid loss of the desired product. Thus, the catalytic activity must be moderated relative to the case of gasoline production from a paraffinic feed, where dehydrocyclization and hydrocracking play an important part.

The acid activity can be obtained by means of halogens (usually fluorine or chlorine up to approximately 1% w/w in catalyst) or silica incorporated in the alumina base. The platinum content of the catalyst is normally in the range of 0.3%–0.8% w/w. At higher levels there is some tendency to effect demethylation and naphthene ring opening, which is undesirable; at lower levels the catalysts tend to be less resistant to poisons.

Most processes have a means of regenerating the catalyst as needed. The time between regeneration, which varies with the process, the severity of the reforming reactions, and the impurities of the feedstock, ranges from every few hours to several months. Several processes use a nonregenerative catalyst that can be used for a year or more, after which it is returned to the catalyst manufacturer for reprocessing. The processes that have moving beds of catalysts utilize continuous regeneration of the catalyst in separate regenerators.

The processes using bauxite (Cycloversion) and clay (Isoforming) differ from other catalytic reforming processes in that hydrogen is not formed and hence none is recycled through the reactors. Since hydrogen is not concerned in the reforming reactions, there is no limit to the amount of olefin that may be present in the feedstock. The Cycloversion process is also used as a catalytic cracking process and as a desulfurization process. The Isoforming process causes only a moderate increase in octane number.

13.7.2 Isomerization Processes

Isomerization reactions are usually reversible reactions and attain equilibrium at lower temperature with highest concentration of isomeric products. The role of catalyst in isomerization is, therefore,
extremely important. The intensity of unwanted side reactions diminishes at lower temperatures as higher temperature favors unwanted cracking, hydrogenation, polymerization reactions. For that reason, isomerizing catalysts must ensure the optimal rate of reactions at as low temperature as possible. To prevent coke deposition, isomerization is carried out at an elevated pressure in a hydrogen atmosphere.

During World War II, 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 in the range of 370°C–480°C (700°F–900°F) and 300–750 psi; aluminum chloride plus hydrogen chloride is universally used for the low-temperature processes. However, aluminum chloride is volatile at commercial reaction temperatures and is somewhat soluble in hydrocarbons, and techniques must be employed to prevent its migration from the reactor. This catalyst is nonregenerable and is utilized in either a fixed-bed or liquid contactor.

Catalysts commonly used for modern isomerization process are (in addition to the aforementioned Friedel–Crafts catalyst, AlCl₃) tungsten sulfide, bifunctional catalysts, zeolite-containing catalysts with noble metals such as platinum (Pt) or palladium (Pd), and complex (bifunctional and zeolite-containing Friedel–Crafts catalysts).

In the presence of certain catalysts, such as aluminum chloride with promoters, isomerization of paraffins can be carried out at the room temperature. In fact, the isomerization of paraffinic hydrocarbons in the presence of aluminum chloride is accelerated substantially if the reaction mixture contains traces of olefins. Catalysts of this type are however strong acids and can cause the corrosion of the equipment, because of which they are not used widely in the industry. Other catalysts for isomerization processes (except for Friedel–Crafts-type catalysts) require higher temperature and higher pressure of hydrogen, which results in the formation of a significant amount of unwanted by-products.

The isomerization of olefins can proceed by the formation of iso-olefins or by double bond transfer. Isomerization of naphthene constituents occurs with the transformation into olefins or with a change in the number of carbon atoms in the cycle. There are many other types of isomerization reaction, for instance, isomerization of alkyl benzene hydrocarbons, including xylenes and the reactions occur by the common carbocation mechanism. The isomerization reaction takes place in the hydrogen atmosphere whose role is to suppress polymerization and cracking reactions which might deactivate the catalyst.

The isomerization reaction is a thermoneutral reaction and requires no heat supply to the reactors from outside and hence can be carried out in a single reactor.

13.7.3 Alkylation Processes

Sulfuric acid, hydrogen fluoride, and aluminum chloride are the only catalysts used commercially. Sulfuric acid is used with propylene and higher-boiling feeds, but not with ethylene, because it reacts to form ethyl hydrogen sulfate and a suitable catalyst contains a minimum of 85% titratable acidity. The acid is pumped through the reactor and forms an air emulsion with reactants; the emulsion is maintained at 50% acid. The rate of deactivation varies with the feed and iso-butane change rate. Butene feedstocks cause less acid consumption than propylene feeds.

Aluminum chloride is not widely used as an alkylation catalyst, but when employed hydrogen chloride is used as a promoter and water is injected to activate the catalyst. The form of catalyst is an aluminum chloride–hydrocarbon complex, and the aluminum chloride concentration is 63%–84%.

Hydrogen fluoride is used for alkylation of higher-boiling olefins. The advantage of hydrogen fluoride is that it is more readily separated and recovered from the resulting product. The usual concentration is 85%–92% titratable acid with approximately 1.5% v/v water.
13.7.4 POLYMERIZATION PROCESSES

Phosphates are the principal catalysts for polymerization; the commercially used catalysts are liquid phosphoric acid, phosphoric acid on diatomaceous earth, copper pyrophosphate pellets, and phosphoric acid film on quartz. The latter is the least active but the most used and easiest to regenerate simply by washing and recoating; the serious disadvantage is that residue must occasionally be burned off the support. The process using liquid phosphoric acid catalyst is far more responsive to attempts to raise production by increasing temperature than the other processes.

13.8 TREATING PROCESSES

Fractions or streams produced by product improvement processes often contain small amounts of impurities that must be removed. Processes that remove these undesirable components are known as treating processes, and these processes are used not only to finish products for the market but also to prepare feedstocks for other processes (such as catalytic polymerization and reforming) in which catalysts would be harmed by impurities.

The most common impurities are sulfur compounds that are derived from the sulfur compounds that occur in crude oil (Chapter 3), such as sulfides (R'SR') and the foul-smelling thiols (RSH, also called mercaptans). Oxygen compounds in the form of carboxylic acids (RCO2H) and phenols (ArOH, where Ar is an aromatic group) may also be present. Nitrogen-containing compounds derived from those that occur in crude oil (Chapter 3) are also present. Furthermore, olefins (R'CH=CHR') must also be eliminated from a feedstock or aromatics removed from a solvent, and these olefins and aromatics are considered impurities. Similarly, polymerized material, asphaltic material, or resin constituents may be impurities, depending on whether their presence in a finished product is harmful.

Treatment processes for the removal of sulfur-containing and nitrogen-containing compounds from distillates are much less severe than the desulfurization and denitrogenation processes applied to higher-boiling fractions (Chapter 10). In fact, it is generally recognized that the removal or conversion of sulfur and nitrogen compounds in distillates by treatment processes is usually limited to mercaptans and the lower-molecular-weight sulfur compounds. When there is more than a trace amount (>0.1%) of heteroatoms present, it is often more convenient and economical to resort to such methods as those thermal processes (e.g., hydroprocesses) that bring about a decrease in all types of heteroatomic compounds.

Choices of a treatment method depend on the amount and type of impurities in the fractions to be treated and the extent to which the process removes the impurities. Naturally occurring sweet kerosene, for example, may require only a simple treatment with alkali (lye) to remove hydrogen sulfide. If mercaptans are also present in the raw kerosene, a doctor treatment in addition to lye treatment is required, but poor-quality raw kerosene may require, in addition to these treatments, treatment with sulfuric acid and fuller’s earth. The lowest quality raw kerosene requires treatment with strong sulfuric acid, neutralization with lye, and redistillation. Since different fractions have the same impurities, the same treatment process may be used for several different products.

The purpose of this section is to present an outline of the processes that are available for the treatment of the various product streams to remove contaminants from streams that will be eventually used as stock for products. The processes outlined here are not usually shown on a refinery schematic but would be placed in the general area entitled finishing, but only after the processes have been shown on a schematic and prior to the designation of the product.

13.8.1 CAUSTIC PROCESSES

The treating of petroleum products by washing with solutions of alkali (caustic or lye) is almost as old as the petroleum industry itself. Early discoveries that product odor and color could be improved
by removing organic acids (naphthenic acids and phenols) and sulfur compounds (mercaptans and hydrogen sulfide) led to the development of caustic washing.

Caustic treating is an extraction process that removes organic acids (RCOOH), mercaptan sulfur (RSH), and phenolic compounds (ROH) from petroleum fractions. Thus, it is not surprising that caustic soda washing (lye treatment) has been used widely on many petroleum fractions. In fact, it is sometimes used as a pretreatment for sweetening and other processes. The process consists of mixing a water solution of lye (sodium hydroxide or caustic soda) with a petroleum fraction (typically naphtha) and is accomplished by contacting a 5%–20% w/w caustic solution countercurrently with the untreated stream in a packed tower with a ratio of product to caustic on the order of 10:1. The spent caustic can be regenerated either by steam stripping or air contacting. The regeneration conditions depend on the concentration of impurities in the caustic solution but the caustic is not 100% regenerable and makeup solution is necessary.

The major use of caustic treating in current refineries is the removal of mercaptan derivatives from naphtha—caustic losses and lower yields are prevalent (due to the formation of difficult-to-break emulsions) when heavy feedstocks are treated.

13.8.1.1 Dualayer Distillate Process
The Dualayer distillate process is similar in character to the Duosol process in that it uses caustic solution and cresylic acid (cresol, methylphenol, CH₃C₆H₄OH). The process extracts organic acid substances (including mercaptans, RSH) from cracked, or virgin, distillate fuels. In a typical operation, the Dualayer reagent is mixed with the distillate at approximately 55°C (130°F) and passed to the settler, where three layers separate with the aid of electrical coagulation. The product is withdrawn from the top layer; the Dualayer reagent is withdrawn from the bottom layer, relieved of excess water, fortified with additional caustic, and recycled.

13.8.1.2 Dualayer Gasoline Process
The Dualayer gasoline process is a modification of the Dualayer distillate process in that it is used to extract mercaptans from liquid petroleum gas, gasoline, and naphtha using the Dualayer reagents. Thus, gasoline, free of hydrogen sulfide, is contacted with the Dualayer solution at 50°C (120°F) in at least two stages, after which the treated gasoline is washed and stored. The treating solution is diluted with water (60%–70% of the solution volume) and stripped of mercaptans, gasoline, and excess water, and the correct amount of fresh caustic is added to obtain the regenerated reagent.

13.8.1.3 Electrolytic Mercaptan Process
The electrolytic mercaptan process employs aqueous solutions to extract mercaptans from refinery streams, and the electrolytic process is used to regenerate the solution. The charge stock is pre-washed to remove hydrogen sulfide and contacted countercurrently with the treating solution in a mercaptan extraction tower. The treated gasoline is stored; the spent solution is mixed with regenerated solution and oxygen. The mixture is pumped to the cell, where mercaptans are converted to disulfides that are separated from the regenerated solution.

13.8.1.4 Ferrocyanide Process
The Ferrocyanide process is a regenerative chemical treatment for removing mercaptans from straight-run naphtha, as well as natural and recycle gasoline, using caustic–sodium ferrocyanide reagent.

For example, gasoline is washed with caustic to remove hydrogen sulfide and then washed countercurrently in a tower with the treating agent. The spent solution is mixed with fresh solution containing ferricyanide; the mercaptan derivatives are converted to insoluble disulfides and are removed by a countercurrent hydrocarbon wash. The solution is then recycled, and part of the ferrocyanide is converted to ferricyanide by an electrolyzer.
13.8.1.5 Lye Treatment

Lye treatment is carried out in continuous treaters, which essentially consist of a pipe containing baffles or other mixing devices into which the oil and lye solution are both pumped. The pipe discharges into a horizontal tank where the lye solution and oil separate. Treated oil is withdrawn from near the top of the tank; lye solution is withdrawn from the bottom and recirculated to mix with incoming untreated oil. A lye-treating unit may be incorporated as part of a processing unit, for example, the overhead from a bubble tower may be condensed, cooled, and passed immediately through a lye-treating unit. Such a unit is often referred to as a worm-end treater, since the unit is attached to the particular unit as a point beyond the cooling coil or cooling worm.

Caustic solutions ranging from 5% to 20% w/w are used at 20°C–45°C (70°F–110°F) and 5–40 psi. High temperatures and strong caustic are usually avoided because of the risk of color body formation and stability loss. Caustic–product treatment ratios vary from 1:1 to 1:10.

Spent lye is the term given to a lye solution in which approximately 65% of the sodium hydroxide content has been used by reaction with hydrogen sulfide, light mercaptans, organic acids, or mineral acids. A lye solution that is spent, as far as hydrogen sulfide is concerned, may still be used to remove mineral or organic acids from petroleum fractions. Lye solution spent by hydrogen sulfide is not regenerated, whereas blowing with steam can regenerate lye solution spent by mercaptans. This technique reforms sodium hydroxide and mercaptans from the spent lye. The mercaptans separate as a vapor and are normally destroyed by burning in a furnace. Spent lye can also be regenerated in a stripper tower with steam, and the overhead consists of steam and mercaptans, as well as the small amount of oil picked up by the lye solution during treatment. Condensing the overhead allows the mercaptans to separate from the water.

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.

13.8.1.6 Mercapsol Process

The Mercapsol process is another regenerative process for extracting mercaptans by means of sodium (or potassium) hydroxide, together with cresols, naphthenic acids, and phenol. Gasoline is contacted countercurrently with the mercapsol solution, and the treated product is removed from the top of the tower. Spent solution is stripped to remove gasoline, and the mercaptans are then removed by steam stripping.

13.8.1.7 Polysulfide Treatment

Polysulfide treatment is a nonregenerative chemical treatment process used to remove elemental sulfur from refinery liquids. Dissolving 1 pound of sodium sulfide (Na₂S) and 0.1 pound of elemental sulfur in a gallon of caustic solution prepares the polysulfide solution. The sodium sulfide can actually be prepared in the refinery by passing hydrogen sulfide, an obnoxious refinery by-product gas, through caustic solution.

The solution is most active when the composition approximates Na₂S to Na₂S₃, but activity decreases rapidly when the composition approaches Na₂S₄. When the solution is discarded, a portion (ca. 20%) is retained and mixed with fresh caustic–sulfide solution, which eliminates the need to add free sulfur. Indeed, if the material to be treated contains hydrogen sulfide in addition to free sulfur, it is often necessary simply to add fresh caustic.

13.8.1.8 Sodasol Process

A lye solution removes only the lighter or lower boiling mercaptans, but various chemicals can be added to the lye solution to increase its ability to dissolve the heavier mercaptans. The added
chemicals are generally known as solubility promoters or solutizers. Several different solutizers have been patented and are used in processes that differ chiefly in the composition of the solutizers.

In the Sodasol process, the treating solution is composed of lye solution and alkyl phenols (acid oils), which occur in cracked naphtha and cracked gas oil and are obtained by washing cracked naphtha or cracked gas oil with the lye solution. The lye solution, with solutizers incorporated, is then ready to treat product streams, such as straight-run naphtha and gasoline. The process is carried out by pumping a sour stream up a treating tower countercurrent to a stream of Sodasol solution that flows down the tower. As the two streams mix and pass, the solution removes mercaptans and other impurities, such as oxygen compounds (phenols and acids), as well as some nitrogen compounds.

The treated stream leaves the top of the tower; the spent Sodasol solution leaves the bottom of the tower to be pumped to the top of a regeneration tower, where mercaptans are removed from the solution by steam. The regenerated Sodasol solution is then pumped to the top of the treatment tower to treat more material. A variation of the Sodasol process is the Potasol process, which uses potassium hydroxide instead of lye (sodium hydroxide).

13.8.1.9 Solutizer Process

The Solutizer process is a regenerative process using such materials as potassium iso-butyrate and potassium alkyl phenolate in strong aqueous potassium hydroxide to remove mercaptans. After removal of the mercaptans and recovery of the hydrocarbon stream, regeneration of the spent solution may be achieved by heating and steam blowing at 130°C (270°F) in a stripping column in which steam and mercaptans are condensed and separated.

On the other hand, the spent solution may be contacted with carbon dioxide air, after which the disulfides formed by oxidation of the mercaptans are extracted by a naphtha wash.

Air blowing in the presence of tannin (tannin Solutizer process) catalytically oxidizes mercaptans to the corresponding disulfides, but there may be side reactions that can lead to reagent contamination.

13.8.1.10 Steam-Regenerative Caustic Treatment

Steam-regenerative caustic treatment is essentially directed toward removal of mercaptans from such products as light, straight-run gasoline. 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 solution gradually deteriorates because of the accumulation of material that cannot be removed by stripping; the caustic quality must be maintained by both continuous or intermittent discard and replacement of a minimum amount of the operating solution.

13.8.1.11 Unisol Process

The Unisol process is a regenerative method for extracting not only mercaptans but also certain nitrogen compounds from sour gasoline or distillates. The gasoline, free of hydrogen sulfide, is washed countercurrently with aqueous caustic–methanol solution at approximately 40°C (100°F). The spent caustic is regenerated in a stripping tower (145°C–150°C, 290°F–300°F), where methanol, water, and mercaptans are removed.

13.8.2 Acid Processes

Treating petroleum products with acids is, like caustic treatment, a procedure that 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 more commonly used sulfuric acid, but in most instances there is little advantage in using any acid other than sulfuric.

Until about 1930 acid treatment was almost universal for all types of refined petroleum products, especially for cracked gasoline, kerosene, and lubricating stocks. Cracked products were acid
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treated to stabilize against gum formation and color darkening (oxidation) and to reduce sulfur content if necessary. However, there were appreciable losses due to polymer formation (from olefins in cracked products) initiated by the sulfuric acid.

Other processes have now superseded the majority of the acid treatment processes. However, acid treatment has, to some extent, been continued for desulfurizing high-boiling fractions of cracked gasoline, for refining kerosene, for manufacture of low-cost lubricating oil, and for making such specialties as insecticide naphtha, pharmaceutical white oil, and insulating oil.

The reactions of sulfuric acid with petroleum fractions are complex. The undesirable components to be removed are generally present in small amounts; large excesses of acid are required for efficient removal, which may cause marked changes in the remainder of the hydrocarbon mixture.

Paraffin and naphthene hydrocarbons in their pure forms are not attacked by concentrated sulfuric acid at low temperatures and during the short time of conventional refining treatment, but solution of light paraffins and napthenes in the acid sludge can occur. Fuming sulfuric acid (oleum) absorbs small amounts of paraffins when contact is induced by long agitation; the amount of absorption increases with time, temperature, concentration of the acid, and complexity of structure of the hydrocarbons. With napthenes fuming sulfuric acid causes sulfonation as well as rupture of the ring.

The action of sulfuric acid on olefin hydrocarbons is very complex. The main reactions involve ester formation and polymerization. The esters formed by reaction of sulfuric acid with olefins in cracked distillates are soluble in the acid phase but are also to some extent soluble in hydrocarbons, especially as the molecular weight of the olefin increases. The esters are usually difficult to hydrolyze with a view to removal by alkali washing. They are, however, unstable on standing for a long time, and products containing them (acid-treated cracked gasoline) may evolve sulfur dioxide and deposit intractable materials. The esters are quite unstable on heating, so that a redistilled, acid-treated cracked distillate usually requires alkali washing after the customary distillation.

Aromatics are not attacked by sulfuric acid to any great extent under ordinary refining conditions, unless they are present in high concentrations. However, if fuming acid is used or if the temperature is allowed to rise above normal, sulfonation may occur. When both aromatics and olefins are present, as in distillates from cracking units, alkylation can occur.

Thus, as indicated, acid treatment of cracked gasoline distillate brings about losses due to chemical reaction and polymerization of some of the olefins to constituents boiling above the gasoline range. This makes redistillation necessary, and such losses may total several percent, even when refrigeration is employed to maintain a low temperature.

Acid treatment of high-boiling distillates and residua presents different problems. Most of these contain at least a small proportion of dissolved or suspended asphalitic substances, and almost all the acid comes out as sludge (acid tar); its separation is aided by the addition of a little water or alkali solution. However, there may be obvious chemical changes, such as sulfur dioxide evolution, and washed (acid-free) sludge from the treatment of practically sulfur-free oils may contain up to 10% combined sulfur derived from the treating acid.

Although largely displaced for bulk production of both gasoline and lubricating oils, acid treatment still serves many special purposes. Paraffin distillates intended for dewaxing might receive light treatment to facilitate wax crystallization and refining, whereas insulating oils, refrigeration compressor oils, and white oils may be treated more severely.

The sludge produced on acid treatment of petroleum distillates, even gasoline and kerosene, is complex in nature. Esters and alcohols are present from reactions with olefins; sulfonation products from reactions with aromatics, napthenes, and phenols; and salts from reactions with nitrogen bases. In addition, such materials as napthenic acids, sulfur compounds, and asphalitic material are all retained by direct solution. To these constituents must be added the various products of oxidation–reduction reactions: coagulated resins, soluble hydrocarbons, water, and free acid.

Disposal of the sludge is difficult, as it contains unused free acid that must be removed by dilution and settling. The disposal is a comparatively simple process for the sludge resulting from treating
gasoline and kerosene, the so-called light oils. The insoluble oil phase separates out as a mobile tar-like material, which can be mixed and burned without too much difficulty. Sludge from heavy oil and bitumen, however, separates out as granular semisolids, which offers considerable difficulty in handling.

In all cases careful separation of reaction products is important to the recovery of well-refined materials. This may not be easy if the temperature has risen as a consequence of chemical reaction. This will result in a persistent dark color traceable to colloidally distributed reaction products. Separation may also be difficult at low temperature because of high viscosity of the stock, but this problem can be overcome by diluting with light naphtha or with propane.

When acid treatment cannot be applied continuously by mechanical agitation followed by effective separation, the older batch agitators are employed. These devices are vertical reactors holding up to several thousand barrels, provided with conical bottoms for sludge drainage. The contact time is difficult to control and may amount to several hours, but the separation of acid tar is desirable to avoid discoloration by resolution and to permit handling the sludge before it becomes undesirably viscous. Breaking out of the suspended acid tar, often referred to as pepper sludge, is helped by adding a little water and agitating, and the subsequent separation of tar resembles closely the precipitation of a colloidal suspension. The sludge is allowed to settle, and the sour oil is washed with water, usually after transfer to another container, to avoid retention of acid tar in the system during the alkali washing that follows.

Sodium hydroxide solution (10%–25% concentration) may be used for nonviscous products, but for viscous oils more dilute solutions are employed and only a very slight excess of alkali is used, but no attempt is made at its recovery. Emulsion breaking chemicals are sometimes required in alkali washing; the use of aqueous alcohol is customary when fuming acid has been employed, as for sulfonates and white oils. Final water washing followed by air blowing to dry the oils is the customary procedure.

13.8.2.1 Nalfining Process

The Nalfining process is a continuous process that employs acetic anhydride and a caustic rinse to convert contaminants into less objectionable, but oil-soluble, compounds. The anhydride is injected into the product stream, where it reacts with oxygen to form the ester, with sulfur to form the thiaester, with nitrogen to form substituted amides, and with complex organic impurities to form environmentally benign products. The caustic rinse neutralizes the potentially corrosive acetic acid.

13.8.2.2 Sulfuric Acid Treatment

Sulfuric acid treatment is a continuous or batch method that is used to remove sulfur compounds. The treatment will also remove asphaltic materials from various refinery stocks. The acid strength varies from fuming (>100%) to 80%; approximately 93% acid finds the most common use. The weakest suitable acid is used for each particular situation to reduce sludge formation from the aromatic and olefin hydrocarbons.

The use of strong acid dictates the use of a fairly low temperature (−4°C to 10°C, 25°F–50°F), but higher temperatures (20°C–55°C, 70°F–130°F) are possible if the product is to be redistilled.

13.8.3 Clay Processes

Treating petroleum distillates and residua by passing them through materials possessing decolorizing power has been in operation for many years (Speight and Ozum, 2002; Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2011, 2014). For example, various clays and similar materials are used to treat petroleum fractions to remove diolefins, asphaltic materials, resins, acids, and colored bodies. Cracked naphtha were frequently clay treated to remove diolefins that formed gums in gasoline. Other processes have now largely superseded this use of clay treatment,
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in particular by the use of inhibitors, which, added in small amounts to gasoline, prevent gums from forming. Nevertheless, clay treatment 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.

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

13.8.3.1 Alkylation Effluent Treatment
This is a continuous liquid percolation process in which reactor effluent is coalesced in a vessel containing glass wool and steel mesh and then charged, alternately, to two bauxite (medium mesh) towers. Regeneration of the bauxite is effected with a mixture of steam and gas.

13.8.3.2 Arosorb Process
The Arosorb process separates aromatics from various refinery streams by the use of fixed silica gel beds. The feedstock is preheated over activated alumina to remove water, as well as traces of nitrogen, oxygen, and sulfur compounds. The material is then passed into one of several gel cases and, after a suitable residence time (ca. 30 minutes), conveyed to a second gel case. The first container (case) is then fed with the desorbent (e.g., crude xylene stream) that removes the saturate compounds from the bed and then displaces the adsorbed aromatics (e.g., benzene and toluene).

13.8.3.3 Bauxite Treatment
This process is essentially the same as the previous process, except in this case a vaporized petroleum fraction is passed through beds of a porous mineral known as bauxite. The bauxite acts as a catalyst to convert many different sulfur compounds, in particular mercaptans, into hydrogen sulfide, which is subsequently removed by a lye treatment. Bauxite is used to treat gasoline, naphtha, and kerosene products that have unusually high mercaptan contents.

A typical bauxite treatment unit consists of a fire-heated coil, two bauxite treatment towers, a bubble tower, a superheater for steam and air, and the usual exchangers, coolers, and pumps. Naphtha, raw kerosene, or other stock to be treated is preheated in heat exchangers and passed through the heating coil where it is heated to 415°C (780°F). At this temperature the stock is superheated. The vaporized feed is then passed downward through one of two bauxite towers at a pressure of approximately 40 psi. Three beds of catalyst in the tower convert mercaptans to hydrogen sulfide to enter a continuous lye treatment unit where hydrogen sulfide is removed.

After a time the bauxite towers are switched, since the bauxite progressively loses its catalytic activity. The spent catalyst is restored to its original activity by regeneration. Regeneration involves by passing superheated steam and air, carefully scheduled in proportions and rate, downward through the catalyst beds. The carbonaceous material that has accumulated on the catalyst is burned off. Combustion progresses downward through the beds; care is taken to prevent temperatures exceeding 595°C (1100°F), which would harm the bauxite. Air alone is finally used to burn away the last traces of carbonaceous material, after which the bauxite is ready for use again.

13.8.3.4 Continuous Contact Filtration Process
This is a continuous clay treatment process in which finely divided adsorbent is mixed with the charge stock and heated to 95°C–175°C (200°F–350°F). The slurry is then conveyed to a steam-stripping tower, after which it is cooled, vacuum filtered, and then vacuum stripped for further product specification control.
13.8.3.5 Cyclic Adsorption Process

The cyclic adsorption process is used for the separation of aromatics from petroleum product streams. Like the Arosorb process, the cyclic adsorption process employs fixed beds of silica gel. The various stages of the process are (1) extraction of the adsorbable material from the feedstock (refining), (2) concentration of the adsorbed phase (enriching), and (3) stripping for recovery of the extract and regeneration of the gel using a light gasoline or pentane fraction.

13.8.3.6 Gray Clay Treatment

This is a continuous vapor-phase process for selectively polymerizing the diolefin constituents of, and removing other gum-forming agents from, thermal gasoline. Two or more towers (10 ft in diameter and approximately 25 ft high) are used in parallel, and the hydrocarbon vapors are passed through the bed at temperatures (120°C–245°C, 250°F–475°F) just above the condensation point. The diolefins polymerize and drain from the base of the tower or they are separated from the gasoline by fractionation. Spent clay is either discarded or regenerated in kilns.

13.8.3.7 Percolation Filtration Process

This is a continuous-flow cyclic-regenerative liquid-phase process in which oil is filtered through a bed (containing 10–50 tons of fuller’s earth) before storage. Two or more beds are used alternately on an operating and regenerating cycle. The spent clay is regenerated by washing it with naphtha, steaming, and burning.

13.8.3.8 Thermofer Continuous Percolation Process

The Thermofer continuous percolation process is a continuous regenerative process for stabilizing and decolorizing lubricants or waxes that have been distilled, solvent refined, or acid treated. The charge stock is heated to 50°C–175°C (125°F–350°F), injected into the base of a clay-filled tower, and allowed to percolate in countercurrent flow through the bed. Spent clay is continuously withdrawn from the base of the tower; regenerated clay is added to the top of the bed to maintain a constant level.

13.8.4 Oxidative Processes

Oxidative treatment processes are, in fact, processes that have been developed to convert the objectionable-smelling mercaptans to the less objectionable disulfides by oxidation. However, disulfides tend to reduce the tetraethyl lead susceptibility of gasoline, and recent trends are toward processes that are capable of completely removing the mercaptans.

13.8.4.1 Bender Process

The Bender process is a fixed-bed catalytic treatment method that employs a lead sulfide catalyst. Controlled amounts of sulfur, alkali, and air are added to the product stream, which is passed through lead sulfide catalyst beds.

In this method, the sulfur required to oxidize the mercaptide derivatives is also furnished by the air oxidation of lead sulfide:

\[
PbS + \frac{1}{2}O_2 \rightarrow PbO + S
\]

\[
PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O
\]

\[
Na_2PbO_2 + 2RSH \rightarrow Pb(RS)_2 + 2NaOH
\]

\[
Pb(RS)_2 + S \rightarrow PbS + R_2S_2
\]
When larger quantities of air must be supplied for treating gasoline of high mercaptan content, there is a tendency toward excessive plumbite formation and also excessive sulfur formation. In such cases, a controlled quantity of aqueous sodium sulfide is simultaneously added to reconvert the extra plumbite back to lead sulfide. The presence of the remaining extra sulfur is not desirable, and therefore it is advantageous to control the air oxidation carefully. The lead sulfide is essentially a catalyst, as only oxygen is consumed in the process; there is, however, a certain loss of alkali to sodium sulfate and thiosulfate.

13.8.4.2 Copper Sweetening Process

The oxidizing power of cupric (Cu$^{2+}$) salts is also utilized to convert mercaptans directly into disulfides; free sulfur is not employed, and polysulfide derivatives are not obtained. The process employs cupric chloride in the presence of strong salt solutions, which are generally made up by dissolving copper sulfate in an aqueous solution of sodium chloride.

\[
4RSH + 2CuCl_2 \rightarrow R_2S_2 + 2CuSR + 4HCl \\
2CuSR + 2CuCl_2 \rightarrow R_2S_2 + 4CuCl \\
4CuCl + 4HCl + O_2 \rightarrow 4CuCl_2 + H_2O
\]

The cuprous chloride (CuCl) is soluble in the salt solution, and there is no precipitation. Under operating conditions a certain amount of copper is retained by the sweetened petroleum fraction, probably as cuprous mercaptide derivatives or cuprous chloride–olefin addition products, but these can be removed by washing the material with aqueous sodium sulfide. Air blowing the cuprous chloride solution, after or during the sweetening operation, regenerates the cupric chloride. The copper chloride solution may be employed as such, or the sour fraction may be percolated through a porous mass saturated with the treating agent. Alternatively, the gasoline may be mixed with a solid carrier for the reagent, dispersed as a slurry.

Three methods of mechanical application of the copper chloride are used. If air will not cause the petroleum fraction to change color or form gum, a fixed-bed process may be used in which the sour material is passed through beds of an adsorbent that have been impregnated with cupric chloride. Air continuously regenerates the cupric chloride almost simultaneously with the sweetening reaction.

In the solution process, a solution of cupric chloride is continuously mixed in a centrifugal pump with the sour fraction. The mixture then enters a settling tank where the spent treatment solution separates from the petroleum liquid, and the treatment solution is withdrawn to a tank where blowing with air regenerates cupric chloride.

The slurry process makes use of clay or a similar material impregnated with cupric chloride. The clay is mixed with a small amount of, say, naphtha to form a slurry, which is pumped into the sour naphtha stream. Air or oxygen gas is added with the sour stream and continuously regenerates the cupric chloride. The treated material and clay slurry flow into a settling tank and separate, and then the clay slurry is recycled.

13.8.4.3 Doctor Process

The doctor process is a method of treating sour (sulfur-containing) distillates consists of agitating the distillate with alkaline sodium plumbite (doctor solution) in the presence of a small amount of free sulfur. A black precipitate of lead sulfide is formed, and the material, which has improved odor, has been rendered sweet.

In practice, sour distillates are usually given an alkali wash before the doctor treatment to remove traces of hydrogen sulfide and some of the lower-molecular-weight mercaptans; this process has a marked effect in reducing the plumbite requirement. Slightly more sulfur than the theoretical is
required as a result of the formation of complex lead intermediates. In the presence of lead mer-
captide derivatives the extra sulfur acts to form alkyl polysulfide derivatives, which are chemically
analogous to peroxide.

The precipitating effect is evidently a result of the presence of these polysulfide derivatives or
possibly of sodium sulfide formed between mercaptans, sulfur, and the alkaline solution. The doctor
solution leaving the reactor consists essentially of a mixture of lead sulfide in free alkali, contain-
ing emulsified hydrocarbons, and this spent solution is pumped to steam-heated vessels, where it
is air-blown for regeneration. Considerable amounts of sodium thiosulfate are also formed and the
thiosulfate, in turn, may react with the alkali present to form sodium sulfite (Na$_2$SO$_3$) and sodium
sulfide (Na$_2$S). The loss of lead is very low, and the main items of consumption are alkali and sulfur.

13.8.4.4 Hypochlorite Sweetening Process
This process employs sodium or calcium hypochlorite [NaOCl or Ca(OCl)$_2$]. The principal reaction
produces disulfides (R–S-S–R') with some formation of sulfoxides, (R$_2$S=O), and sulfonic acids
(RSO$_2$H). When hydrogen sulfide is present, an alkaline wash prevents the formation of elemental
sulfur. An alkaline afterwash is frequently necessary to remove undesirable chlorinated products.

13.8.4.5 Inhibitor Sweetening Process
This is a continuous process that uses a phenylenediamine-type inhibitor, air, and caustic to sweeten
low-mercaptan-content gasoline. The inhibitor and air are injected between the caustic washing
stages, and the mercaptan disappearance may be attributed to reaction with the caustic and then to
oxidation during both washing and storage. In the absence of caustic, excessive peroxide formation
occurs, which leads to gasoline deterioration.

13.8.4.6 Merox Process
The Merox process is a combination process for mercaptan extraction and sweetening of gasoline or
lower boiling materials. The catalyst is a cobalt salt, which is insoluble in the oil and may be used in
cautic solution or on a suitable solid support. Thus, gasoline is washed with alkali and contact by
the catalyst and caustic in the extractor, air is then injected, and the treated product is stored in the
regeneration step. Caustic is taken from the extractor and mixed with air in the oxidizer, after which
disulfides and excess air are separated from the reagent in the disulfide separator. The regenerated
caustic solution is recirculated to the top of the extractor.

13.8.5 Solvent Processes
Solvent refining processes are of a physical nature rather than a chemical nature. The desirable
constituents, as well as the undesirable constituents, of the mixture can be recovered unchanged and
in the original state. In addition, the processes that use solvent as a means of refining are extremely
versatile, insofar as both low-boiling and high-boiling fractions can be used as feedstocks. In gen-
eral, the solvent processes can be classified as (1) deasphalting, (2) dewaxing, and (3) solvent refin-
ing. The two former process types have been dealt with elsewhere in this text (Chapter 12) and,
therefore, are excluded from this section.

Solvent refining (solvent treatment) is a widely used method of refining lubricating oils, as well
as a host of other refinery stocks. The solvent processes yield products that meet the desired spec-
fications by removing undesirable constituents (such as aromatics, naphthenes, and unsaturated
compounds) from the charge material. There are, however, solvent refining processes in which the
desirable continents are aromatics and are extracted by the solvent from the petroleum fraction.

Nevertheless, the original object of solvent extraction, or solvent treatment, was to remove
aromatic compounds from feedstocks, such as lubricating oils. Thus, a suitable solvent can con-
vert inferior raw lubricating oil stocks into oils with as high a quality as desired and is higher
than could ever be obtained with, say, sulfuric acid. In contrast to sulfuric acid treatment (which
depends on chemical reaction for a large part of its effect), solvent treatment is a physical process in which undesirable olefin compounds, asphaltic compounds, aromatic compounds, and sulfur compounds are selectively dissolved in the solvent and removed with the solvent. After separation of the solvent by distillation from both the unwanted materials and the treated oil, the solvent can be reused.

The most widely used extraction solvents are phenol, furfural, and cresylic acid. The last is used with propane in the Duosol process. Other solvents less frequently used are liquid sulfur dioxide, nitrobenzene, and chlorex (2,2-dichloroethyl ether). All lubricating oil solvent extraction processes operate on the principal of mixing the oil with the solvent and then allowing the solvent to settle from the treated oil. The solvent carries the unwanted materials with it. The nature of the raw lubricating oil stock is important in determining the type of process to use and the extent to which treatment should be carried out. The greater is the extent of treatment, the smaller the yield of treated oil but the higher the quality.

It is possible to make oil of any desired quality from any raw lubricating oil stock. In fact, it is possible to overtreat lubricating oils, causing a loss in lubricating properties. White oils, for example, are lubricating oils that have been deliberately overtreated with very strong sulfuric acid to remove all traces of color. Such oils are so overrefined that they are not used as lubricating oils; their lubricating properties are inferior to oils refined specifically for use as lubricants. Thus, solvent extraction is a complex operation requiring the selective removal of only those components that reduce the lubricating qualities of the oil being treated.

The phenol treatment process is the most widely used. Phenol, also known as carbolic acid, is a poisonous solid that can cause serious flesh burns. It melts at 41°C (106°F) and boils at 183°C (361°F). In the phenol treatment process, phenol is used in the liquid state by maintaining the temperature at over 35°C (100°F).

In the process, raw lubricating oil is pumped into the bottom of the tower and phenol into the top; the phenol descends through the oil and is mixed with the oil by means of baffles or other mechanical mixing devices. The treated oil or raffinate leaves the top of the tower. The phenol that collects at the bottom of the tower contains the extract (aromatic, unsaturated, asphaltic, and sulfur compounds extracted from the raw oil) and is known as spent phenol.

The raffinate is heated to 260°C (500°F) and pumped to a pair of fractional vacuum distillation towers operated in series. Here, the phenol in the raffinate is removed overhead. The bottom product from the second tower is the finished product.

The phenol is recovered from the spent phenol in a phenol recovery unit, which consists of another pair of fractional distillation towers and a stripper tower. The spent phenol is heated and passed into the primary tower, where process water is removed as an overhead product and some of the phenol recovered as a side-stream product. The bottom product from the primary tower is heated to approximately 240°C (460°F) and pumped into the secondary tower, where the majority of the remaining phenol is recovered as an overhead product. The extract (the bottom product) is heated to 345°C (650°F) and pumped into a vacuum stripper tower, where steam removes the phenol from the extract. The phenol obtained from the various distillation units is pumped to a heated storage tank for reuse. The extract may be used as a special-purpose product when high-molecular-weight aromatic hydrocarbons are needed; it may be added to heavy fuel oils, or it may be used as a cracking stock.

Liquid sulfur dioxide was first used commercially as an extraction solvent in 1909 to remove aromatic hydrocarbons from kerosene (Edeleanu process), when it was noted that aromatic and unsaturated hydrocarbons would dissolve in liquid sulfur dioxide but paraffinic and naphthenic hydrocarbons would not. The process was widely used for light distillates, such as kerosene, but was not used for heavier oils, such as lubricating oils, until about 1930.

The process is carried out in much the same way as phenol treatment, except that treatment takes place at approximately 0°C (32°F) and under sufficient pressure to maintain the sulfur dioxide as a liquid. The feedstock is contacted with liquid sulfur dioxide and the aromatic portion is
concentrated in the extract phase, which is in turn contacted with a wash oil (such as kerosene) to remove the lower boiling nonaromatic compounds. The streams are then stripped and fractionated to recover sulfur dioxide and the wash oil for recycling to the extraction tower.

Sulfur dioxide alone does not effectively dissolve the high-boiling aromatic hydrocarbons in lubricating oils and therefore is used in conjunction with benzene for treating lubricating oils. Mixing benzene with the sulfur dioxide increases the solvent capacity but at the same time retains the selectivity for aromatic and nonparaffinic hydrocarbons. The percentage of benzene in the solvent mixture makes it possible to select the most advantageous treatment conditions for any particular feedstock to produce a product with the desired specifications.

**Furfural** is a heavy, straw-colored liquid that boils at 162°C (323°F). The process is carried out in the same manner as phenol treatment, but the raffinate or treated oil has so little furfural dissolved in it that distillation is not used to remove it; steam stripping is all that is required. The treatment (Figure 13.12) is conducted in countercurrent towers, or multistage units, which normally operate at a temperature of 40°C–120°C (100°F–250°F). A high-temperature gradient in the treatment section permits a high yield of the refined oil.

**Hydrogen fluoride treatment** is a liquid–liquid extraction process removing sulfur and potential coke-forming materials from naphtha, middle distillates, and gas oil. The feedstock is contacted countercurrently with liquid hydrofluoric acid in an extraction tower, after which the overhead product is sent to a tower for removal of hydrogen fluoride. The solvent is recovered from the extract by use of evaporators and a stripper. The process is relatively insensitive to variations in temperature and pressure, but normally temperatures of 50°C (120°F) and pressures below 100 psi are employed.

The **Udex extraction process** is a liquid–liquid recovery method for the selective extraction of aromatic compounds from hydrocarbon mixtures by the use of a diethylene glycol (90%–92%), water (8%–10%), and solvent system. The feedstock, which may be pretreated to eliminate high conjugated dienes or alkenyl aromatics, rises countercurrent to the descending solvent. The stripper recovers the solvent for recycling; the overhead from the extractor is treated with clay and fractionated to separate the aromatics. The temperatures employed in the process are usually fairly low (120°C, 250°F); the pressures are just high enough to maintain liquid-phase conditions.

**Sulfolane** has been used primarily for the extraction of aromatics, such as benzene, toluene, and xylene(s). The chemicals usually arise from catalytic reforming of various feedstocks. Thus, the feedstock is contacted with the solvent in an extractor, and the mixture is conveyed to an extractive

![Diagram of Aromatics extraction using furfural](http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html)
Product Improvement

distillation column. The bottom product from this column is a mixture of solvent and aromatic compounds. Vacuum and steam stripping remove the final traces of hydrocarbons in the bottom part of the recovery column.

REFERENCES
