

Modern separation processes

14.8.2 MODERN PROCESSES

14.8.2.1 Thermal Reforming

In carrying out thermal reforming, a feedstock such as 205°C (400°F) end-point naphtha or a straight-run gasoline is heated to 510°C to 595°C (950°F to 1100°F) in a furnace, much the same as a cracking furnace, with pressures from 400 to 1000 psi (27 to 68 atm). As the heated naphtha leaves the furnace, it is cooled or quenched by the addition of cold naphtha. The material then enters a fractional distillation tower where any heavy products are separated. The remainder of the reformed material leaves the top of the tower to be separated into gases and reformate. The higher octane number of the reformate is due primarily to the cracking of longer-chain paraffins into higher-octane olefins.

The products of thermal reforming are gases, gasoline, and residual oil or tar, the latter being formed in very small amounts (about 1%). The amount and quality of the gasoline, known as reformate, is very dependent on the temperature. A general rule is: the higher the reforming temperature, the higher the octane number, but the lower the yield of reformate.

Thermal reforming is less effective and less economical than catalytic processes and has been largely supplanted. As it used to be practised, a single-pass operation was employed at temperatures in the range of 540°C to 760°C (1000°F to 1140°F) and pressures of about 500 to 1000 psi (34 to 68 atm). The degree of octane number improvement depended on the extent of conversion, but was not directly proportional to the extent of crack per pass. However at very high conversions, the production of coke and gas became prohibitively high. The gases produced were generally olefinic and the process required either a separate gas polymerization operation or one in which C3 to C4 gases were added back to the reforming system.

More recent 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 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.

14.8.2.2 Catalytic Reforming

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 to 1959 time period.

Like thermal reforming, catalytic reforming converts low-octane gasoline into high-octane gasoline (reformate). When thermal reforming could produce reformate with research octane numbers of 65 to 80 depending on the yield, catalytic reforming produces reformate with octane numbers on the order of 90 to 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 feedstock. This more modern concept actually rendered thermal reforming somewhat obsolescent.

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 used mixed nonprecious 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.

Catalytic reformer feeds are saturated (i.e., not olefinic) materials; in the majority of cases that feed may be a straight-run naphtha, but other byproduct low-octane naphtha (e.g., coker

naphtha) can be processed after treatment to remove olefins and other contaminants. Hydrocracker naphtha that contains substantial quantities of naphthenes is also a suitable feed.

Dehydrogenation is a main chemical reaction in catalytic reforming, and hydrogen gas is consequently produced in large 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 byproduct.

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 temperature, 450°C to 520°C (840°F to 965°F), and then passed through fixed-bed catalytic reactors at hydrogen pressures of 100 to 1000 psi (7 to 68 atm) (Figure 14.12). Normally, pairs of reactors are used in series with heaters which are located between adjoining reactors in order to compensate for the endothermic reactions taking place. Sometimes as many as four or five reactors are kept on stream in series, whereas one or more is regenerated.

The on-stream cycle of any one reactor may vary from several hours to many days, depending on the feedstock and reaction conditions.

14.8.2.3 Catalysts

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, chromia–alumina, or platinum on a silica–alumina or alumina base. The nonplatinum catalysts are widely used in

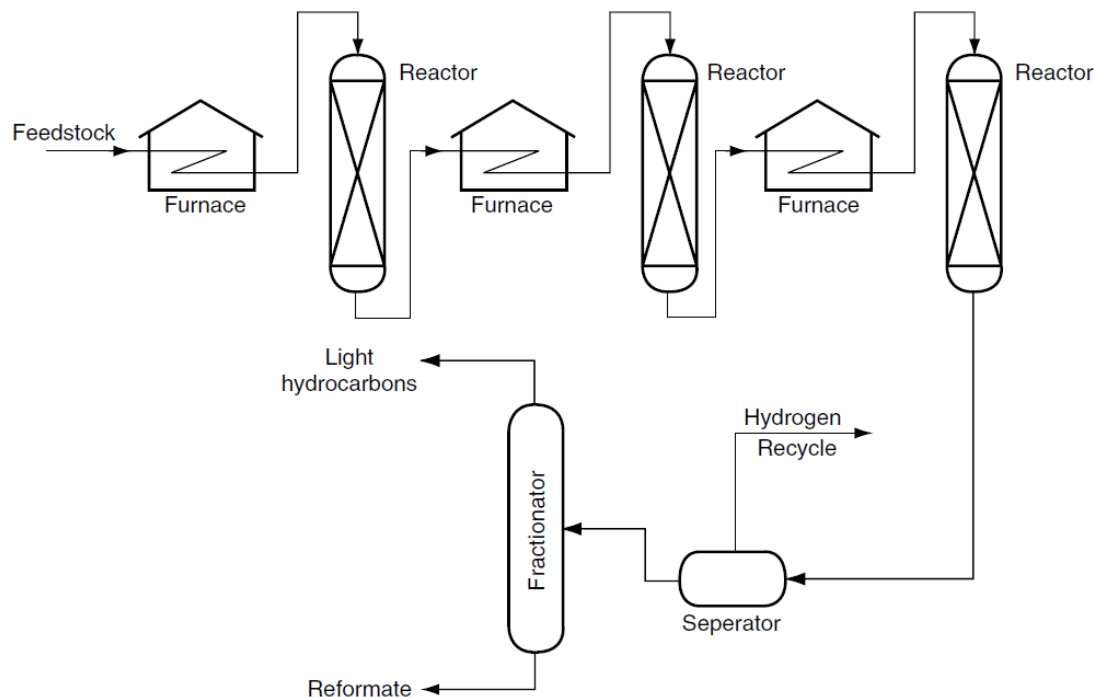


FIGURE 14.12 Catalytic reforming. (From OSHA Technical Manual, Section IV, [Chapter 2](#), Petroleum Refining Processes.)

regenerative process for feeds containing, for example, sulfur, which poisons platinum catalysts, although pretreatment processes (e.g., hydrodesulfurization) may permit platinum catalysts to be employed.

The purpose of platinum on the catalyst is to promote dehydrogenation and hydrogenation reactions, i.e., 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 fact, in the production of aromatics from cyclic saturated materials (naphthenes), it is important that hydrocracking be minimized to avoid loss of the desired product and, 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.

14.9 ISOMERIZATION

Catalytic reforming processes provide high-octane constituents in the heavier gasoline fraction but the normal paraffin components of the lighter gasoline fraction, especially butanes, pentanes and hexanes, have poor octane ratings. The conversion of these normal 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.

14.9.1 HISTORICAL DEVELOPMENT

Isomerization, another “child of the twentieth century,” 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 led to the majority of the butane isomerization units being shut down. In recent years, the greater demand for high-octane motor fuel has resulted in new butane isomerization units being installed.

The earliest process of note was the production 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. In the process, pure butane or a mixture of isomeric butanes (Figure 14.13), is mixed with hydrogen (to inhibit olefin formation) and passed to the reactor, at 110°C to 170°C (230°F to 340°F) and 200 to 300 psi (14 to 20 atm). The product is cooled, the hydrogen separated and the cracked gases are then removed in a stabilizer column. The stabilizer bottom product is passed to a superfractionator where the normal butane is separated from the *iso*-butane.

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Present isomerization applications in petroleum refining are used with the objective of providing additional feedstock for alkylation units or high-octane fractions for gasoline blending (Table 14.5). Straight-chain paraffins (*n*-butane, *n*-pentane, *n*-hexane) are converted to respective *iso*-compounds by continuous catalytic (aluminum chloride, 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% to 60% conversion per pass are characteristic of the isomerization reaction.

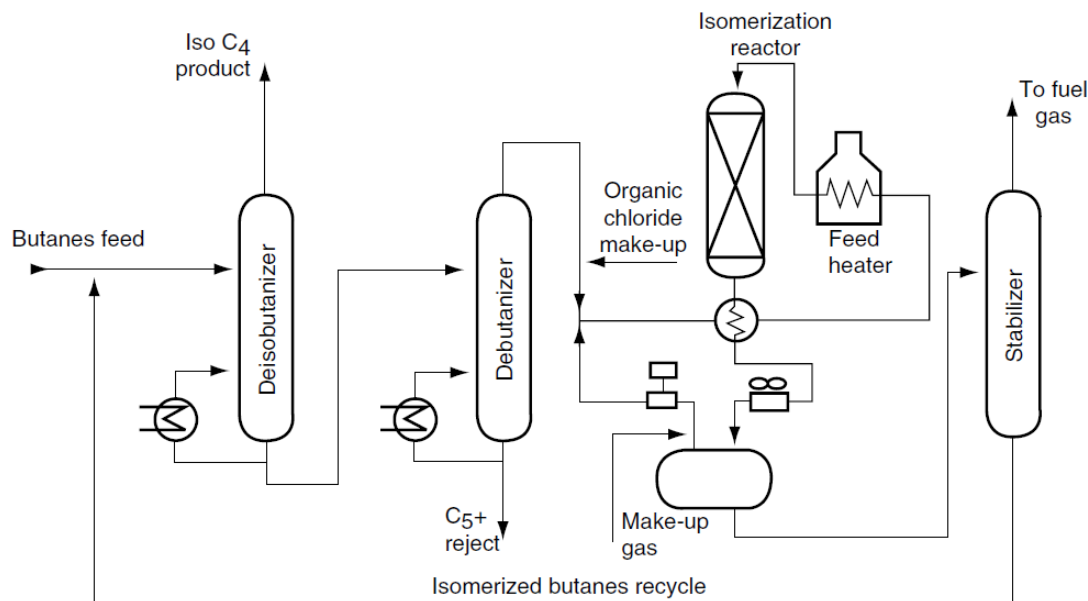


FIGURE 14.13 A butane isomerization unit. (From OSHA Technical Manual, Section IV, Chapter 2, Petroleum Refining Processes.)

14.9.3 CATALYSTS

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 which operate in the range of 370°C to 480°C (700°F to 900°F) and 300 to 750 psi of (20 to 51 atm), while aluminum chloride and hydrogen chloride are universally used for the low-temperature processes.

TABLE 14.5
Component Streams for Gasoline

Stream	Producing Process	Boiling Range	
		°C	°F
<i>Paraffinic</i>			
Butane	Distillation Conversion	0	32
<i>Iso-pentane</i>	Distillation Conversion Isomerization	27	81
Alkylate	Alkylation	40–150	105–300
Isomerate	Isomerization	40–70	105–160
Naphtha	Distillation	30–100	85–212
Hydrocrackate	Hydrocracking	40–200	105–390
<i>Olefinic</i>			
Catalytic naphtha	Catalytic cracking	40–200	105–390
Cracked naphtha	Steam cracking	40–200	105–390
Polymer	Polymerization	60–200	140–390
<i>Aromatic</i>			
Catalytic reformat	Catalytic reforming	40–200	105–390

Nonregenerable aluminum chloride catalyst is employed with various carriers in a fixed-bed or liquid contactor. Platinum or other metal catalyst processes utilized fixed-bed operation and can be regenerable or nonregenerable. The reaction conditions vary widely depending on the particular process and feedstock, 40°C to 480°C (100°F to 900°F) and 150 to 1000 psi (10 to 68 atm).

14.10 ALKYLATION PROCESSES

The combination of olefins with paraffins to form higher *iso*-paraffins is termed *alkylation*. Since olefins are reactive (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*-butene or normal butene and *iso*-octane is the product. Although alkylation is possible without catalysts, commercial processes use aluminum chloride, 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 which 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 values. All alkylates, however, have high octane numbers (>87) which makes them particularly valuable.

14.10.1 HISTORICAL DEVELOPMENT

Alkylation is another twentieth century refinery innovation, and developments in petroleum processing in the late 1930s and during World War II were directed toward production of high-octane liquids 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, but motor-gasoline quality requirements rose sharply. Wherever practical, refiners shifted the use of alkylate to premium motor fuel. To aid in the improvement of 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.

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The alkylation reaction as now practised in petroleum refining is the union, through the agency of a catalyst, of an olefin (ethylene, propylene, butylene, and amylene) with *iso*-butane to yield high-octane branched-chain hydrocarbons in the gasoline boiling range. Olefin feedstock is derived from the gas produced in a catalytic cracker, while *iso*-butane is recovered by refinery gases or produced by catalytic butane isomerization.

To accomplish this, either ethylene or propylene is combined with *iso*-butane at 50°C to 280°C (125°F to 450°F) and 300 to 1000 psi (20 to 68 atm) in the presence of metal halide catalysts such as aluminum chloride. Conditions are less stringent in catalytic alkylation; olefins (propylene, butylenes or pentylenes) are combined with *iso*-butane in the presence of an acid catalyst (sulfuric acid or hydrofluoric acid) at low temperatures and pressures (1°C to 40°C, 30°F to 105°F and 14.8 to 150 psi; 1 to 10 atm) (Figure 14.14).

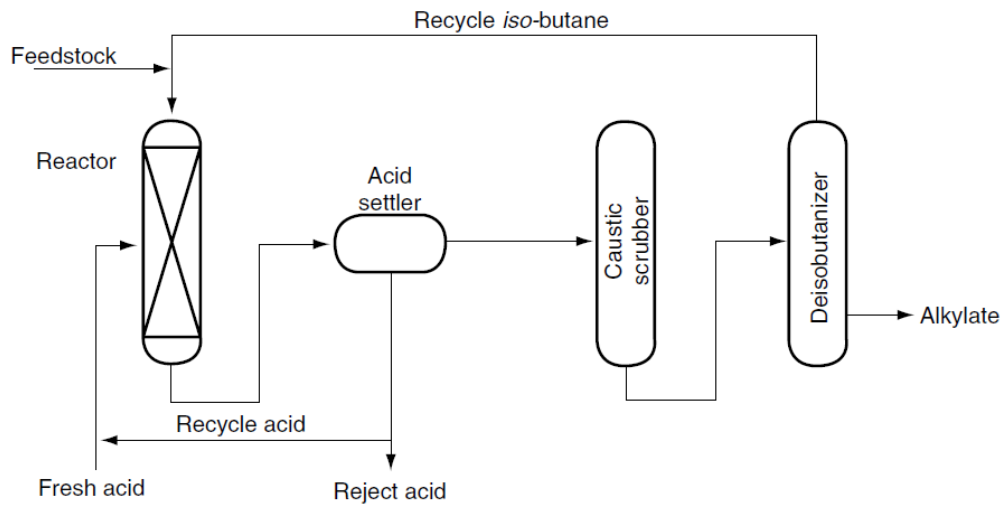


FIGURE 14.14 An alkylation unit (sulfuric acid catalyst). (From OSHA Technical Manual, Section IV, Chapter 2, Petroleum Refining Processes.)

14.10.3 CATALYSTS

Sulfuric acid, hydrogen fluoride, and aluminum chloride are the general 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. The acid is pumped through the reactor and forms an air emulsion with reactants, and the emulsion is maintained at 50% acid. The rate of deactivation varies with the feed and *iso*-butane charge rate. Butene feeds cause less acid consumption than the 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 as an aluminum chloride or hydrocarbon complex. Hydrogen fluoride is used for alkylation of higher-boiling olefins and the advantage of hydrogen fluoride is that it is more readily separated and recovered from the resulting product.