

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 those 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.



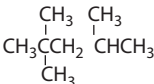
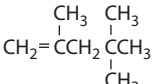
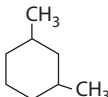
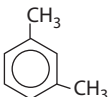
## 24.2 REFORMING

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 24.1). 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

**TABLE 24.1**  
**Structure and Octane Numbers of Selected Hydrocarbons**

Compound	<i>n</i> -Hexane	1-Hexane	Cyclohexane	Benzene
Formula	C <sub>6</sub> H <sub>14</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>6</sub>
Structure	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	CH <sub>2</sub> -CH(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>		
RON	25	76	83	123 (est.)
Compound	2,2,4-Trimethylpentane (Isooctane)	2,4,4-Trimethyl-1-pentane (Isooctane)	Cis 1,3-dimethyl-cyclohexane	1,3-Dimethylbenzene
Formula	C <sub>8</sub> H <sub>18</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>8</sub> H <sub>16</sub>	C <sub>8</sub> H <sub>10</sub>
Structure				
RON	100	106	72	118

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  $(R + M)/2$ . RON and MON are two different test methods that quantify the antiknock qualities of a fuel. Since the MON is a test under more severe conditions than the RON test, for any given fuel, the RON is always higher than the MON.

Unfortunately, the desulfurized light and heavy naphtha fractions of crude oils have very low octane numbers. The heavy naphtha fraction has an octane number on the order of  $50 (R + M)/2$ . 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 (Chapter 26), 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 24.2). The ether derivatives are also high-octane oxygenates (Table 24.3) 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

**TABLE 24.2**  
**Oxygenates Allowed in Gasoline**

Oxygenate	Maximum, Vol %
Methanol	3
Ethanol	5
Isopropyl alcohol	10
Isobutyl alcohol	10
<i>tert</i> -Butyl alcohol	7
Ether (5 or more C atoms)	15
Other oxygenates	10

**TABLE 24.3**  
**Various Oxygenates Used in Gasoline**

Name	Formula	Structure	Oxygen Content Mass %	Blending Research Octane Number (BRON)
Ethanol (EtOH)	$C_2H_6O$	$CH_2CH_2OH$	34.73	129
Methyl tertiary-butyl ether (MTBE)	$C_5H_{12}O$	$\begin{array}{c} CH_3 \\   \\ CH_3O-C-CH_3 \\   \\ CH_3 \end{array}$	18.15	118
Ethyl tertiary-butyl ether (ETBE)	$C_6H_{14}O$	$\begin{array}{c} CH_3 \\   \\ CH_3CH_2O-C-CH_3 \\   \\ CH_3 \end{array}$	15.66	119
Tertiary-amyl methyl ether (TAME)	$C_6H_{14}O$	$\begin{array}{c} CH_3 \\   \\ CH_3O-C-CH_2CH_3 \\   \\ CH_3 \end{array}$	15.66	112

as iso-butene and iso-pentene, under the influence of acid catalysts. In the mid-1990s methyl-*t*-butyl ether (MTBE) (Table 24.3), 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.

Environmental issues with MTBE have made it more desirable to dimerize iso-butene from the catalytic cracking unit rather than etherify it. Fortunately, iso-butene *dimerization* may be achieved with minimal modifications to existing MTBE plants and process conditions, using the same acidic catalysts. Where olefin levels are not restricted, the extra blending octane boost of the *di-isobutylene* can be retained. Where olefin levels are restricted, the *di-isobutylene* can be *hydrotreated* to produce a relatively pure iso-octane stream that can supplement alkylate for reducing olefins and aromatics in reformulated gasoline.

### 24.2.1 THERMAL REFORMING

Thermal reforming was a natural development from thermal cracking, since reforming is also 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 (Nelson, 1958).

In 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 reformat. The higher octane number of the product (*reformat*) 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–1140°F) and pressures in the range 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 *reformat* 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 reformat is relatively low. For example, a gasoline with an octane number of 35 when reformed at 515°C (960°F) yields 92.4% of 56 octane reformat; when reformed at 555°C (1030°F) the yield is 68.7% of 83 octane reformat. 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 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 ( $\text{CH}_3\text{CH}=\text{CH}_2$ ), which is associated with propane in the  $\text{C}_3$  fraction, and butylene ( $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$  and/or  $\text{CH}_3\text{CH}=\text{CHCH}_3$ ) and iso-butylene [ $(\text{CH}_3)_2\text{C}=\text{CH}_2$ ], which are associated with butane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ) and iso-butane [ $(\text{CH}_3)_2\text{CHCH}_3$ ] in the  $\text{C}_4$  fraction. When the  $\text{C}_3$  and  $\text{C}_4$  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  $\text{C}_3$  and  $\text{C}_4$  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.

### 24.2.2 CATALYTIC REFORMING

Like thermal reforming, *catalytic reforming* converts low-octane gasoline into high-octane gasoline (reformate) (Kelly et al., 1997). Although thermal reforming can produce reformate with an RON in the range 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 1953–1959 time period (Bland and Davidson, 1967; Riediger, 1971). As a result, thermal reforming is now somewhat obsolete (Schwarzenbek, 1971).

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 naphthene 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 a 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 24.1) which operate at temperatures of  $\sim 480^\circ\text{C}$  ( $900^\circ\text{F}$ ). The hydrocarbons are reheated by direct-fired furnaces in

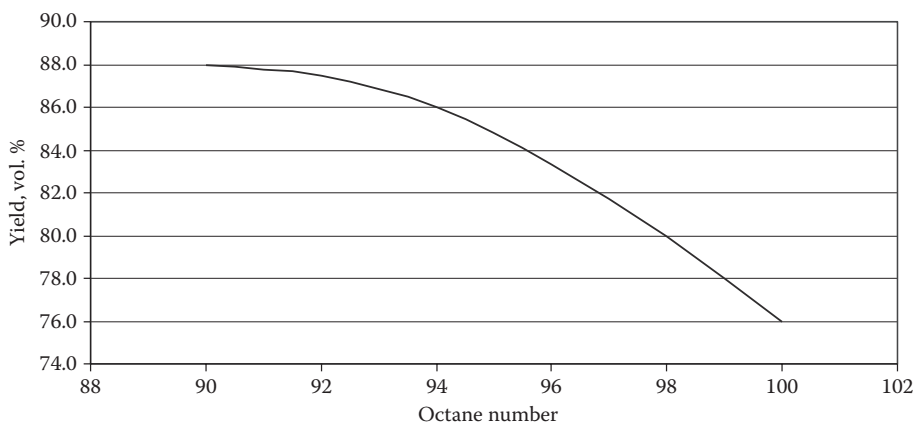


FIGURE 24.1 Octane number and reformate yield.

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 on-stream in series while one or more is being regenerated. The on-stream 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 24.4) 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 non-precious 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 semi-regenerative process is the simplest configuration but does require that the unit be shutdown 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.

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**TABLE 24.4**  
**Composition of Catalytic Reformer**  
**Product Gas**

Constituent	% by Volume
Hydrogen	75–85
Methane	5–10
Ethane	5–10
Ethylene	0
Propane	5–10
Propylene	0
Butane	<5
Butylenes	0
Pentane plus	<2

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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 one catalyst; and cracking, isomerization, and olefin polymerization 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 ( $H_2S$ ) 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 gasoline 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, which 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 about 190°C (375°F), partially because of increased coke deposition on the catalyst as the end point during processing at about 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.

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 by-product.

#### 24.2.2.1 Fixed-Bed Processes

Fixed-bed, continuous catalytic reforming can be classified by catalyst type: (1) cyclical regenerative with non-precious 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 on-stream.

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.

#### 24.2.2.1.1 Hydroforming

The Hydroforming process made use of molybdena–alumina ( $\text{MoO}_2\text{--Al}_2\text{O}_3$ ) 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 at  $400^\circ\text{C}$ – $540^\circ\text{C}$  ( $900^\circ\text{F}$ – $1000^\circ\text{F}$ ) 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  $205^\circ\text{C}$  ( $400^\circ\text{F}$ ).

After 4–16 h on process cycle, the catalyst was regenerated. This was done by burning carbon deposits from the catalyst at a temperature of  $565^\circ\text{C}$  ( $1050^\circ\text{F}$ ) 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.

#### 24.2.2.1.2 Iso-Plus Houdriforming

This is a combination process using a conventional Houdriformer operated at moderate severity for product production (Table 24.5), 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  $\text{C}_3$  and  $\text{C}_4$  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.

#### 24.2.2.1.3 Platforming

The first step in the Platforming process (Figure 24.2; Dachos et al., 1997) is preparation of the naphtha feed. For motor gasoline manufacture, the naphtha feed is distilled to separate a fraction boiling in the  $120^\circ\text{C}$ – $205^\circ\text{C}$  ( $250^\circ\text{F}$ – $400^\circ\text{F}$ ) range. Since sulfur adversely affects the platinum catalyst, the naphtha fraction may be treated to remove sulfur compounds. Otherwise, the hydrogen-rich

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**TABLE 24.5**  
**Feedstock and Product Data for the**  
**Houdriforming Process**

<b>Feedstock</b>	
API	52.6
Boiling range	
$^\circ\text{C}$	92–192
$^\circ\text{F}$	197–377
Composition, % v/v	
Paraffins	53
Naphthenes	38
Aromatics	9
<b>Product</b>	
Research octane number	100
Composition, % v/v	
Paraffins	21
Naphthenes	2
Aromatics	77

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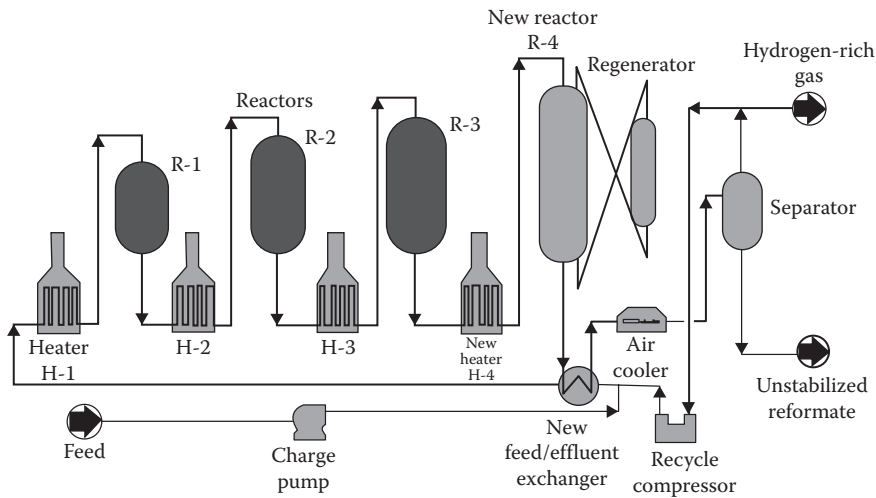


FIGURE 24.2 Catalytic reforming process.

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 reformat stream (Table 24.6). The catalyst is composed of 1/8 in. pellets of alumina containing chlorine and about 0.5% platinum. Each pound of catalyst reforms up

**TABLE 24.6**  
**Feedstock and Product Data for the Platforming Process**

Feedstock			
API	59.0		
Boiling range			
°C	92–112		
°F	197–233		
Composition, % v/v			
Paraffins	69		
Naphthenes	21		
Aromatics	10		
Process operation	Semiregenerative	Continuous	
Pressure			
Psi	295	123	49
kPa	2040	850	340
Product			
Research octane number	100	100	100
Composition, % v/v			
C <sub>5+</sub>	70	78	82
Aromatics	46	55	58
Hydrogen, % w/w	2	3	4



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 ( $\text{Al}_2\text{O}_3$ ), silica–alumina ( $\text{SiO}_2\text{--Al}_2\text{O}_3$ ) 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 the mild conditions of the guard-bed operation.

#### 24.2.2.1.4 Powerforming

The cyclic *Powerforming* process is based on frequent regeneration by 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 shutdown 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 reformat (Table 24.7). Choice between the semi-regenerative process and the cyclic process depends on the size of plant required, type of feedstocks available, and the octane number needed in the product.

#### 24.2.2.1.5 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  $27^\circ\text{C}$  ( $50^\circ\text{F}$ ) 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 avoided. The glycol solvent in the aromatic extraction section is designed to extract low-boiling high-octane iso-paraffins as well as aromatics.

#### 24.2.2.1.6 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 200–600 psi and  $315^\circ\text{C}$ – $450^\circ\text{C}$  ( $600^\circ\text{F}$ – $900^\circ\text{F}$ ). The catalyst used in the selectoforming process is non-noble

**TABLE 24.7**  
**Feedstock and Product Data for the**  
**Powerforming Process**

Feedstock		
API	57.2	
Composition, % v/v		
Paraffins	57	
Naphthenes	30	
Aromatics	13	
Process operation	Semiregenerative	Cyclic
Product		
Research octane number	99	101
Composition, % v/v		
$\text{C}_1\text{--C}_4$	13	11
$\text{C}_{5+}$	79	79
Hydrogen, % w/w	2	3

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.

### 24.2.2.2 Moving-Bed Processes

#### 24.2.2.2.1 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 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.

#### 24.2.2.2.2 Thermoform Catalytic Reforming

This is also a moving-bed process that uses a synthetic bead co-precipitated chromia (CrO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) catalyst. Catalyst-naphtha ratios have little effect on product yield or quality when varied over a wide range. The catalyst flows 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.

### 24.2.3 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 (Mo<sub>2</sub>O<sub>3</sub>, 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 about 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.