REVIEW OF CATALYTIC REFORMING

Catalytic reforming is a refining process that uses selected operating conditions and selected catalysts to convert naphthenes and paraffins to aromatics and isoparaffins. Hydrocarbon molecules are reconstructed, or reformed, without changing their carbon numbers (Sterba et al., 1976). The reactions, which include isomerization, hydrogenation, dehydrocyclization, and dehydrogenation, among others, lead to a marked improvement in fuel quality as measured by the octane number, as described in chapter 3.

This chapter reviews an introductory description of the .products from reforming, feedstocks for reforming, catalytic reforming for aromatics, and catalytic reformers, together with detailed accounts of the commercial processes.

2.1 Products from Reforming

Catalytic reforming in a petroleum refinery produces high-octane blending stock for motor fuel and also produce high-value aromatic hydrocarbons such as benzene, toluene, and xylenes (BTX). Hydrogen is a valuable reforming product and its yield is the source of part or all of the hydrogen used for hydrotreating, hydrocracking, or hydrorefining processes.

A reformer that is operated to make high-octane blending stock is a motor fuel reformer. When operated to make aromatics, it is a BTX refomer. The primary product from reforming is called reformate. Because reformer feedstocks contain paraffins, a BTX reformer yields a mixture of aromatics and paraffins; further processing such as extraction is necessary to recover aromatics of marketable purity. After removal of aromatics from the reformate, the remainder is called raffinate. In some refineries, a catalytic reformer may operate part time as a motor fuel unit and part time as a BTX unit. The position of the catalytic reforming unit (or cat reformer) in a typical fuels refinery processing scheme is shown in Figure 2-1.

2.2 Feedstocks for Reforming

Because gasoline and distillates are usually higher-priced refinery products, refinery processing units are designed to maximize conversion of crude oil to these products. Two of the lighter (lower boiling) streams from crude distillation are light straight-run (lt. st. run) naphtha and heavy straight-run (hvy. st. run) naphtha. Both these streams are in the gasoline boiling range (about 80-400 °F). When the stream goes directly to motor fuel, it is called gasoline in refiner jargon. If the stream (that is, the feedstock) is charged to a process unit, it is generally called naphtha.

In Figure 2-1, the light straight-run (80-180 °F boiling range) fraction is hydrodesulfurized and blended directly to gasoline. The pentanes and hexanes in this boiling range are not converted to the desired aromatics in a cat reformer because
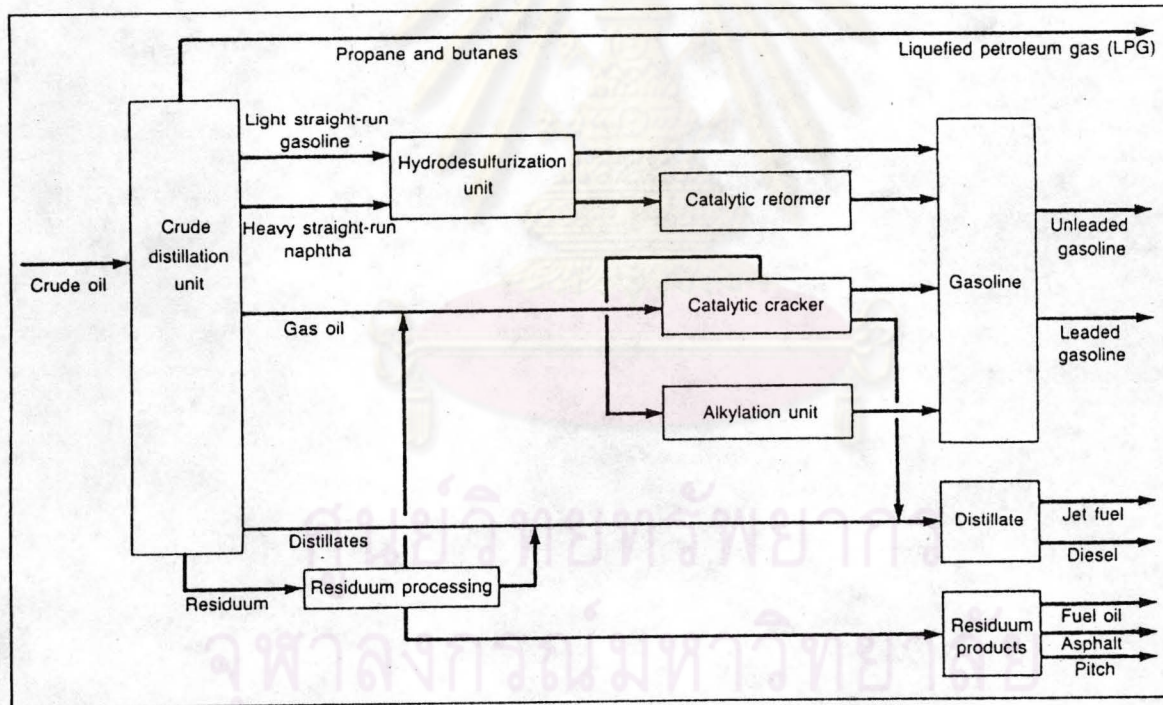
Fig. 2−1   Motor fuel refinery with catalytic reforming (Little, 1985)

they are not good cat reforming feedstock. The heavy straight-run naphtha is hydrodesulfurized and then charged to the cat reformer. The product from the cat reformer is blended with other refinery stocks to make finished gasoline.

Thus, the feedstock to the cat reformer from the crude unit is gasoline boiling range hydrocarbons, which are in the raw crude. These are separated from other crude hydrocarbons by fractionation. The gasoline (hvy. st. run naphtha), obtained directly from crude oil, is almost always of such low octane number that a refiner cannot use it in motor fuel. The other refinery blending stocks are usually not high enough in octane number to raise the motor fuel blends to the required octane number specification. So the purpose of the cat reformer is to raise the octane number of gasoline to a higher octane number.

2.3 Catalytic Reforming for Aromatics

Although catalytic reformers are most widely used for increasing octane number, many refiners find it economical to reform for certain aromatic hydrocarbons that can be sold as petrochemicals, usually at a much higher price than gasoline. These aromatics are benzene, toluene, and xylenes.

Cat reformers are particularly suited to yield these aromatics because refinery naphtha feedstocks contain a significant amount of naphthenes, which in the reformer are dehydrogenated to aromatics, and of paraffins, which are cyclized to aromatics. Operating conditions in reformer reactors are such that aromatics, once formed, are relatively stable and resist destruction or conversion to nonaromatics. A procedure for aromatics production follows.

The refinery process scheme of Figure 2-1 must be changed
to produce marketable aromatics. A new BTX catalytic reformer
would be added. The installation of fractionation and extraction
facilities would be required to separate and purify the
benzene, toluene, and xylenes to specification-grade aromatics.
The feedstock to the BTX reformer would likely be a straight-run
naphtha. The refinery configuration would then be as shown in
Figure 2-2.

2.4 Process Design of Catalytic Reformers

The process design of a catalytic reforming unit follows
the basic configuration of most refinery catalytic process
units. The generalized flow scheme is:

Feed Preparation
|
Temp. Control
|
Reactor(s)
|
Product Recovery
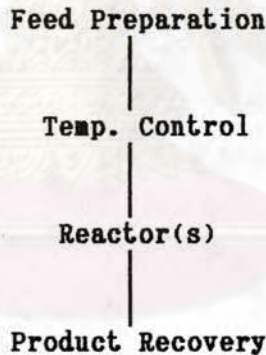
Each component of the flow scheme is engineered to the
needs of a particular process. For example, the reactor of a
fluid cat cracker (FCC) differs in size, shape, and metallurgy
from that of a catalytic reformer, but each is designed so
desired reactions can take place.

The reaction section of an FCC unit rarely has more than
one reactor. A catalytic reformer may have from three to five
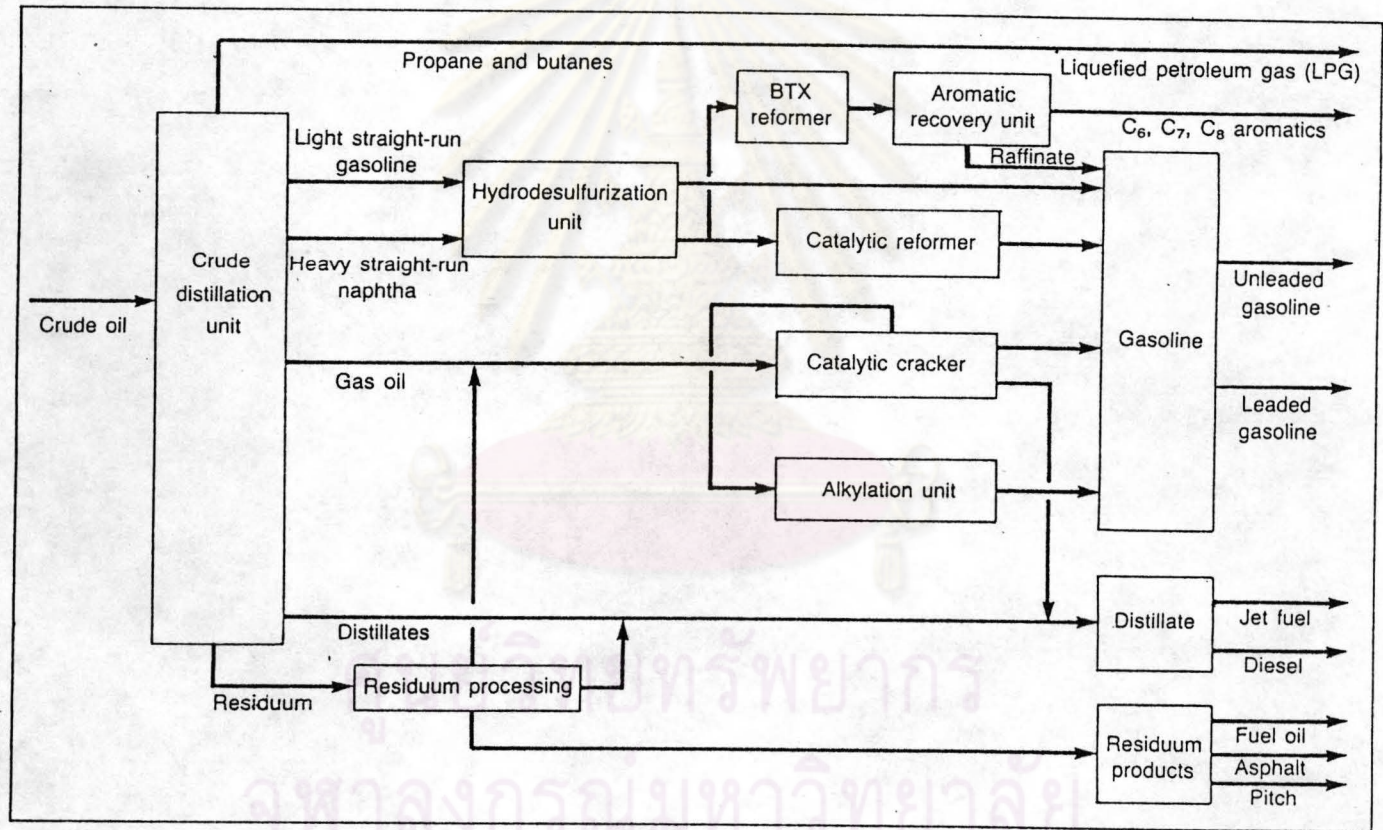reactors in its reaction section. Variations within a unit are

Fig. 2-2   Refinery with motor fuel and BTX catalytic reforming   (Little, 1985)

necessary, but the basic flow scheme is still recognizable.

Figure 2-3 shows the basic elements of a catalytic reformer for a step-by-step description of the process.

2.4.1 Feed Preparation

The charge, or feedstock, to the cat reformer is a naphtha that has been processed in a feed-preparation unit to remove contaminants such as sulfur, nitrogen, arsenic, and lead. These contaminants are either temporary or permanent poisons to the catalyst and must be eliminated for satisfactory catalyst performance.

The feed-preparation unit itself is a catalytic unit using a cobalt-molybdenum (Co-Mo) or a nickel-molybdenum (Ni-Mo) catalyst. Hydrogen is included with the feed to the feed-preparation units. These feed-preparation units are called hydrodesulfurization (HDS) units, or hydrotreaters.

After passing over the Co-Mo or Ni-Mo catalyst, the naphtha goes to a stripper or fractionator that removes the hydrogen sulfide, ammonia, water, and light hydrocarbons formed in the hydrotreater reactor. The feed stripper could be either on the tail end of the hydrotreater or on the front end of the reformer. In the flow scheme (Figure 2-3), the reformer naphtha charge is fractionated to the correct end point, probably at the crude unit. Only the initial boiling point is adjusted in the feed stripper.

2.4.2 Temperature Control

The reactor charge must be raised to the proper temperature for the reforming reactions to occur when the charge contacts the catalyst. As shown in Figure 2-3, total

reactor charge is heated, at first by heat exchange with effluent from the last reactor, and is finally brought up to the NO. 1 reactor inlet temperature in the charge heater. (Effluent is total vapor flowing out of the last reactor.)

The reactor effluent-to-feed exchanger is one key to energy conservation in a catalytic reformer. The reactor effluent, which may run at temperature as high as 950-1,000 °F, must be cooled to 90-125 °F for flash separation -separation of vapor and liquid without fractionation- of hydrogen from the reformate.

The reactor effluent-to-feed exchanger is sometimes called the combined feed exchanger. This exchanger cools reactor effluent and, at the same time, adds heat to the incoming total reactor charge. In reformers built in the 1950s and 1960s, this heat exchange consists of several banks of heat exchangers, arranged for parallel flow. Newer units use one large single-pass vertical exchanger.

2.4.3 Reactor

Catalytic reforming is a vapor-phase process. After passing through the reactor effluent-to-feed exchanger and the charge heater, the total reactor charge is 100% vapor and is ready to contact the reforming catalyst of reaction temperature.

The flow scheme (Figure 2-3) shows three reactors. Reformers have been built with four or five reactors. Although the Figure 2-3 flow sheet shows all reactors of the same size, reactors sizes are different in many units, with the smallest reactor in the No. 1 position and the largest as the last reactor.
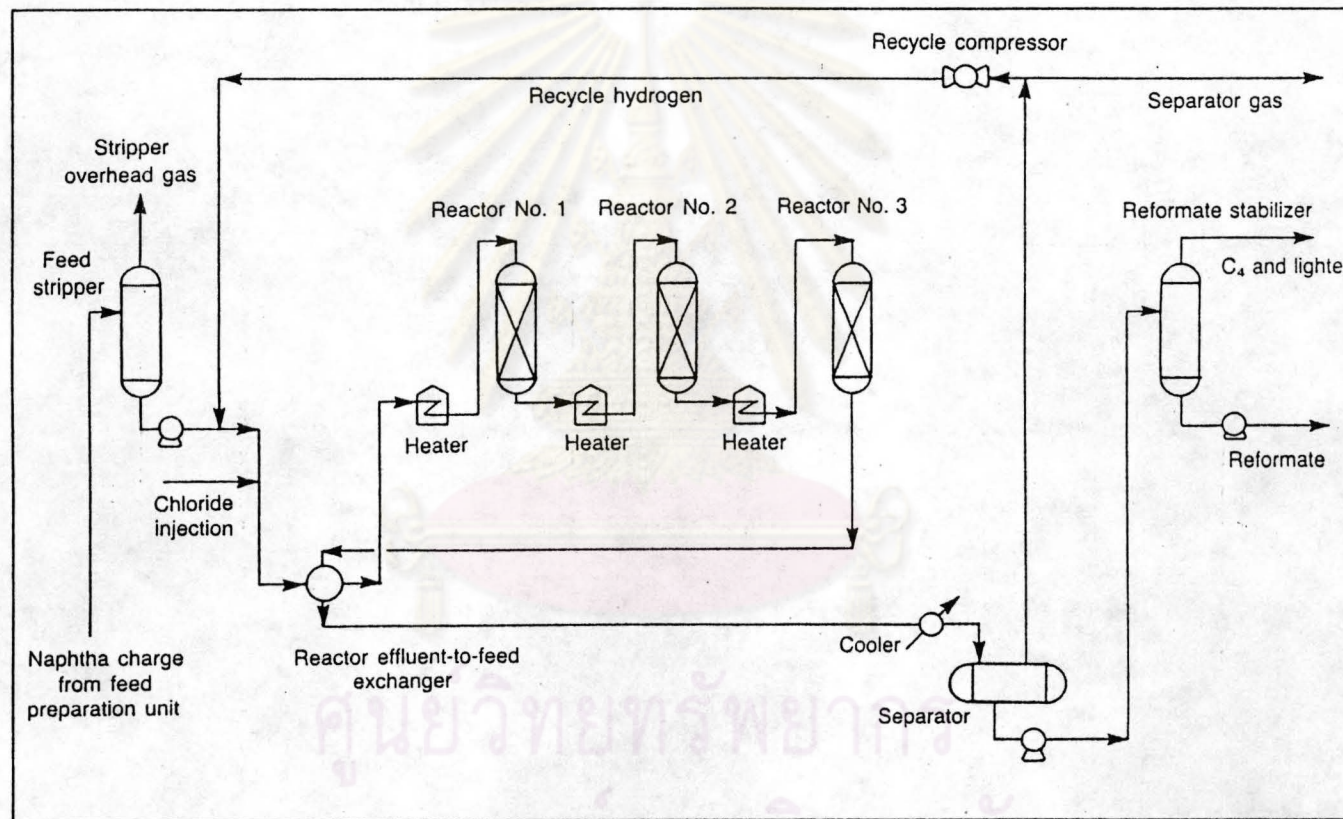
Fig.2-3 Process flow scheme of a catalytic reformer (Little, 1985)

Some units originally built with three reactors have been revamped by adding one or more reactors. The additional reactors increase catalyst volume, which permits increased time between catalyst regenerations, increased charge rate, or higher-octane-number reformate.

The major reactions, such as dehydrogenation, are endothermic and very fast. The first contact with catalyst causes a rapid decrease in temperature. Very quickly the temperature in the reactor drops so low that the reaction rate becomes too slow for commercial operation. It is not unusual in the No. 1 reactor to have a temperature decrease between inlet and outlet of 180-280 °F. For this reason, catalytic reformers are designed with multiple reactors and with heaters between reactors to maintain reaction temperatures at operable levels.

As total reactor charge passes through the reactor train (three or more reactors in series flow), the reactions become less and less endothermic and temperature differential across the reactors decrease. In fact, the last reactor may show zero endotherm or, in some cases, a small temperature increase.

The flow scheme of Figure 2-3 shows a separate heater for each reactor. A number of units have heaters arranged this way, but there are also units with two or more heating coils in one large heater. The coils are separated within the heater by a bridgewall arrangement. A bridgewall is firebrick between heating coils.

2.4.4 Product Recovery

The effluent from the last reactor, at temperatures from 950-1000 °F, is cooled by heat exchange with the reactor

charge, then further cooled by air and water exchangers to 100-125 °F.

The stream then enters the separator vessel (called the product separator), where flash separation of hydrogen and some of the light hydrocarbons- primarily methane and ethane takes place. The flashed vapor, containing 60-90 mol % hydrogen, passes to a compressor and then circulates to join the naphtha charge from the feed stripper. The hydrogen circulating to the naphtha charge is called hydrogen recycle. Excess hydrogen from the separator is yielded to fuel gas or to hydrogen-consuming units in the refinery hydrotreaters.

The separator liquid, comprised mostly of the desired reformate product but also containing hydrogen, methane, ethane, propane, and butanes, is pumped to the reformate stabilizer or fractionator. Reformate off the bottom of the stabilizer is sent to storage for gasoline blending or, in the case of a BTX reformer, to an aromatic-extraction unit. Some refiners separate the stabilizer to leave sufficient butane in the reformate to meet Reid vapor pressure (Rvp) specifications when making gasoline blends.

2.5 Reformer Classification

The flow diagram of Figure 2-3 is purposely simplified. This reformer can be classed as one of four types of reformers generally used in the petroleum industry. The four reformer classifications are as follows.

1. Semiregenerative. This means the reformer processes feedstock for a time and then shuts down for regeneration and

rejuvenation of the catalyst. The time between regeneration is called cycle and is expressed in months. (A cycle is sometimes reported as barrels of feed per pound of catalyst.) Cycles vary from three months to three years. A cycle may be terminated for a number of reasons, but the most common is poor catalyst performance. This shows up as a loss of reformate yield or as too high reactor-inlet temperatures approaching the maximum allowable for reactor metallurgical construction.

The generation procedure, which includes rejuvenation, restores the catalyst to fresh-catalyst condition. The reformer, as a semiregenerative unit, will have a few connections not shown in Figure 2-3 for regeneration purposes. These connections allow addition of air and nitrogen or oxygen and nitrogen, injection of hydrogen chloride, instrumentation, and neutralizing solution to be circulated. The catalyst in a semiregenerative unit is expected to retain its usefulness over multiple regenerations and to have an ultimate life of 7-10 years or longer.

2. Nonregenerative. Some reformers do not regenerate catalyst because the cycle is long enough for the refiner to justify replacing – instead of regenerating – the catalyst. The reformer of Figure 2-3 can easily operate in this manner.

3. Cyclic. The unique feature of a cyclic reformer is that it has a special valving-and-manifold system so any reactor can be isolated and regenerate catalyst while the other reactors are reforming. In contrast to a semiregenerative reformer, which requires a shutdown of the entire unit to regenerate catalyst, a cyclic unit can continue operation over long periods between shutdowns. Note, however, that a cyclic unit can operate as a semiregenerative reformer.

Since the usual reason for regeneration is to burn off carbon that has fouled the catalyst, a cyclic unit can reform at lower pressure and higher severity than semiregenerative units, even though rapid coking results. The cycles (switching reactors in a cyclic unit) vary from a few hours to weeks or months. Although the reactors can be operated in any sequence, the last reactor is usually the one taken off-line for regeneration.

4. Moving-bed or continuous catalyst regeneration. These units, as the names imply, permit the catalyst to be moved continuously through the reactors, to be withdrawn from the last reactor, to be regenerated in a regeneration section, and to be returned to the first reactor as fresh catalyst. Compared to a fluid cat-cracking unit, the rate of catalyst flow in a reformer is very slow. Whereas FCC catalyst circulation is measured in tons per hour, reforming catalyst circulation is a few hundred or a few thousand pounds per hour.

The moving-bed reformer operates in a semiregenerative mode by shutting down the regeneration section. In fact, a number of new units are designed to operate initially as semiregenerative, with the provision that a regeneration section can be added later.

2.6 Commercial Processes

2.6.1 Historical development

The first catalytic reforming went on stream in November 1940 at the Pan American Refining Corp. (now American Oil Co.) refinery at Texas City, Texas. Hydroforming, the name of the new technology, was a fixed-bed cyclic unit with two reactors on regeneration and two on process. The catalyst was about 9 wt%

molybdenum oxide on activated alumina granules or pellets.

Catalytic reforming was a logical outcome of catalytic developments in petroleum processing in the 1930s. Thermal cracking of naphtha, gas oil, and residuum dominated refinery processing in the early 1930s. Houdry catalytic cracking, a fixed-bed catalytic cracking process, conceived and developed by Eugene J. Houdry, went on stream in 1973 at the Sun Oil Co. refinery in Marcus Hook, Pennsylvania.

The article on Houdry catalytic cracking indicates Sun Oil was receptive to the Houdry process because Sun was one of the few companies not using tetraethyllead (TEL) as octane-number booster, and they were concerned about meeting competition. At the same time, some companies foresaw that, in the event of war, there would be a far greater demand for high-octane aviation gasoline than thermal cracking of naphtha could produce.

Hydroforming was the only catalytic reforming process in use during World War II. Three units were built before the war, and five more were constructed during the war. Catalytic reforming made an important contribution to the war effort, producing toluene for trinitrotoluene (TNT, for explosives) and for aviation gasoline. Cycloversion, a process developed by Phillips Petroleum Co. about 1940, raised the octane number of straight-run naphtha by desulfurization over a bauxite catalyst. About 1943, the units were made cyclic, to combine desulfurization and reforming. Reforming was mild.

Platforming (a combination of platinum and reforming) was announced by Universal Oil Products Co. (now UOP Inc.) in March 1949. This process was the first commercial reforming technology to use a catalyst containing platinum. Platformers did not regenerate. The platinum catalyst operated about 9-18 months,

then was removed and replaced with new catalyst. The usual reason for replacement was loss of reformate yield.

Platforming technology was first used commercially in October 1949 on a revamped thermal reformer at Old Dutch Refining Co.'s refinery in Muskegon, Michigan. Three hours after start-up, the unit went down because of high reactor-shell temperature. The problem was soon solved, and the unit made about a nine month run.

As it turned out, catalytic reforming was just getting a good start. Within five years of the announcement of the UOP process, nine new catalytic reforming processes were introduced to the petroleum industry. A chronological development of catalytic reforming is shown in Table 2-1.

2.6.2 Licensed Reforming Processes

At least six reforming processes are available for license with in the United Stated. Most are available either in semiregerative form or in cyclic or continuous form. The processes are listed in Table 2-2 in alphabetical order and are presented in that sequence.

(1) IFP Catalytic Reforming.

The IFP catalytic reforming process is licensed by Institute Francais du Petrol, which first developed a semiregenerative technology, followed a few years after by a continuous regenerative one. This last process (Figure 2-4) is characterized by continuous circulation of the catalyst by the moving-bed system. Catalyst regeneration is carried out in a fixed-bed regenerator using the same procedures as the one duly proven in the semiregenerative process.

TABLE 2-1
Catalytic reforming processes (Little, 1985)

Process	Developed by[a]	Date Process Announced	Date of First Commercial Use	Type of Process
Fixed-bed Hydroforming	Standard Oil Development Co., M. W. Kellogg Co., and Standard Oil Co. (Indiana)	1939	March 1940	Cyclic
Platforming	Universal Oil Products Co.	March 1949	October 1949	Semiregenerative
Catforming	Atlantic Refining Co.	February 1951	August 1952	Semiregenerative
Houdriforming	Houdry Process Corp.	May 1951	November 1953	Semiregenerative
Thermofor Catalytic Reforming	Socony-Vacuum Oil Co. Inc.	May 1951	March 1955	Moving-bed
Fluid Hydroforming	Standard Oil Development Co. and M. W. Kellogg Co.	May 1951	December 1952	Fluid Bed
Hyperforming	Union Oil Co. of California	February 1952	May 1955	Moving-bed
Orthoforming	M. W. Kellogg Co.	July 1953	April 1955	Fluid Bed
Ultraforming	Standard Oil Co. (Indiana)	November 1953	May 1954	Semiregenerative
Sovaforming	Socony-Vacuum Oil Co.	January 1954	November 1954	Semiregenerative
Powerforming	ESSO Research and Engineering Co.	March 1956	1956	Cyclic or Semiregenerative
Magnaforming	Engelhard and Atlantic Richfield Co.	1965	May 1967	Semiregenerative
IFP Reforming[b]	Institut Francais du Petrole	1960	1961	Semiregenerative
Rheniforming	Chevron Research Co.	1967	January 1970	Semiregenerative
Continuous Catalyst Regeneration Platforming	UOP Process Div. of UOP Inc.	1971	January 1971	Moving-bed

Notes: Phillips Petroleum Co.'s perco cycloversion process was on stream in 1940, raising octane number of straight-run naphtha primarily by desulfurization. By 1944 the process, using bauxite as catalyst, was expanded to a cyclic unit, raising octane number by combined desulfurization and reforming.

The above list does not include combination processes, that is, catalytic reforming plus aromatic extraction.

This tabulation does not include announcements of better catalysts. For example, the RD–150 catalyst of Baker and Co. with Sinclair Refining Co. (1954), or the new bimetallic catalysts announced from 1970 to 1980.

[a] Process developers are identified by company name at time of the process's announcement or its going into commercial service. Some companies have since changed names or merged with others. Companies offering processes for license in 1984 (Appendix V) are reviewed in chapter 7; their addresses are listed in Appendix VI.

[b] IFP continuously regenerative process was announced in 1968. The first unit was licensed in Italy in 1968.

TABLE 2-2

Commercial catalytic reforming processes (Little, 1985).

Process Name	Licensor	Process Type
IFP Catalytic Reforming	Institut Francais du Petrole	Semiregenerative, moving bed
Magnaforming	Engelhard Industries Div. of Engelhard Corp.	Semiregenerative, semicyclic
Platforming	UOP Process Div. of UOP Inc.	Semiregenerative, continuous catalyst regeneration
Powerforming	Exxon Research and Engineering Co.	Cyclic, semiregenerative, semicyclic
Rheniforming	Chevron Research Co.	Semiregenerative
Ultraforming	Standard Oil Co. (Indiana) Amoco Research and Development Dept.	Cyclic, semiregenerative, semicyclic

1. Upper hopper
2. Lift pot
3. Surge drum, used catalyst
4. Regeneration reactor
5. Surge drum, fresh catalyst
6. Heater
7. Heat exchanger
8. Air cooler
9. Regeneration gas compressor
10. Heater
11. Lower hopper
12. Dryer
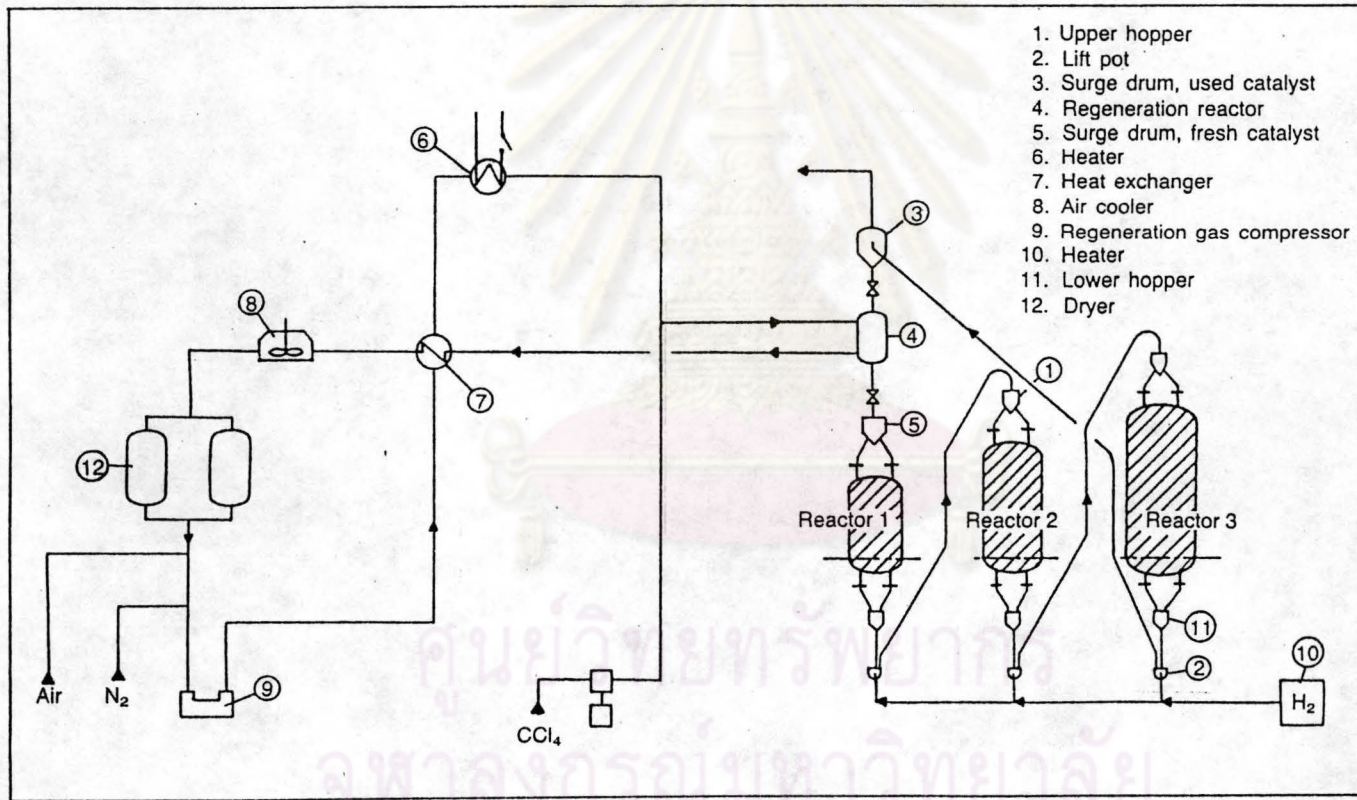
Fig. 2-4 IFP continuous regenerative system (Little, 1985)
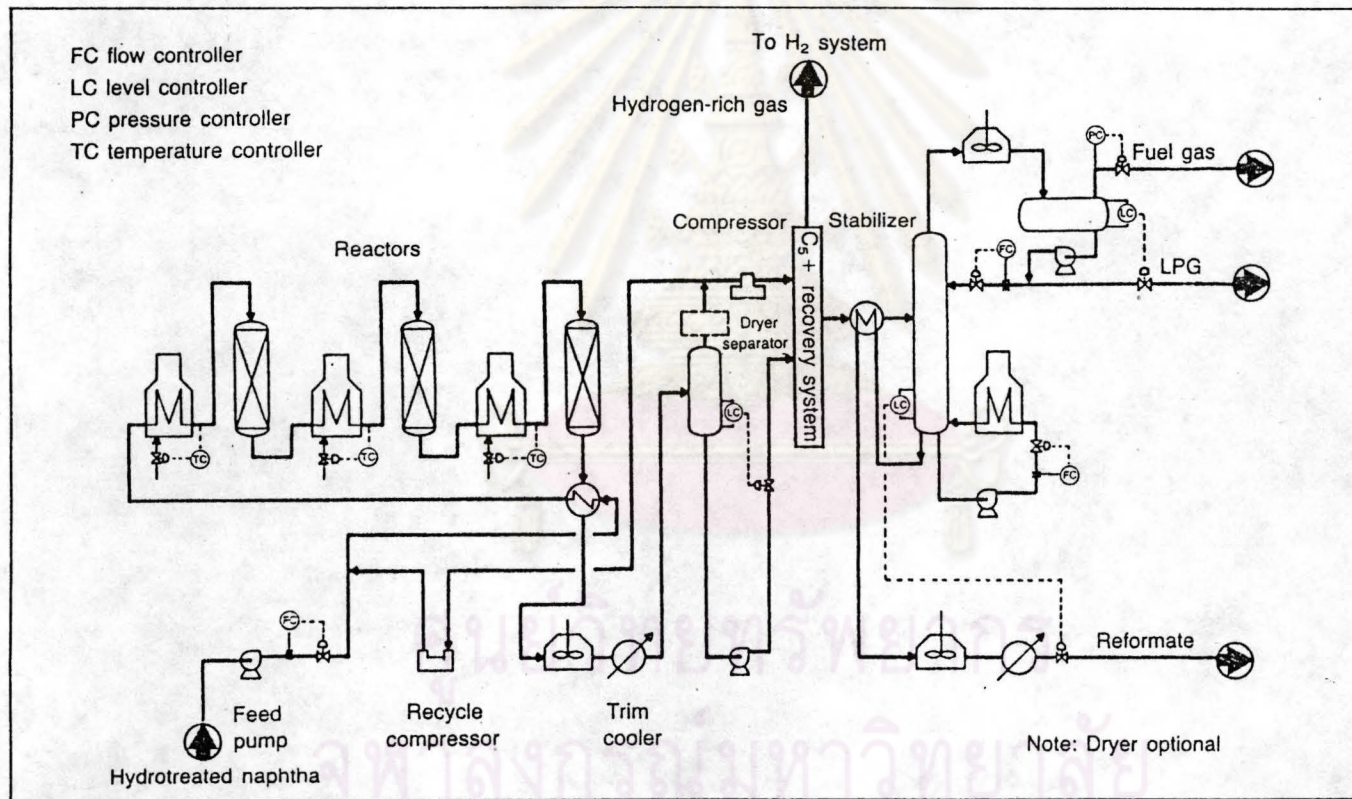
Fig. 2-5 IFP semiregenerative reformer.

Labels within figure:

FC flow controller
LC level controller
PC pressure controller
TC temperature controller

Reactors
Compressor
Stabilizer
To H₂ system
Hydrogen-rich gas
Dryer separator
C₅ + recovery system
Fuel gas
LPG
Feed pump
Recycle compressor
Trim cooler
Reformate
Hydrotreated naphtha
Note: Dryer optional

In the semiregenerative process (Figure 2-5) a mean reactor pressure of 200 psig provides a acceptable cycle length with most feedstock. With regenerative process this pressure can be reduced to as low as 110 psig to take advantage of better yields.

(2) Magnaforming

Magnaforming is licensed by Engelhard Industries, Div. of Engelhard Corp. The process design is based on an optimization of catalyst distribution, reactor inlet temperature, gas recycle ratio, and operating pressure. Magnaforming design principles are shown in the process flow scheme of Figure 2-6. The increasing sizes of the reactors from front end to tail end indicate controlled catalyst distribution. The divided hydrogen recycle indicates control of hydrogen-to-hydrocarbon ratio.

(3) Platforming

Platforming is licensed by the UOP Process Div. of UOP Inc. This was the first commercial catalytic reforming process to use a platinum catalyst. Platforming was first announced at the 1949 Western Petroleum Refiners Assoc. annual meeting. The process has gone through a series of developments. Older units are still serving as nonregenerative or as semiregenerative reformers. In 1971, UOP introduced their concept of continuous catalyst regeneration as a commercial reforming process.

A process flow diagram of the reaction and product recovery sections of a UOP continuous catalyst regeneration unit is shown in Figure 2-7. Figure 2-8 illustrates the catalyst regeneration section. The hydrocarbon flow pattern is essentially

the same as it is in conventional fixed-bed reformers. Reactor feed combined with recycle hydrogen is raised to reactor temperature by heat exchange and a fired heater and is charged to the reactor section.

Temperature is maintained across the reactor section by interheaters. Effluent from the last reactor is cooled by heat exchange, followed by air and water cooling, and passes to the product-recovery section. The hydrogen-rich separator gas is recycled to the combined feed exchanger and then to the reactors. Excess hydrogen is sent to hydrogen-consuming units or to fuel gas.

In the continuous process, unlike fixed-bed units, the catalyst is continuously withdrawn from the last reactor. The catalyst is continuously regenerated in the regeneration system (Figure 2-7) and is then returned to the top of the NO. 1 reactor (Figure 2-8). The ability to continuously remove catalyst from the reactor system, restore it to fresh-catalyst condition, and return it to the reactor system permits the unit to operate continuously at high-severity conditions, that is, producing high-octane reformate.

(4) Powerforming

Powerforming, the catalytic reforming process licensed by Exxon Research and Engineering, can be designed for either semiregenerative or cyclic reforming. The process flow of Figure 2-9 shows a semiregenerative scheme and the additional equipment needed for cyclic operation. For most operations, the low-cost semiregenerative process is employed. Powerforming, operating in the cyclic scheme, is the preferred alternative if a very high octane rating or if the maximum yield of aromatics
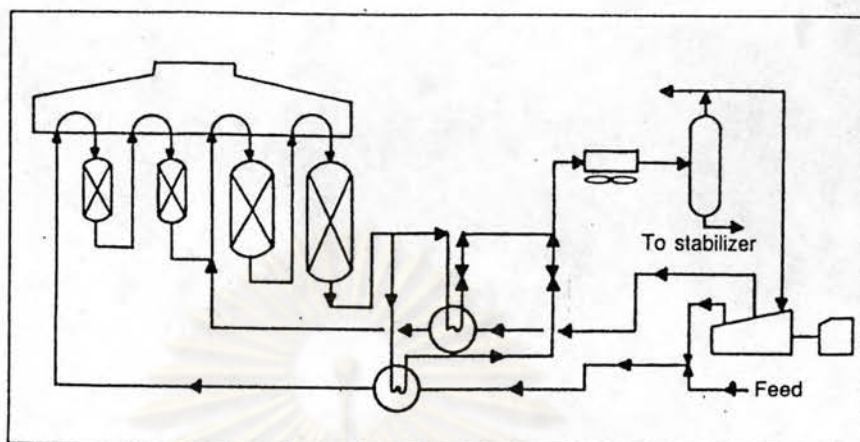
Fig. 2-6 Magnaforming flow diagram (Little, 1985)
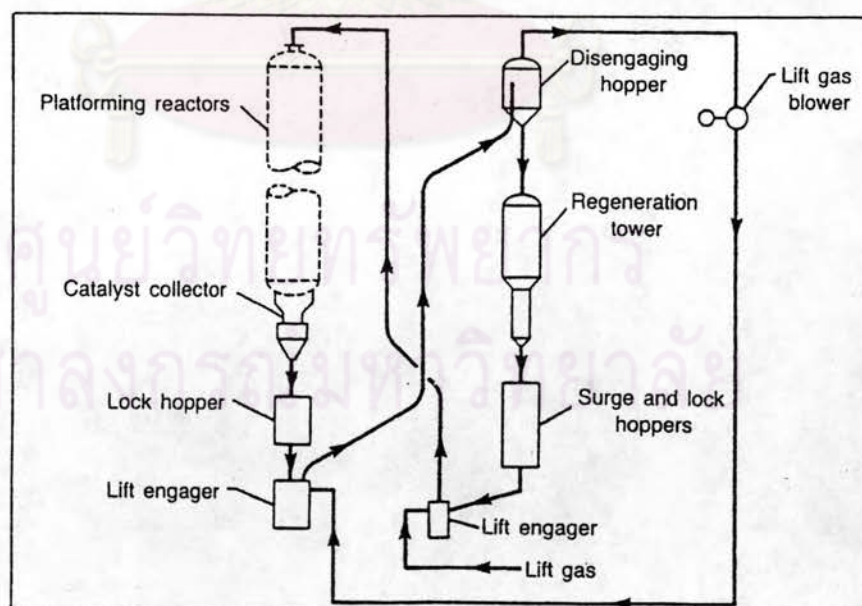

Fig. 2-7 Catalyst regeneration section for UOP continuous catalyst regeneration process (Little, 1985)
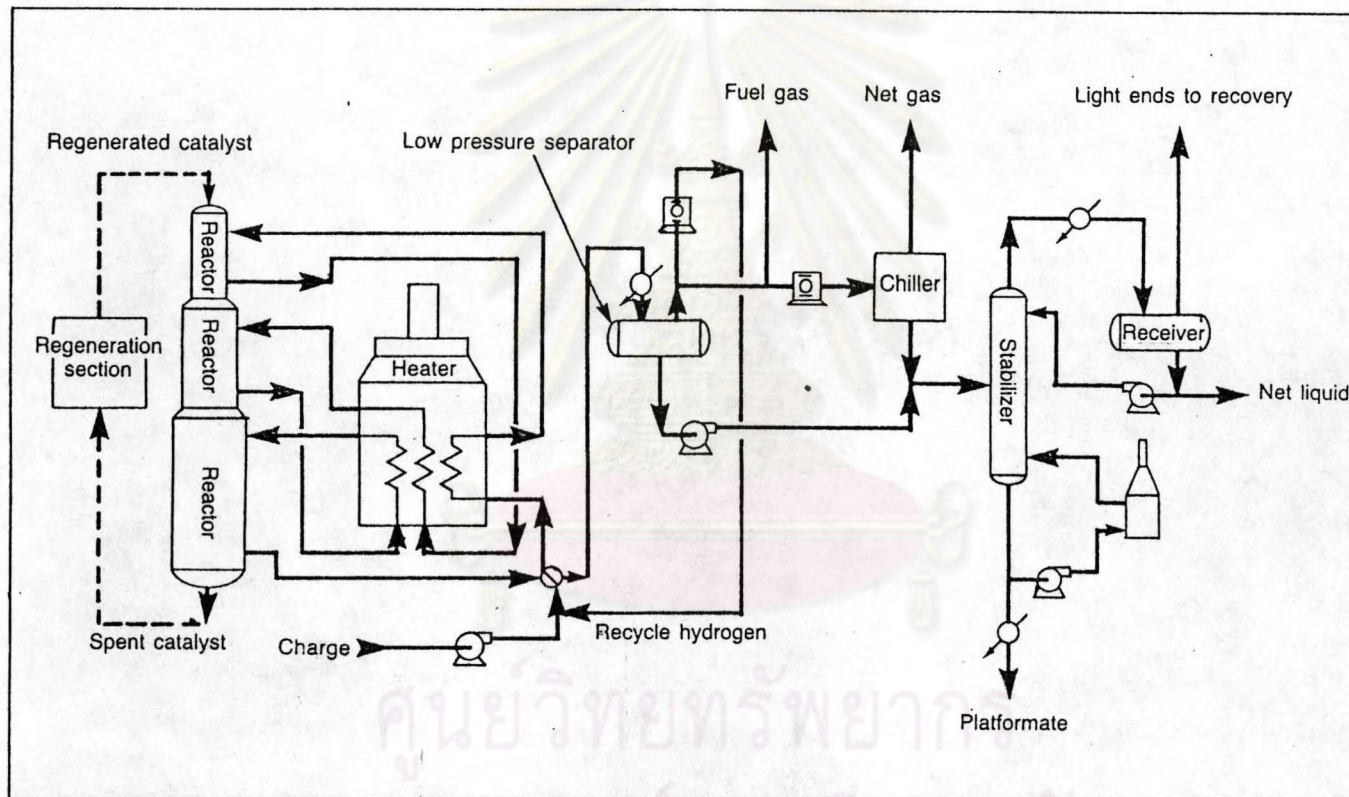
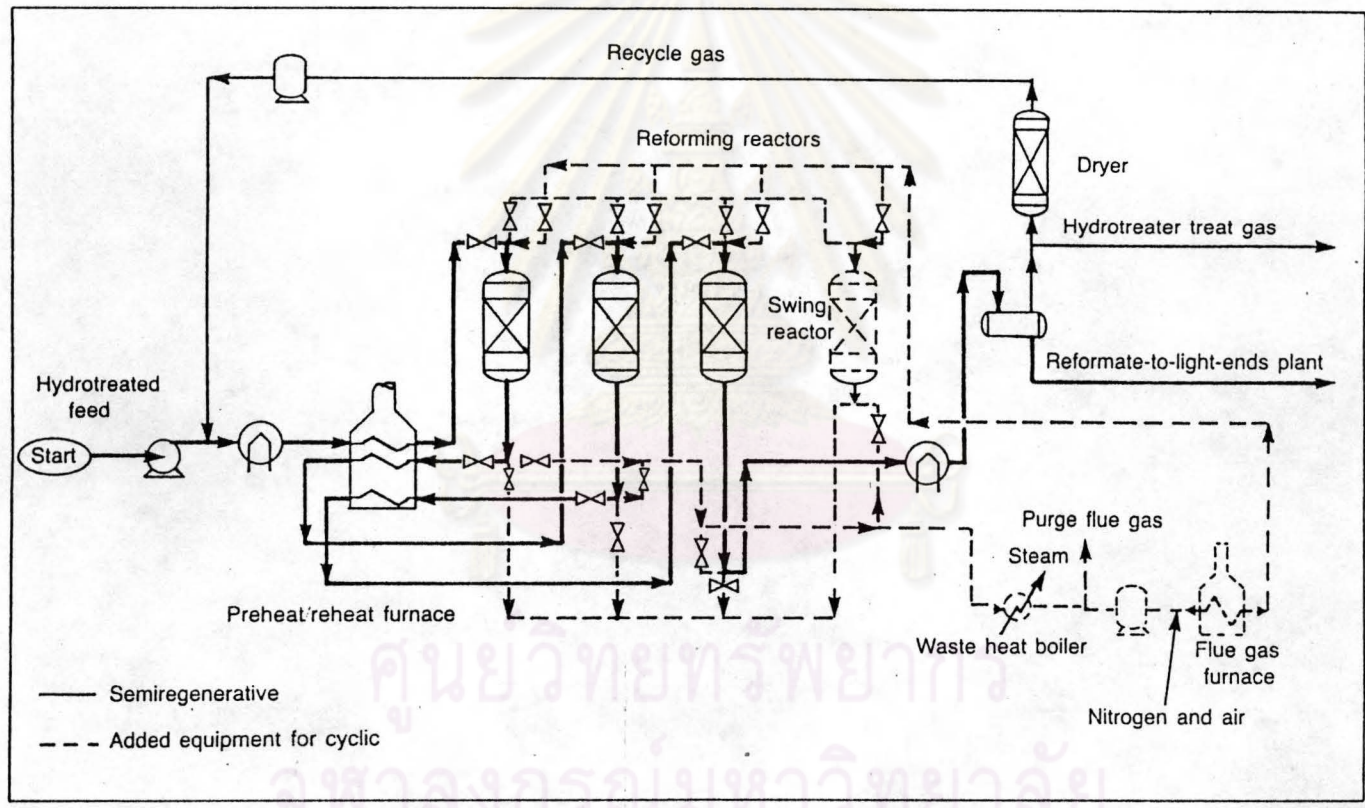**Fig.** 2-8   Platforming, UOP continuous catalyst regeneration process   (Little, 1985)

Fig. 2-9   Powerforming unit   (Little, 1985)

(benzene, toluene, or xylenes) per barrel of feed is desired. Semicyclic operations of an existing cyclic unit are anything between cyclic and semiregenerative.

(5) Rheniforming

Rheniforming is a catalytic reforming process licensed by Chevron Research Co. Rheniforming (Figure 2-10) is a semiregenerative, low-pressure, fixed-bed catalytic reforming process which employs a bimetallic platinum-rhenium catalyst and special operating techniques.

Chevron Research Co. introduced platinum-rhenium reforming to the refining industry in 1967. Improvements have since been made in the catalyst, in the process design, in operating procedures, and in regeneration procedures.

Rheniforming features design simplicity, energy efficiency, optimum operation, and a rugged, completely regenerable catalyst.

(6) Ultraforming

Ultraforming is licensed by Standard Oil Co. (Indiana). The technical aspects of licensing are handled by Standard's wholly-owned affiliate, Amoco Oil Co. Ultraforming's first commercial unit went on stream in 1954, utilizing a proprietary platinum-on-alumina catalyst. Starting in the late 1960s Amoco developed and made extensive use of its own proprietary bimetallic (platinum-rhenium) catalyst. Amoco also developed and proved in commercial operation the technology, including regeneration, involved in utilizing this catalyst.

Ultraforming (Figure 2-11) employs a swing-reactor design, which permits on-stream regeneration for high-severity

high-octane-reformate or high aromatics yields) operation. For lower-octane reformate, the process can be designed as a semiregenerative unit.
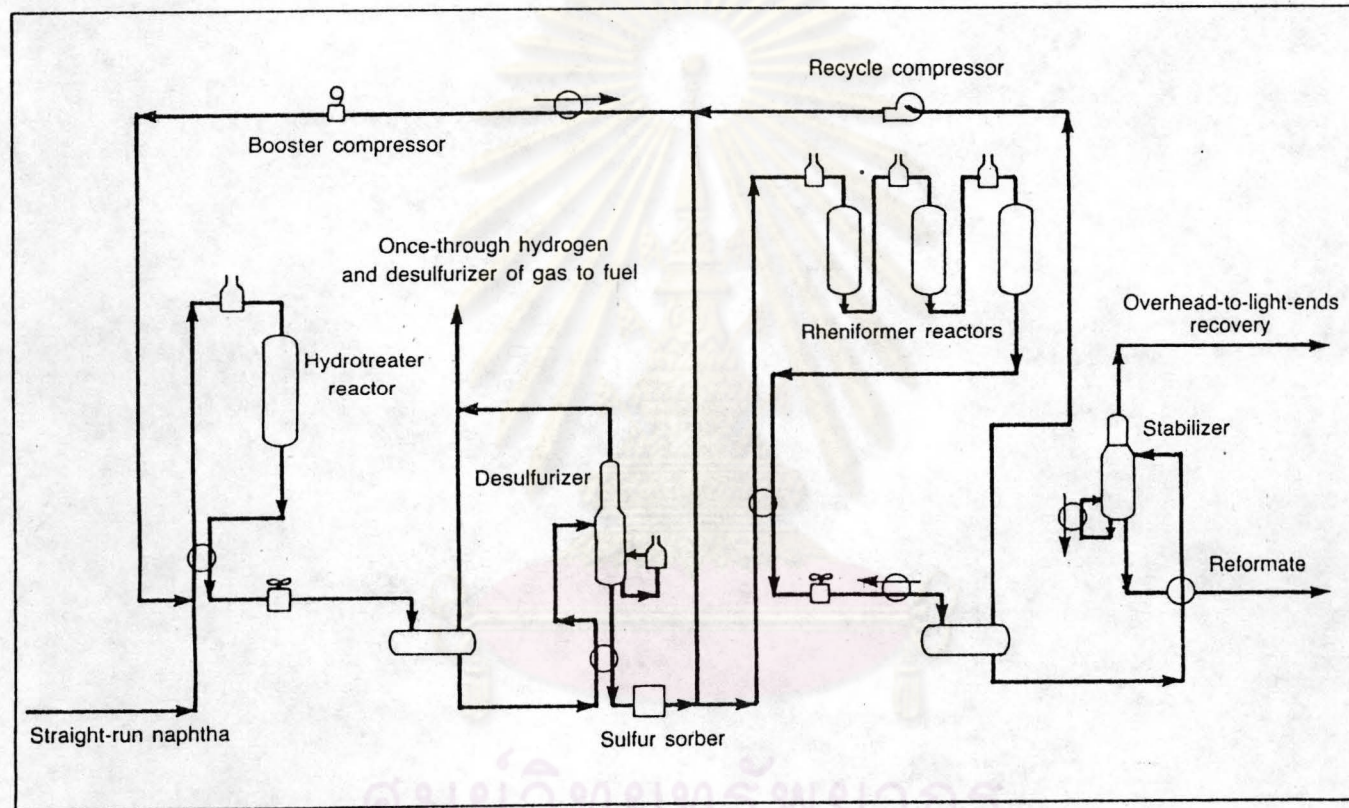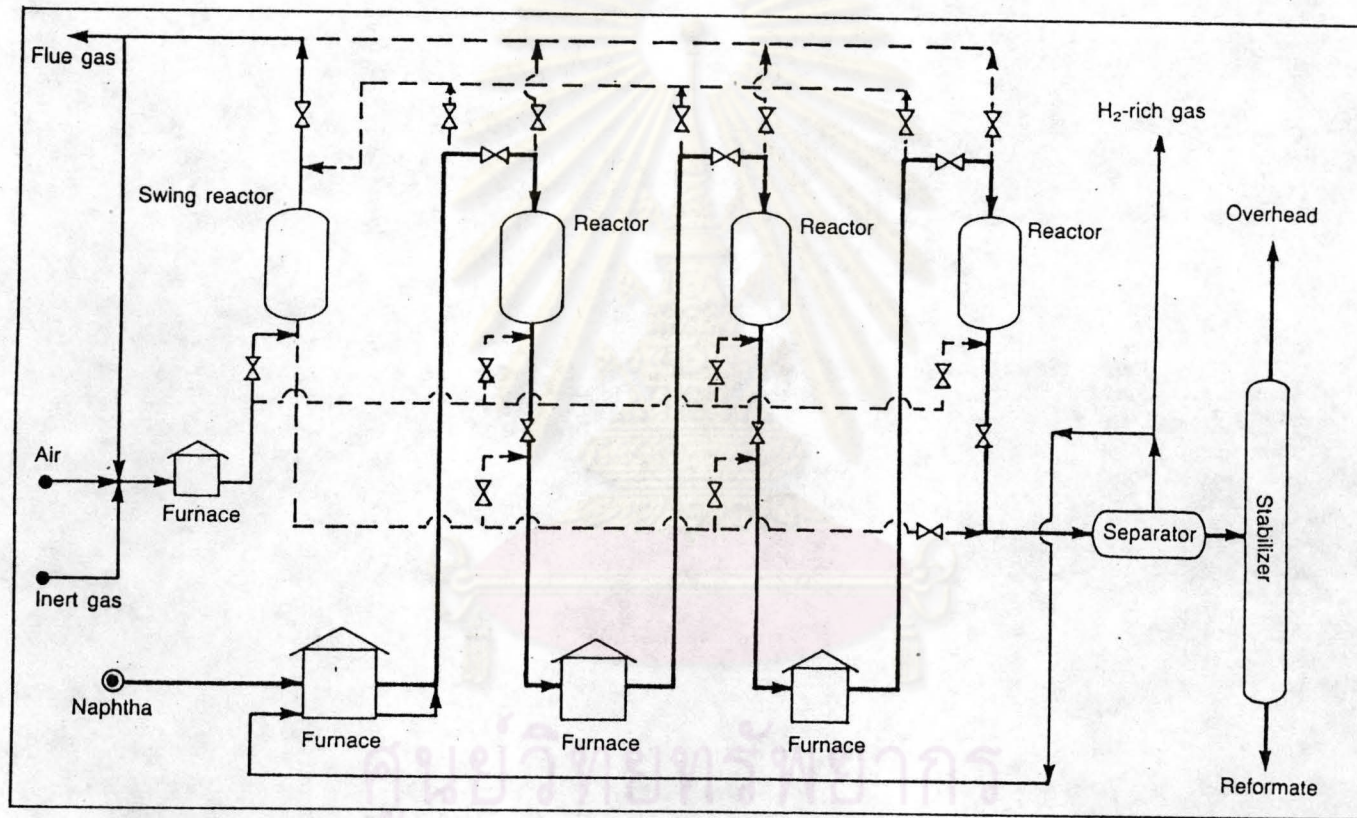
Fig. 2-10 Rheniforming process with hydrotreater (Little, 1985)

Fig. 2–11 Ultraforming process.