CHAPTER 2

REVIEW OF CATALYTIC REFORMING

Catalytic reforming is a process that converts naphthenes and paraffins to aromatics and isoparaffins. These hydrocarbons are reconstructed, or reformed, without changing the number of carbon atoms in the molecule.

Catalytic Reforming for Aromatics

Catalytic reforming is suitable to yield aromatics (benzene, toluene, and xylenes(BTX)) because naphtha feedstocks contain a significant amount of naphthenes, which in the reforming processes 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 refinery configuration is shown in Figure 2-1. 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.

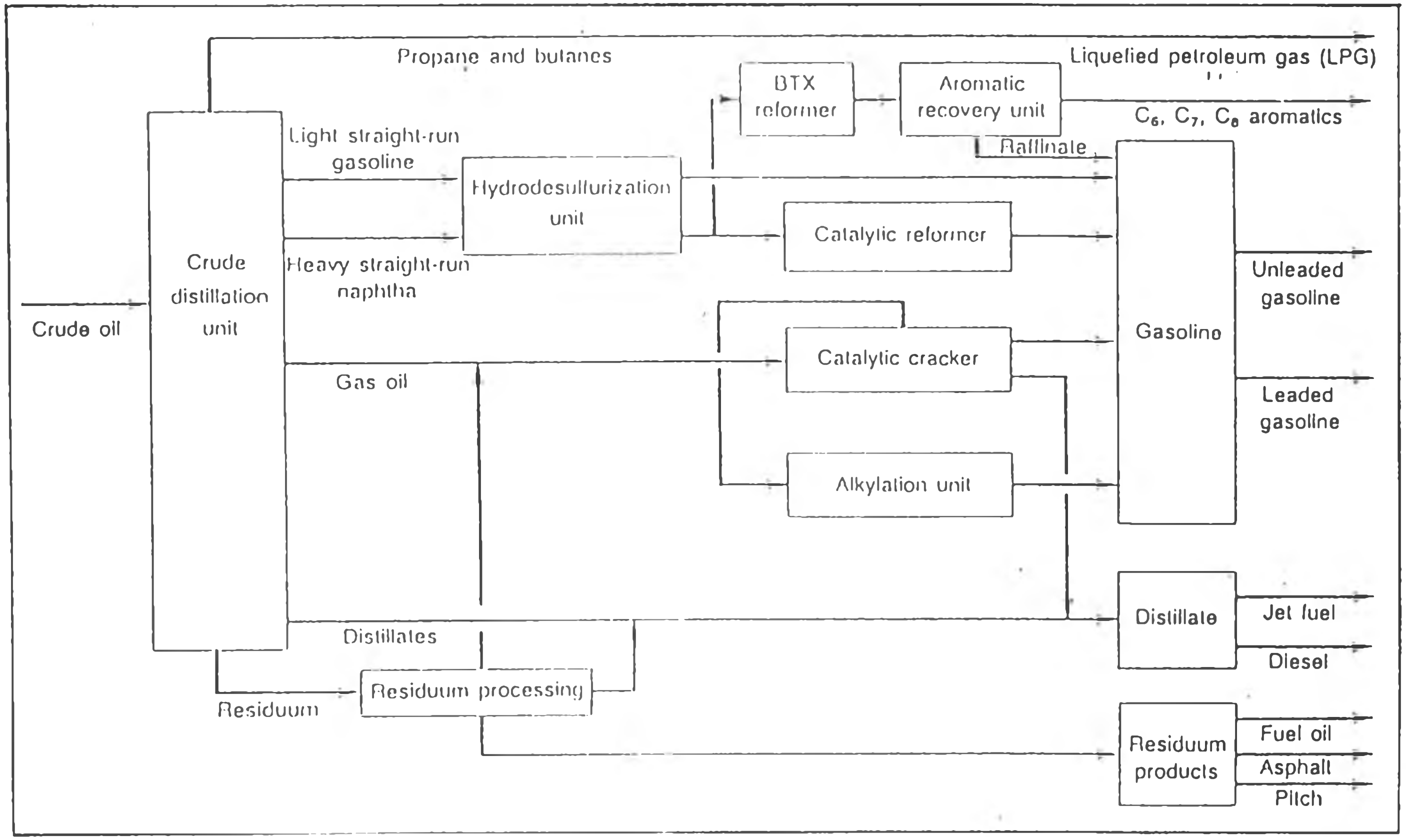


Figure 2-1 Refinery with motor fuel and BTX catalytic reforming (Little, 1985)

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. The lower boiling streams from crude distillation are naphthas. These streams are in the gasoline boiling range(about 80-400 °F). When the stream goes directly to motor fuel, it is called *gasoline*. 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 catalytic reformer because they are not good catalytic reforming feedstock. The heavy straight-run naphtha is hydrodesulfurized and then charged to the catalytic reformer. The product from the catalytic reformer is blended with other refinery stocks to make finished gasoline.

The feedstock to the catalytic reforming 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.

Products from Reforming

Catalytic reforming produces high-value aromatic hydrocarbons such as benzene , toluene , and xylenes. 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.

Theory of Reforming Reactions

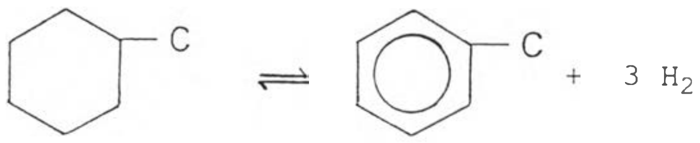
Catalytic reforming for BTX entails a number of reactions, the most important of which are dehydrogenation of naphthenes and dehydrocyclization of paraffins. These reactions convert selected naphthas charged to BTX reformers to high yield of aromatics such as benzene, toluene, orthoxylene, metaxylene, and paraxylene. The nature of the catalytic reaction is as follows

1. Reforming Reactions

Reforming catalyst and operating conditions are designed to promote certain reactions and to inhibit others. Reactions most prevalent in catalytic reforming are dehydrogenation , isomerization , dehydrocyclization, and hydrocracking.

(1) Dehydrogenation

A principal reforming reaction is dehydrogenation because it produces aromatics that have high octane numbers or are valuable petrochemicals:



(2-1)

Methylcyclohexane Toluene Hydrogen

C_7H_{14} C_7H_8 H_2

Dehydrogenation is strongly influenced by temperature and by hydrogen partial pressure, the extent of reaction increases as temperature increases and hydrogen partial pressure decreases.

(2) Isomerization

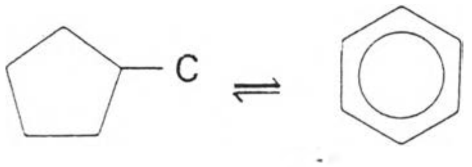
Isomerization of a paraffin rearranges the molecule with essentially no change in volume but with a marked increase in octane number.

$$\text{C-C-C-C-C-C} \rightleftharpoons \text{C-}\overset{\text{C}}{\overset{|}{\text{C}}}\text{-}\overset{\text{C}}{\overset{|}{\text{C}}}\text{-C} \qquad (2\text{-}2)$$

n-Hexane 2,2-Dimethylbutane(22DMB)

C_6H_{14} C_6H_{14}

Naphthene hydrocarbons may also isomerize in reforming reactors. When this happens, they almost immediately undergo dehydrogenation to aromatics. For example, a naphthene isomerization is the conversion of methylcyclopentane(MCP) to benzene :



+ 3 H_2 (2-3)

MCP Benzene Hydrogen

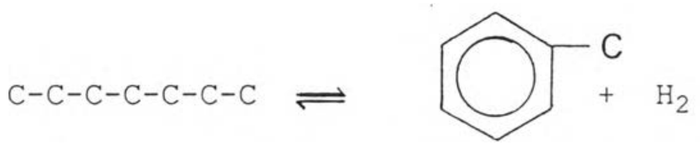
C_6H_{12} C_6H_6 H_2

Methylcyclopentane is generally acknowledged to isomerize first to cyclohexane, which then dehydrogenates to benzene. Volume decreases, but octane number increases. Apparently this reaction involves ring opening, with a likelihood of forming paraffins as well as aromatics. On the other hand, paraffins can be cyclized to aromatics by what is known as dehydrocyclization.

(3) **Dehydrocyclization**

Dehydrocyclization is the most difficult reaction in reforming process. It is a required reaction for production of a satisfactory yield of high-octane-number reformate. Most reforming feedstocks contain a substantial quantity of low-octane-number paraffins. The dehydrogenation and isomerization reactions of paraffins alone cannot produce enough aromatics and isoparaffins to yield high-octane-number reformate.

A typical dehydrocyclization is :



(2-4)

n-Heptane Toluene Hydrogen

C_7H_{16} C_7H_8 H_2

As with naphthene isomerization , there are intermediate steps between the paraffin and the aromatic. The reaction is favored by high temperature and low pressure.

For cyclization, a paraffin with at least a six carbon straight chain is needed. Consequently, n-pentane does not cyclize, nor does 2-methylpentane nor 2,2-dimethylpentane. However, n-heptane will cyclize to benzene. The longer straight-chain paraffins will dehydrocyclize more readily than the shorter chains.

(4) **Hydrocracking**

The breaking of the C-C bond in reforming operations is called hydrocracking. Hydrocracking can break a paraffin molecule into two molecules of lower molecular weight and can open the ring of a naphthene. Aromatics present in the feed or produced in the reactors do not normally undergo ring opening at reforming temperatures and pressures. Examples of hydrocracking reactions are :

$$\underset{\substack{\text{n-Heptane} \\ C_7H_{16}}}{C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}C} + \underset{\substack{\text{Hydrogen} \\ H_2}}{H_2} \longrightarrow \underset{\substack{\text{Propane} \\ C_3H_8}}{C\text{-}C\text{-}C} + \underset{\substack{\text{Butane} \\ C_4H_{10}}}{C\text{-}C\text{-}C\text{-}C} \qquad (2\text{-}5)$$

High temperature and high pressure accelerate hydrocracking. It usually takes place on the acidic sites of the catalyst but can also cause pyrolysis(chemical decomposition by heat) at temperatures above 1,100 °F. Hydrocracking produces coke precursors that cover active catalyst sites.

Hydrocracking is not all bad. For example, n-decane can split into n-heptane and propane. The n-heptane can then dehydrocyclize to toluene, a high-octane-number aromatic.

2. Reaction Rate

All the above reactions occur in reforming, but all do not proceed at the same rate. For the most part, an engineer assigned to a reforming unit will think more about relative rates of reactions of broad classes of hydrocarbons rather than the reaction rates of individual components. It is well known in reforming that naphthene dehydrogenation is a relatively fast reaction, is endothermic, and is favored by low hydrogen partial pressure.

A general characterization of relative reaction rates are :

Reaction	Relative Rate	Comments
Dehydrocyclization	1	Endothermic; promoted by low pressure and high temperature
Hydrocracking	4	Exothermic; promoted by high pressure and high temperature
Isomerization	12	Mildly exothermic ; promoted by high temperature, only slightly affected by pressure
Naphthene dehydrogenation	100^{+}	Endothermic ; promoted by low pressure and high temperature

The above relative rates are broad generalizations For example, the rate of dehydrocyclization of n-heptane is much faster than that of n-hexane. In general, the higher the number of carbon atoms per molecule, the more rapid the rates for the above reactions.

3. Rate Equation

An attempt to formulate a rate equation for solid-catalyzed reactions starts from the basic laws of chemical kinetics encountered in the treatment of homogeneous reactions. In order to develop the kinetics for complex reaction, Hougen and Watson(1947) formulated an expression that relates the rate and amount of adsorption of the component.

The kinetic equations for reactions catalyzed by solids based on the chemisorption mechanism may always be written as a combination of three groups (Yang and Hougen (1950)).

In general form of the overall rate is :

$$r_A = \frac{(\text{kinetic factor})(\text{driving-force group})}{(\text{adsorption group})^n} \qquad (2-6)$$

where n is the exponent of adsorption group.

Summaries of these groups for various kinetic schemes are given in Appendix B.

In model discrimination and parameter estimation in heterogeneous catalysis, the form of the rate equation (of the model) is not known a priori, although physico-chemical insight and several formalisms limit the spectrum of possible models. Also unknown, of course, are the values of the rate coefficients and of the adsorption coefficients K_A, K_R, K_S, or in other words, the parameters of the model. The estimation of parameters should be accompanied by extensive statistical testing. The kinetic investigation consists mainly of two parts : model discrimination and parameter estimation. The methodology of kinetic analysis, by both the differential and the integral method, has been discussed in detail by Froment (1975).

4. Catalyst

The catalyst in the reactors promotes the desired reforming reactions and makes catalytic reforming a commercially feasible process.

The catalysts are composed of a base or support material, usually alumina (Al_2O_3), to which has been added certain metals catalytically active for the desired reforming reaction. The metals(examples:platinum, iridium, rhenium, germanium) comprise less than 1 wt% of the catalyst and are highly dispersed on the surface and in the pores of the alumina support.

The catalyst is manufactured in a manner that deposits the metals on the catalyst as extremely small, amost atomic-size crystallites. When reduced with hydrogen to the metallic state, these crystallites become active sites for catalytic reforming reactions. To make the catalyst even more active, a promoter such as chloride and fluoride is added to enhance the isomerization reactions.

(1) **Development of Reforming Catalyst**

The first reforming catalysts based on chromia oxides or molybdenum oxides were used to catalyze the hydrogenation and dehydrogenation reactions were required to produce high-octane aromatics.

The support or base material was the subject of extensive research. Steiner(1950) demonstrated that molybdenum and chromia oxides were inactive by themselves but were active and stable when supported by alumina. Silica and silica alumina were also used, but Haensel(1983) reported that, with silica alumina, hydrocracking was more difficult to control than with alumina alone. Thus, before the introduction of platinum on alumina catalyst by UOP in 1949, reforming catalysts were molybdenum oxide on alumina.

Reforming catalysts were developed in the following steps :

1. Better-quality alumina base gave longer life (stability)
2. Platinum replaced molybdenum and chromia, giving better yields
3. Regeneration technology gave redispersion of platinum, restoring catalyst activity and selectivity to that of fresh catalyst
4. Bimetallic and multimetallic catalyst

markedly improved activity, selectivity, and stability

Since the introduction of bimetallics in 1967, improvements have been slow and mostly in the structure of the alumina base.

(2) **Multifunctional Catalyst**

An outstanding feature of reforming catalyst, even from the beginning, is the incorporation of more than one function in a single catalyst. For this reason, reforming catalysts have been termed dual functional, bifunctional and, recently, multifunctional.

Technologists involved in the development of reforming catalysts recognize that reforming reactions require at least two different functions. One is a metal to catalyze the dehydrogenation of naphthenes to aromatics and to hydrogenate olefins formed by dehydrogenation and hydrogenolysis of paraffins. It is generally acknowledged that the metal component also contributes to dehydrocyclization and isomerization. The second function needed is an acid to catalyze isomerization, cyclization, and hydrocracking. The contribution of catalyst components to reactions that occur in reforming and the effect of environmental variables, although the subjects of vast research, are still not well understood. The general consensus is that the catalyst-metal function and the acid function are both necessary and both contribute, sometimes individually and sometimes collectively.

One of the better visualizations of the dual function of reforming catalyst and reforming reactions is presented in Figure 2-2. This figure has appeared in a number of reforming articles and was first published by Mills et al. (1953). In this simplified representation of reforming reaction network, reactions indicated by vertical arrows are catalyzed by the metal function of the catalyst. Reactions indicated by horizontal arrows are catalyzed by the acid function of the catalyst. For example, the mechanism for producing benzene from n-hexane is dehydrogenation to methylcyclopentane on a metal site, isomerization to cyclohexane on an acid site, then dehydro-genation on a metal site to cyclohexadiene, and, finally, benzene.

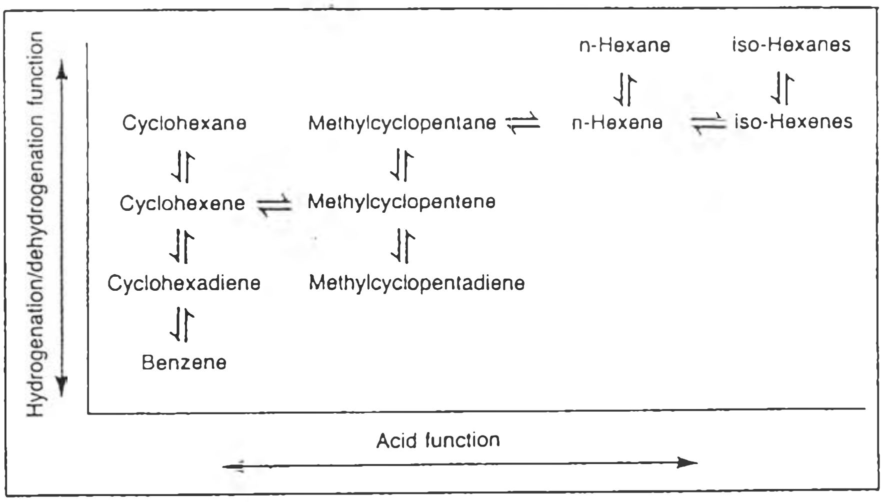


Figure 2-2 Reactions of a multifunction reforming catalyst (Mills et al.(1953))

(3) **Catalyst Poisons**

Reforming catalyst poisons are classified as either temporary or permanent. *Temporary poisons* are those which can be removed from the catalyst without a shutdown, and the catalyst is restored to proper activity and selectivity. A temporary poison is sulfur which, when present in amounts greater than 0.5 ppm wt, causes a significant activity loss (octane number decrease) in a bimetallic catalyst.

A *permanent poison* is one that impairs catalyst performance to the point that the unit must be shut down and the catalyst replaced because there is no way to restore it to a satisfactory performance level. A permanent catalyst poison is arsenic, which deposits on the catalyst and causes a rapid loss in activity.

Poisons of catalytic reforming are :

Sulfur. Sulfur deactivates the hydrogenation-dehydrogenation function of the catalyst by forming metal sulfides. The reaction, however, is reversible. When sulfur is removed from the feed, the sulfur leaves the catalyst and appears as hydrogen sulfide in reformer products.

Nitrogen. Organic nitrogen compounds in reformer feed are converted to ammonia, which poisons the acid function of the catalyst. This generally means ammonia reacts with the chloride component. When organic nitrogen is eliminated from the feed, the catalyst gives up ammonium chloride and recovers its acid function if chloride is brought up to the proper level by chloride addition. Molecular nitrogen (N_2) apparently does not react at reforming conditions and so is not a catalyst poison.

Halides. Too much chloride increases the acid function of the catalyst beyond an optimum required for balanced catalyst performance. When excess chloride is eliminated from the feed, chloride leaves the catalyst. Balance is restored by control of chloride injection. Fluoride has the same effect as chloride, except fluoride is very difficult to strip from the catalyst and makes controlling the acid-catalyzed hydrocracking reaction more difficult.

Water. It comes from moisture in the feed or from oxygenated hydrocarbons converted to water at reforming conditions. Although some moisture is required to activate the alumina support, excess water can throw the acid function of the catalyst out of balance by stripping chlorides from the catalyst. Balance of catalyst functions is restored by elimination of the excess water source and by chloride injection.

Metals. Trace quantities of metal such as arsenic or lead can enter a reformer with reactor charge.

Metals deposit nearly quantitatively on the catalyst and deactivate the metal(platinum) function of the catalyst. The effect is irreversible; the arsenic of lead cannot be removed to restore the reforming functions of the catalyst. Preventing arsenic or lead from entering the unit and replacing the poisoned catalyst are necessary to bring unit performance up to its proper level.

Carbon on Catalyst. Rapid buildup of carbon on the catalyst accelerates loss of activity and selectivity. Carbon laydown is generally attributed to condensation of aromatics into polycyclic aromatics. These polycyclic aromatics strongly adhere to the catalyst and are ultimately converted to coke. At some level of coke on the catalyst about 7-10 wt% for platinum-only catalyst and 20-40 wt% for bimetallic catalyst activity and selectivity are so low that the catalyst must be regenerated by burning off the coke. A high rate of carbon laydown and coking is frequently a result of high-boiling hydrocarbons in reactor charge.

(4) **Catalyst Regeneration**

Catalyst regeneration of an acidic platinum of multimetallic Al_2O_3 catalyst will always involve at least the following :

(1) Purging of hydrogen and hydrocarbon

(2) Burning off the coke with very dilute air at first and then with more concentrated air.

(3) Adjusting the catalyst acidity.

(4) Purging all oxygen from the system.

(5) Reducing the catalyst with hydrogen.