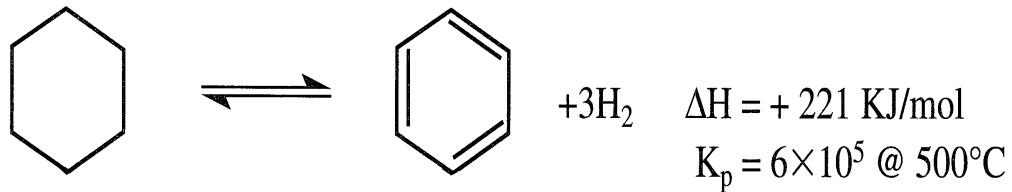


# Lecture Six

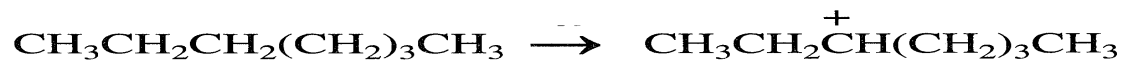
**Aromatization.** The two reactions directly responsible for enriching naphtha with aromatics are the dehydrogenation of naphthenes and the dehydrocyclization of paraffins. The first reaction can be represented by the dehydrogenation of cyclohexane to benzene.



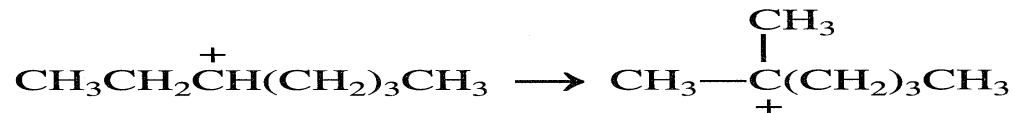
This reaction is fast; it reaches equilibrium quickly. The reaction is also reversible, highly endothermic, and the equilibrium constant is quite large ( $6 \times 10^5 @ 500^\circ\text{C}$ ).

**Isomerization.** Reactions leading to skeletal rearrangement of paraffins and cycloparaffins in a catalytic reactor are also important in raising the octane number of the reformat product. Isomerization reactions may occur on the platinum catalyst surface or on the acid catalyst sites. In the former case, the reaction is slow. Most isomerization reactions, however, occur through formation of a carbocation. The formed carbocation could rearrange through a hydride-methide shift that would lead to branched isomers. The following example illustrates the steps for the isomerization of n-heptane to 2-methylhexane through 1,2-methide-hydride shifts:

Carbocation Formation:



1,2-Methide-Hydride Shift:



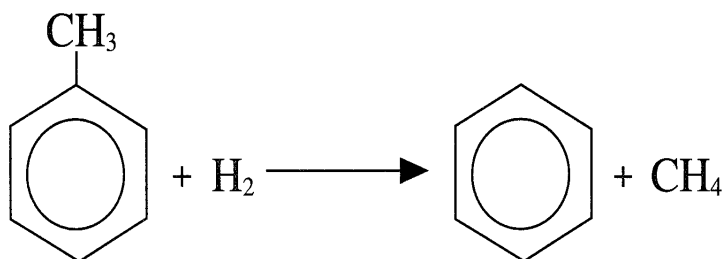
**Hydrocracking.** Hydrocracking is a hydrogen-consuming reaction that leads to higher gas production and lower liquid yield. This reaction is favored at high temperatures and high hydrogen partial pressure. The following represents a hydrocracking reaction:



Bond breaking can occur at any position along the hydrocarbon chain. Because the aromatization reactions mentioned earlier produce hydrogen and are favored at high temperatures, some hydrocracking occurs also under these conditions. However, hydrocracking long-chain molecules can produce C<sub>6</sub>, C<sub>7</sub>, and C<sub>8</sub> hydrocarbons that are suitable for hydrode-cyclization to aromatics.

For more aromatics yield, the end point of the feed may be raised to include higher molecular weight hydrocarbons in favor of hydrocracking and dehydrocyclization. However, excessive hydrocracking is not desirable because it lowers liquid yields.

**Hydrodealkylation.** Hydrodealkylation is a cracking reaction of an aromatic side chain in presence of hydrogen. Like hydrocracking, the reaction consumes hydrogen and is favored at a higher hydrogen partial pressure. This reaction is particularly important for increasing benzene yield when methylbenzenes and ethylbenzene are dealkylated. Although the overall reaction is slightly exothermic, the cracking step is favored at higher temperatures. Hydrodealkylation may be represented by the reaction of toluene and hydrogen.



As in hydrocracking, this reaction increases the gas yield and changes the relative equilibrium distribution of the aromatics in favor of benzene.

**Table 3-7 shows the properties of feed and products from Chevron Rheiniforming process**

<b>Yields: Typical yields for severe reforming</b>		
<b>Naphtha Feed</b>	<b>Hydrotreated</b>	<b>Hydrocracked</b>
Feed type	Paraffinic	Naphthenic
Boiling range,°F	200-330	200-390
Paraffins,LV%	68.6	32.6
Naphthenes,LV%	23.4	55.5
Aromatics,LV%	8.0	11.9
Sulfur,ppm	<0.2	<0.2
Nitrogen,ppm	<0.5	<0.5

## **Reforming Process**

Catalytic reformers are normally designed to have a series of catalyst beds (typically three beds). The first bed usually contains less catalyst than the other beds. This arrangement is important because the dehydrogenation of naphthenes to aromatics can reach equilibrium faster than the other reforming reactions. Dehydrocyclization is a slower reaction and may only reach equilibrium at the exit of the third reactor. Isomerization and hydrocracking reactions are slow. They have low equilibrium constants and may not reach equilibrium before exiting the reactor.

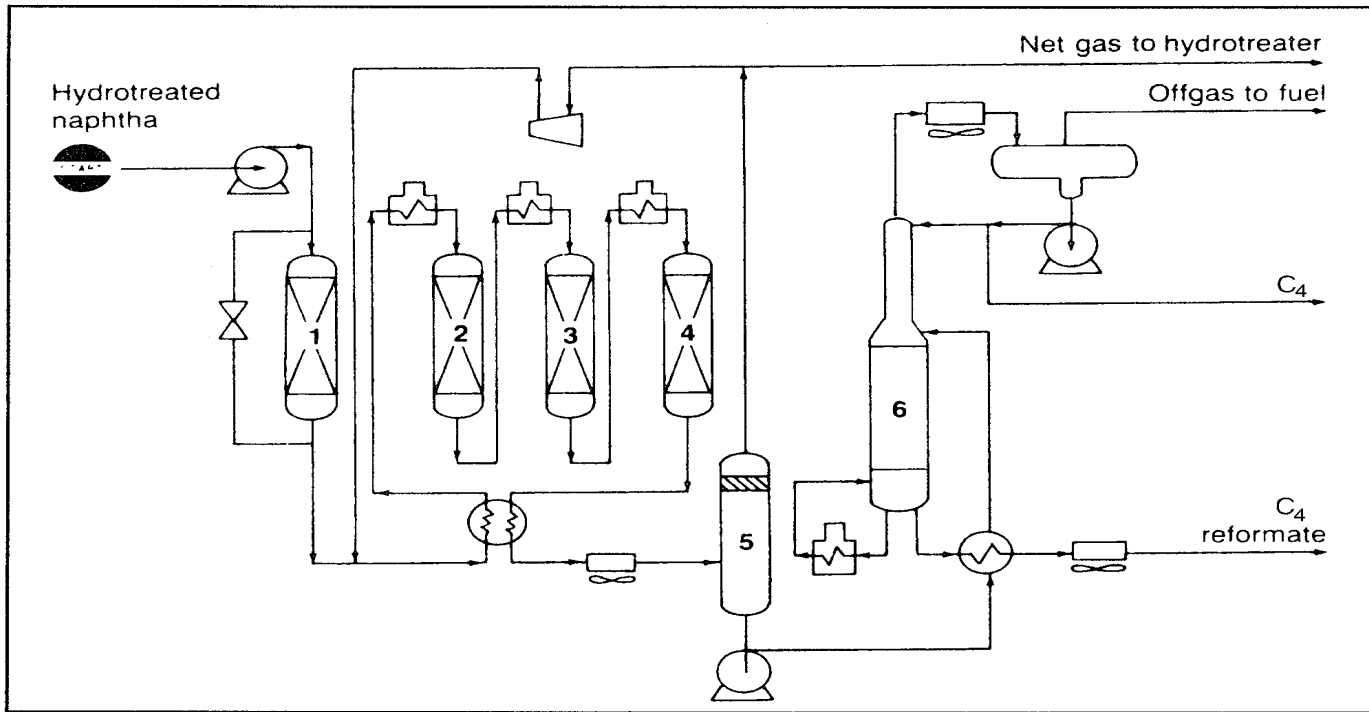
The second and third reactors contain more catalyst than the first one to enhance the slow reactions and allow more time in favor of a higher yield of aromatics and branched paraffins. Because the dehydrogenation of naphthenes and the dehydrocyclization of paraffins are highly endothermic, the reactor outlet temperature is lower than the inlet temperature. The effluent from the first and second reactors are reheated to compensate for the heat loss.

Normally, catalytic reformers operate at approximately 500–525°C and 100–300 psig, and a liquid hourly space velocity range of 2–4 hr<sup>-1</sup>. Liquid hourly space velocity (LHSV) is an important operation parameter expressed as the volume of hydrocarbon feed per hour per unit volume of the catalyst. Operating at lower LHSV gives the feed more contact with the catalyst.

Regeneration of the catalyst may be continuous for certain processes that are designed to permit the removal and replacement of the catalyst during operation. In certain other processes, an additional reactor is used (Swing reactor). When the activity of the catalyst is decreased in one of the reactors on stream, it is replaced with the stand-by (Swing) reactor.

In many processes, regeneration occurs by shutting down the unit and regenerating the catalyst (Semi-regenerative). Figure 3-5 shows a Chevron Rheiniforming semiregenerative fixed three-bed process. Products from catalytic reformers (the reformate) is a mixture of aromatics, paraffins and cycloparaffins ranging from C<sub>6</sub>-C<sub>8</sub>. The mixture has a high octane rating due to presence of a high percentage of aromatics and branched paraffins. Extraction of the mixture with a suitable solvent produces an aromatic-rich extract, which is further fractionated to separate the BTX components.





**Figure 3-5.** Flow diagram of a Chevron Rheiniforming unit:(1) sulfur sorber,(2–4) reactors, (5) separator, (6) stabilizer.

## Catalytic Cracking

Catalytic cracking (Cat-cracking) is a remarkably versatile and flexible process. Its principal aim is to crack lower-value stocks and produce higher-value light and middle distillates. The process also produces light hydrocarbon gases, which are important feed stocks for petrochemicals. Catalytic cracking produces more gasoline of higher octane than thermal cracking. This is due to the effect of the catalyst, which promotes isomerization and dehydrocyclization reactions.

Products from catalytic cracking units are also more stable due to a lower olefin content in the liquid products. This reflects a higher hydrogen transfer activity, which leads to more saturated hydrocarbons than in thermally cracked products from delayed coking units, for example.

The feeds to catalytic cracking units vary from gas oils to crude residues. Heavier feeds contain higher concentrations of basic and polar molecules as well as asphaltenes. Examples are basic nitrogen compounds, which are readily adsorbed on the catalyst acid sites and lead to instantaneous albeit temporary deactivation. Polycyclic aromatics and asphaltenes contribute strongly to coke formation. These feed stocks are often pretreated to decrease the metallic and asphaltene contents. Hydrotreatment, solvent extraction, and propane deasphalting are important treatment processes.

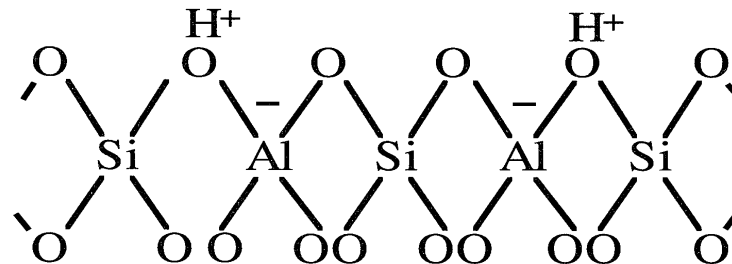
Excessive asphaltene and aromatics in the feed are precursors to carbon formation on the catalyst surface, which substantially reduces its activity and produces gasolines of lower quality.

Residuum fluid catalytic cracking (RFCC) has gained wide acceptance due to a larger production of gasoline with only small amounts of low-value products. Pretreating the feed in a low-severity residue desulfurization (RDS) increased the gasoline yield by 7.4%.

## **Cracking Catalysts**

Acid-treated clays were the first catalysts used in catalytic cracking processes, but have been replaced by synthetic amorphous silica-alumina, which is more active and stable. Incorporating zeolites (crystalline alumina-silica) with the silica/alumina catalyst improves selectivity towards aromatics. These catalysts have both Lewis and Bronsted acid sites that promote carbonium ion formation. An important structural feature of zeolites is the presence of holes in the crystal lattice, which are formed by the silica-alumina tetrahedra. Each tetrahedron is made of four oxygen anions with either an aluminum or a silicon cation in the center. Each oxygen anion with a  $-2$  oxidation state is shared between either two silicon, two aluminum, or an aluminum and a silicon cation.

The four oxygen anions in the tetrahedron are balanced by the +4 oxidation state of the silicon cation, while the four oxygen anions connecting the aluminum cation are not balanced. This results in  $-1$  net charge, which should be balanced. Metal cations such as  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , or protons ( $\text{H}^+$ ) balance the charge of the alumina tetrahedra. A two-dimensional representation of an H-zeolite tetrahedra is shown:



Bronsted acid sites in HY-zeolites mainly originate from protons that neutralize the alumina tetrahedra. When HY-zeolite (X- and Y-zeolites are cracking catalysts ) is heated to temperatures in the range of  $400\text{--}500^\circ\text{C}$ , Lewis acid sites are formed.

Zeolites as cracking catalysts are characterized by higher activity and better selectivity toward middle distillates than amorphous silica-alumina catalysts. This is attributed to a greater acid sites density and a higher adsorption power for the reactants on the catalyst surface.

The higher selectivity of zeolites is attributed to its smaller pores, which allow diffusion of only smaller molecules through their pores, and to the higher rate of hydrogen transfer reactions. However, the silica- alumina matrix has the ability to crack larger molecules. It has been recently demonstrated the importance of the interaction of the zeolite with the silica-alumina matrix. In a set of experiments using gas oil and rare earth zeolite/silica-alumina, the yield of gasoline increased when the matrix was used before the zeolite. This was explained by the mechanism of initial matrix cracking of large feedstock molecules to smaller ones and subsequent zeolite cracking of the smaller molecules to products. Aluminum distribution in zeolites is also important to the catalytic activity. An imbalance in charge between the silicon atoms in the zeolite framework creates active sites, which determine the predominant reactivity and selectivity of FCC catalyst. Selectivity and octane performance are correlated with unit cell size, which in turn can be correlated with the number of aluminum atoms in the zeolite framework.

Deactivation of zeolite catalysts occurs due to coke formation and to poisoning by heavy metals. In general, there are two types of catalyst deactivation that occur in a FCC system, reversible and irreversible. Reversible deactivation occurs due to coke deposition. This is reversed by burning coke in the regenerator. Irreversible deactivation results as a combination of four separate but interrelated mechanisms: zeolite dealumination, zeolite decomposition, matrix surface collapse, and contamination by metals such as vanadium and sodium.

Pretreating the feed stocks with hydrogen is not always effective in reducing heavy metals, and it is expensive. Other means that proved successful are modifying the composition and the microporous structure of the catalyst or adding metals like Sb, Bi or Sn, or Sb-Sn combination. Antimony organics have been shown to reduce by 50% gas formation due to metal contaminants, especially nickel.

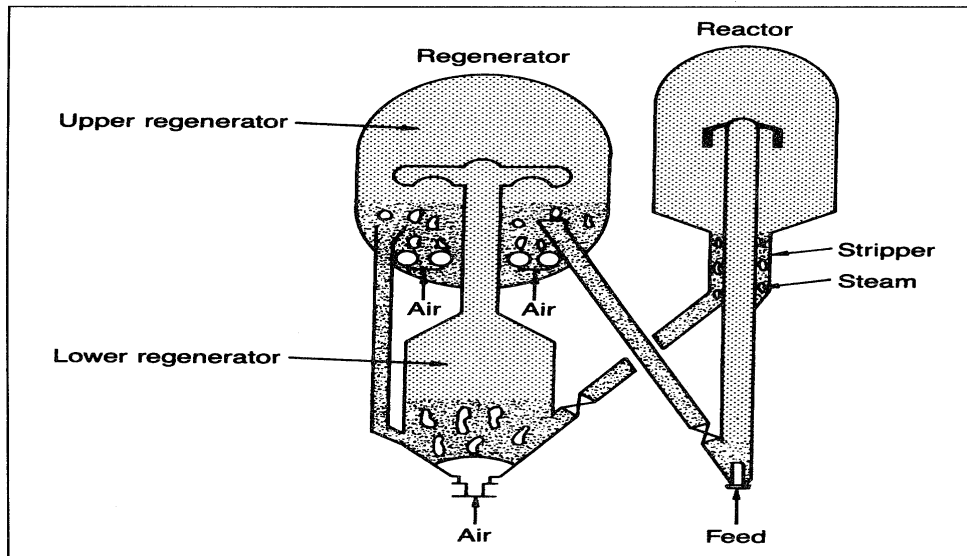
## **Cracking Reactions**

A major difference between thermal and catalytic cracking is that reactions through catalytic cracking occur via carbocation intermediate, compared to the free radical intermediate in thermal cracking. Carbocations are longer lived and accordingly more selective than free radicals. Acid catalysts such as amorphous silica-alumina and crystalline zeolites promote the formation of carbocations.

## Cracking Process

Most catalytic cracking reactors are either fluid bed or moving bed. In the more common fluidized bed process (FCC), the catalyst is an extremely porous powder with an average particle size of 60 microns. Catalyst size is important, because it acts as a liquid with the reacting hydrocarbon mixture. In the process, the preheated feed enters the reactor section with hot regenerated catalyst through one or more risers where cracking occurs. A riser is a fluidized bed where a concurrent upward flow of the reactant gases and the catalyst particles occurs. The reactor temperature is usually held at about 450–520°C, and the pressure is approximately 10–20 psig. Gases leave the reactor through cyclones to remove the powdered catalyst, and pass to a fractionator for separation of the product streams. Catalyst regeneration occurs by combusting carbon deposits to carbon dioxide and the regenerated catalyst is then returned to the bottom of the riser. Figure 3-6 is a typical FCC reactor/regeneration system. Fluid catalytic cracking produces unsaturates, especially in the light hydrocarbon range  $C_3$ – $C_5$ , which are used as petrochemical feed stocks and for alkylate production. In addition to hydrocarbon gases, FCC units produce gasolines with high octane numbers (due to the high aromatic content, branched paraffins and olefins), gas oils, and tar. The ratio of these products depends greatly on the different process variables. In general, higher conversions increase gas and gasoline yields. Higher conversion also increases coke formation. Process variables that increase conversion are higher temperatures, longer residence times, and higher catalyst/oil ratio.

In the moving bed processes, the preheated feed meets the hot catalyst, which is in the form of beads that descend by gravity to the regeneration zone. As in fluidized bed cracking, conversion of aromatics is low, and a mixture of saturated and unsaturated light hydrocarbon gases is produced. The gasoline product is also rich in aromatics and branched paraffins.

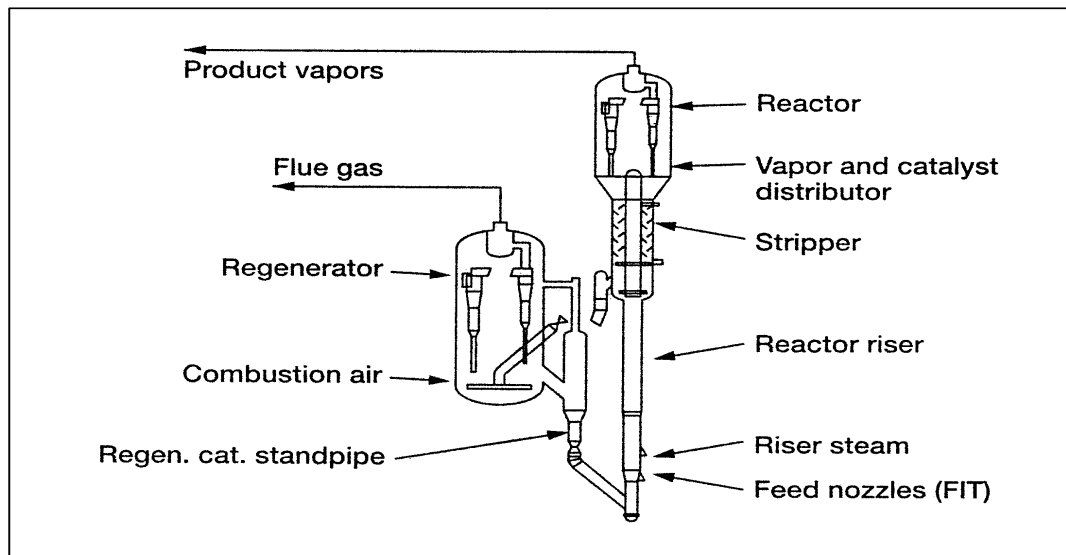


**Figure 3-6.** Typical FCC reactor/regenerator.



## Deep Catalytic Cracking

Deep catalytic cracking (DCC) is a catalytic cracking process which selectively cracks a wide variety of feed stocks into light olefins. The reactor and the regenerator systems are similar to FCC. However, innovation in the catalyst development, severity, and process variable selection enables DCC to produce more olefins than FCC. In this mode of operation, propylene plus ethylene yields could reach over 25%. In addition, a high yield of amylene ( $C_5$  olefins) is possible. Figure 3-7 shows the DCC process.



**Figure 3-7.** Deep catalytic cracking process.

## **Hydrocracking Process**

Hydrocracking is essentially catalytic cracking in the presence of hydrogen. It is one of the most versatile petroleum refining schemes adapted to process low value stocks. Generally, the feed stocks are not suitable for catalytic cracking because of their high metal, sulfur, nitrogen, and asphaltene contents. The process can also use feeds with high aromatic content.

Products from hydrocracking processes lack olefinic hydrocarbons. The product slate ranges from light hydrocarbon gases to gasolines to residues. Depending on the operation variables, the process could be adapted for maximizing gasoline, jet fuel, or diesel production.

## **Hydrocracking Catalysts and Reactions**

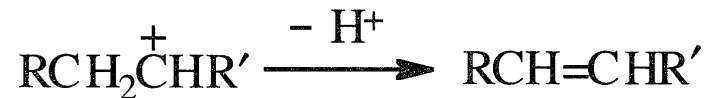
The dual-function catalysts used in hydrocracking provide high surface area cracking sites and hydrogenation-dehydrogenation sites. Amorphous silica-alumina, zeolites, or a mixture of them promote carbonium ion formation. Catalysts with strong acidic activity promote isomerization, leading to a high iso/normal ratios. The hydrogenation-dehydrogenation activity, on the other hand, is provided by catalysts such as cobalt, molybdenum, tungsten, vanadium, palladium, or rare earth elements.

As with catalytic cracking, the main reactions occur by carbonium ion and beta scission, yielding two fragments that could be hydrogenated on the catalyst surface. The main hydro-cracking reaction could be illustrated by the first-step formation of a carbocation over the catalyst surface.



The carbocation may rearrange, eliminate a proton to produce an olefin, or crack at a beta position to yield an olefin and a new carbocation.

Under an atmosphere of hydrogen and in the presence of a catalyst with hydrogenation-dehydrogenation activity, the olefins are hydrogenated to paraffinic compounds. This reaction sequence could be represented as follows



As can be anticipated, most products from hydrocracking are saturated. For this reason, gasolines from hydrocracking units have lower octane ratings than those produced by catalytic cracking units; they have a lower aromatic content due to high hydrogenation activity. Products from hydrocracking units are suitable for jet fuel use. Hydrocracking also produces light hydrocarbon gases (LPG) suitable as petrochemical feed stocks.