

**Lecture 6**

# **Catalytic Reforming**

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## CATALYTIC REFORMING

Catalytic reforming is a major conversion process in petroleum refinery and petrochemical industries. The reforming process is a catalytic process which converts low octane naphthas into higher octane reformat products for gasoline blending and aromatic rich reformat for aromatic production. Basically, the process re-arranges or re-structures the hydrocarbon molecules in the naphtha feedstocks as well as breaking some of the molecules into smaller molecules. Naphtha feeds to catalytic reforming include heavy straight run naphtha. It transforms low octane naphtha into high-octane motor gasoline blending stock and aromatics rich in benzene, toluene, and xylene with hydrogen and liquefied petroleum gas as a byproduct. With the fast growing demand in aromatics and demand of high - octane numbers, catalytic reforming is likely to remain one of the most important unit processes in the petroleum and petrochemical industry. Various commercial catalytic reforming processes is given in [Table M-VI 6.1](#).

**Table M-VI 6.1: Various Catalytic Reforming Processes**

Process	Licensor
Rheniforming	Chevron oil
Power forming	ESSO Oil/EXXON
Magna forming	Altalntic Richfield oil
Ultra forming	British petroleum
Houdriforming	Houdry process
CCR Plateforming	UOP
Octanising	Axen

## OCTANE NUMBER OF HYDROCARBONS

Octane number is a measurement of antiknock characteristics of fuels

- Among the same carbon number compounds, the order of RONC is (Research Octane Number )

Paraffins < Naphthenes < Aromatics

- Branched paraffins also have high octane. It increases with degree of branching.

Therefore, octane number of naphtha can be improved by reforming the hydrocarbon molecule (Molecular rearrangement). Octane number of various hydrocarbons is mention in [Table M-VI](#)

6.2. Such rearrangement takes place in reforming reactors in presence of catalyst by way of numerous complex reactions.

**Table M-VI 6.2: Octane Number of Various Hydrocarbons**

Hydrocarbon	Octane number
n-Butane	94.0
i-Butane	102.0
n-Pentane	61.8
i-Pentane	93.0
n-Heptane	
octane	100.0
toluene	119.7

Feed consists of Heavy straight run gasoline (HSR), Naphtha, Heavy hydro cracker naphtha and Naphtha containing (C<sub>6</sub>-C<sub>11</sub>) chain paraffins, olefins, naphthenes & aromatics.

## PROCESS STEPS IN CATALYTIC REFORMING

Basic steps in catalytic reforming involve

- Feed preparation: Naphtha Hydrotreatment
- Preheating: Temperature Control,
- Catalytic Reforming and Catalyst Circulation and Regeneration in case of continuous reforming process
- Product separation: Removal of gases and Reformate by fractional Distillation
- Separation of aromatics in case of Aromatic production

## NAPHTHA HYDRO TREATMENT

Naphtha hydrotreatment is important steps in the catalytic reforming process for removal of the various catalyst poisons. It eliminates the impurities such as sulfur, nitrogen, halogens, oxygen, water, olefins, di olefins, arsenic and other metals presents in the naphtha feed stock to have longer life catalyst. [Figure M-VI 6.1](#) illustrate hydrotreatment of naphtha.

- Sulphur: Mercaptans, disulphide, thiophenes and poison the platinum catalyst. The sulphur content may be 500 ppm.
- Maximum allowable sulphur content 0.5 ppm or less and water content <4 ppm.
- Fixed bed reactor containing a nickel molybdenum where both hydro de sulphurisation reactions and hydro de nitrification reactions take place.
- The catalyst is continuously regenerated. Liquid product from the reactor is then stripped to remove water and light hydrocarbons.

### Various sections in the naphtha hydro treatment unit are:

**Charge Heater:** Preheating reactor feedstock to reaction temperature of 340 °C. Charge heater has four passes four gas burners. Heater tubes are made up of SS-321

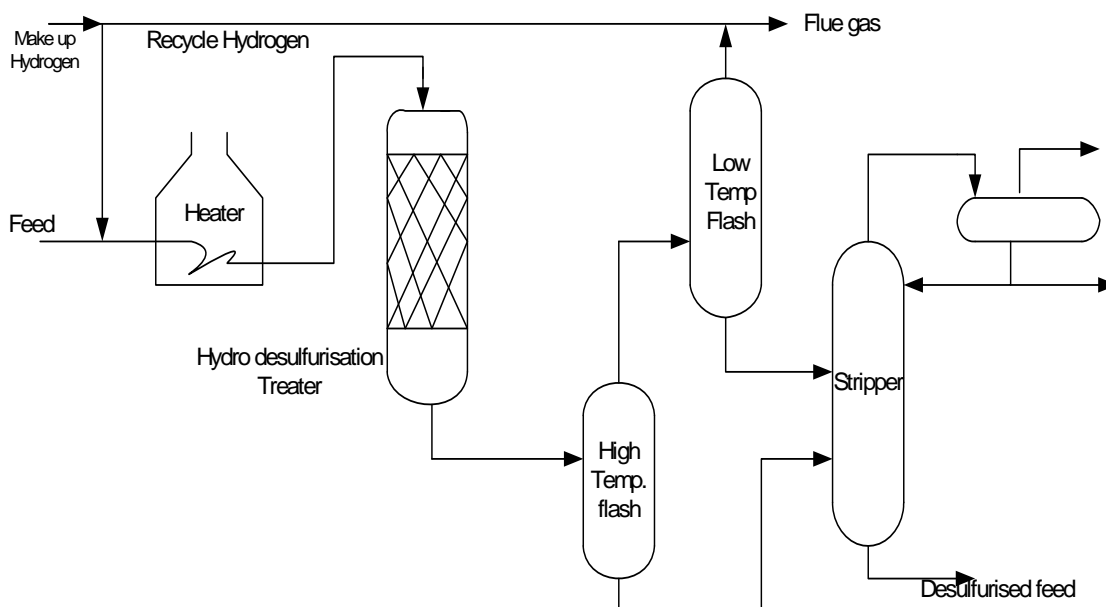
**Reaction Section:** The reactor consists of two catalyst beds.

**Stripping Section:** Stripping section uses air for stripping the light ends mainly hydrogen sulfide from reactor product, stripper temperature 14 kg/ cm<sup>2</sup> and temp. 172 °C

**Stripper Reboiler:** Stripper reboiler supply heat required for stripper

### Operating Variables Naphtha Hydrotreatment

- Reactor temperature
- Space velocity
- Hydrogen partial pressure
- H<sub>2</sub>/HC ratio, feed quality
- Stripper bottom temperature



**Figure M-VI 6.1: Hydrotreatment of Naphtha**

### CLASSIFICATION OF PROCESSES

- Semi Regenerative catalytic reforming
- Cyclic catalytic reforming
- Continuous catalytic reforming(CCR)

## Various Types of Catalytic Reformers

***Semi-Regenerative Fixed Bed reactors:*** In this type of reformers the catalyst generally has a life of one or more years between regeneration. The time between two regeneration is called a cycle. The catalyst retains its usefulness over multiple regeneration.

***Cyclic Fixed Bed Reformers:*** Cyclic reformers run under more severe operating conditions for improved octane number and yields. Individual reactors are taken offline by a special valving and manifold system and regenerated while the other reformer unit continues to operate.

***Continuous Reformers:*** In these reformers the catalyst is in moving bed and regenerated frequently. This allows operation at much lower pressure with a resulting higher product octane,  $C_5+$ , and hydrogen yield. These types of reformers are radial flow and are either separated as in regenerative unit or stacked one above the other.

## Semi- regenerative Catalytic Reforming Process

A semi-regenerative process uses low platinum and regeneration is required only once a year. The process consists of typically three reactor beds & furnace preheaters. The dehydrogenation is highly endothermic and large temperature drop as the reaction proceeds. Multiple reactors with intermediate reheat is required. Dehydrogenation of naphthene takes place in first reactor and requires less catalyst. Preheat of feed is required. Last reactor for isomerization of paraffins. Typical catalyst distribution in three reactors are 20, 30 and 50percent. [Figure M-VI 6.2](#) shows typical catalytic reforming process[ Mall,2007].

## Catalyst Regeneration

Performance of the catalyst decreases with respect to time due to deactivation. Reasons for deactivation

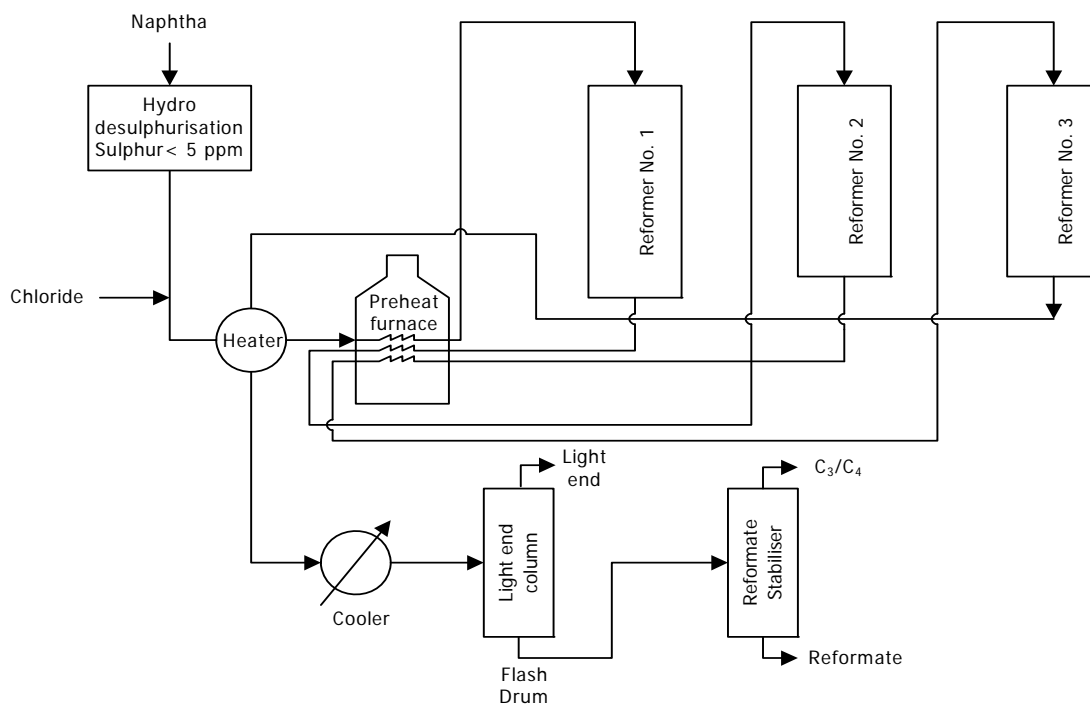
- Coke formation
- Contamination on active sites
- Agglomeration
- Catalyst poisoning

Activity could be restored if deactivation occurred because of coke formation or temporary poisons.

## Objective of Regeneration

- Surface area should be high
- Metal Pt should be highly dispersed

- Acidity must be at a proper level
- Regeneration changes by the severity of the operating conditions
- Coke formation can be offset for a time by increasing reaction temperatures.



**Figure M-VI 6.2: Catalytic Reforming Process**

## REACTIONS IN CATALYTIC REFORMING

Following are the most prevalent main reactions in catalytic reforming

### Desirable

- Dehydrogenation of naphthenes to aromatics
- Isomerisation of paraffins and naphthenes
- Dehydrocyclisation of paraffins to aromatics

### Non-Desirable

- Hydrocracking of paraffins to lower molecular weight compounds

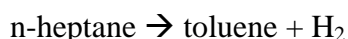
**Dehydrogenation & Dehydrocyclization:** Highly endothermic, cause decrease in temperatures, highest reaction rates, aromatics formed have high B.P so end point of gasoline rises

Dehydrogenation reactions are very fast, about one order of magnitude faster than the other reactions. The reaction is promoted by the metallic function of catalyst



**Dehydrocyclisation:** It involves a dehydrogenation with a release of one hydrogen mole followed by a molecular rearrangement to form a naphthene and the subsequent dehydrogenation of the naphthene.

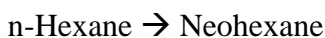
i-paraffins to aromatics of paraffins



**Favourable Conditions:** High temperature, Low pressure, Low space velocity, Low  $\text{H}_2/\text{HC}$  ratio

**Isomerisation:** Branched isomers increase octane rating, Small heat effect, Fairly rapid reactions.

**Favourable Conditions:** High temperature, Low pressure, Low space velocity,  $\text{H}_2/\text{HC}$  ratio no significant effect



**Naphthenes dehydro-Isomerisation:** A ring re-arrangement reaction, Formed alkyl-cyclohexane dehydrogenate to aromatics. • Octane increase is significant, Reaction is slightly exothermic

**Coking:** Coking is very complex group of chemical reactions. Linked to heavy unsaturated products such as poly-nuclear aromatics. Traces of heavy olefines and di-olefines promote coking. High feed FBP favors coking. Poor feed distribution in the reactor promotes coking favored by high temperature

**Hydrocracking:** Exothermic reactions, slow reactions, consume hydrogen, produce light gases, Lead to coking, Causes are high paraffin conc feed

**Favourable conditions:** High temperature, High pressure

## PROCESS VARIABLES

Following variables affect the reformate yield and quality of the product [Little, 1985; Raseev, 2003; Mohan, 2011]. Favorable conditions for different reforming reactions is mention in Table M-VI 1.3.

- Reaction temperature
- Space velocity
- Reaction pressure
- H<sub>2</sub>/HC ratio
- Feedstock Characteristics

**Table M-VI 6.3: Favorable Conditions for Different Reforming Reactions**

Reaction	Pressure	Temperature
Dehydrogenation of naphthenes to aromatics	Low pressure	High temperature
Isomerisation of naphthenes	Indeterminate	Indeterminate
Dehydrocyclisation of paraffins to aromatics	Low pressure	High temperature
Hydrocracking	High pressure	High temperature

## FEED QUALITY

- Naphthenes dehydrogenate very fast and give rise to aromatics. Therefore,  $N + 2A$  is taken as index of reforming. Higher the  $N + 2A$ , better is quality to produce high aromatics.

$N$  = Naphthenes %

$A$  = Aromatics %

- Lighter fraction have a poor naphthene and aromatic content are, therefore, poor feed for reforming. Low IBP feed results in lower aromatics and H<sub>2</sub> yield.
- Heavy fractions have high naphthene and aromatic hydrocarbon content. Therefore, good reforming feed but tendency of coke formation is high.

## REACTION TEMPERATURE



## Temperature is the most important operating parameter

- By simply raising or lowering reactor inlet temperature, operators can raise or lower the octane number of the product.
- Since all the reactor inlet temperatures are not necessarily identical, it is commonly accepted to consider the Weighted Average Inlet Temperature (WAIT)

## SPACE VELOCITY

- Liquid hourly space velocity (LHSV)
- Weight hourly space velocity (WHSV)

$$\text{LHSV} = \frac{\text{Vol/Hour of Reactor Charge (60F \& 14.7 Psia)}}{\text{Vol. of Catalyst}}$$
$$\text{WHSV} = \frac{\text{Weight/Hour of Reactor Charge}}{\text{Weight of Catalyst}}$$

Reforming LHSV range = 1.0 to 3.0 l/hr

Below 1.0 LHSV, undesired side reactions namely hydrocracking occurs which reduce reformate yield i.e., for every rise in LHSV of 0.1 between 1 to 2, about the 2°C rise in temperature is required. The lower the space velocity (i.e., higher contact time), the higher the severity assuming all other conditions unchanged. Lowering the space velocity has the same effects as increasing temperature, i.e. Increase the octane, decrease the product yield, decrease H<sub>2</sub> purity, Increase coke deposit

## REACTION PRESSURE

Reforming reaction pressure ranges (5 – 35 kg/sq. cm.). Decreasing pressure increases dehydrogenation of naphthenes and dehydrocyclisation of paraffins which favours an increase in production of aromatics and hydrogen (increase catalyst coking and shorter cycle life). Higher pressure causes higher rates of hydrocracking reducing reformate yield but decreases coking of catalyst resulting in longer cycle life.

## HYDROGEN TO HYDROCARBON RATIO

$$\text{Hydrogen : Hydrocarbon Ratio} = \frac{\text{Moles of H}_2 \text{ in Recycle Gas}}{\text{Moles of Hydrocarbons}}$$

Main purpose of hydrogen recycle is to increase hydrogen partial pressure in the reaction. H<sub>2</sub> reacts with coke precursors removing them from the catalyst reforming polycyclic aromatics. Higher the H<sub>2</sub>/HC ratio, higher the cyclic length. Two main reasons for reducing H<sub>2</sub>:HC ratio

- Reduction in energy costs for compressing and circulating H<sub>2</sub>.
- Favours naphthene dehydrogenations and dehydrocyclisation reaction

Lowering of H<sub>2</sub>/HC Ratio, From 8 to 4 carbon increase in 1.75 times and from 4 to 2 carbon increase 3.6 times

## CATALYST IN CATALYTIC REFORMING

**Monometallic:** (Pt),

**Bimetallic:** (Pt, Rhenium)

**Acid Activity:** Halogens/silica incorporated in alumina base.

**Metallic Function:** It promote dehydrogenation and hydrogenation. It also contribute to dehydrocyclisation and isomerisation.

**Acid Function:** It promotes isomerisation, the initial step in hydrocracking, participate in paraffin dehydrocyclisation.

### Stages in historical development of reforming catalyst in Indian scene

- Development of low Pt monometallic catalyst IRC-1002 by IPCL for BT Production.
- Commercialization of IRC-1001 catalyst in the first reactor of IPCL's three reactor system for Xylenes Production-1987.
- Scale up and manufacture of bimetallic catalyst IPR-2001 at IPCL's catalyst division
- Commercialization of bimetallic catalyst at MRL for gasoline production 1990
- Commercialization of bimetallic catalyst IRC-1002 by IPCL for BT Production
- Commercialization of monometallic catalyst at IRC-1002 in BPCL Reformer for BT production -1990
- Development of improved versions of reforming catalysts:
  - High Rhenium Catalyst – Recipe ready for scale up.

- Multimetallic Catalyst – Recipe ready for commercial trial.
- Spheroidal Catalyst - CCR operations recipe in advanced stage
  - Catalyst used now a days is platinum on alumina base.
  - For lower pressure stability is increased by combining rhenium with platinum.
  - Pt serve as a catalytic site for hydrogenation and dehydrogenation reactions
  - Chlorinated alumina provides acid site for isomerization, cyclization & hydrocracking reactions.
  - Catalyst activity reduced by coke deposition and chlorine loss
  - As catalyst age's activity of the catalyst decreases so temperature is increased as to maintain the desired severity.

## **Advantages Of Bimetallic And Multimetallic Catalyst Over Monometallic Catalyst**

### **Enhanced Resistance to Coking**

- Lower Fouling
- Higher coke tolerance
- Longer cycle length for S-R units
- Low pressure and low H<sub>2</sub>/HC ratio

### **Operation**

- High Octane
- High aromatics
- High yields of desirable products

Better yield stability

Lower temperature requirement

Better tolerance to high temperature

Better regenerability

High ultimate life

## **CATALYST POISONS**

**Temporary Poisons:** Temporary poisons are those impurities which can be removed during various pretreatment process like sulphur, nitrogen

**Permanent Poisons:** Permanent Poisons are those impurities present in the feed which is irreversible damage to the catalyst

Source and maximum level of catalyst poisons are given in [Table M-VI 1.4](#).

**Table M-VI 1.4: Source and Maximum Level of Catalyst Poisons**

POISONS	MAX. LEVEL WT%	SOURCE
Arsenic	1 PPB	SR or Cracked Naphtha
Lead	5 PPB	Recycle
Copper	5 PPB	Corrosion
Mercury	5 PPB	Naphtha condensate
Iron	5 PPB	Corrosion
Silicon	5 PPB	Foaming additives
Nickel	5 PPB	Corrosion
Chromium	5 PPB	Corrosion

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