
ISOMERIZATION OF C7+ PARAFFINIC NAPHTHA TO INCREASE ITS
OCTANE NUMBER FOR FUTURE FUELS

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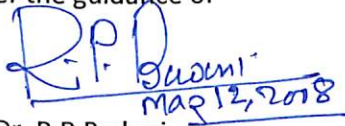
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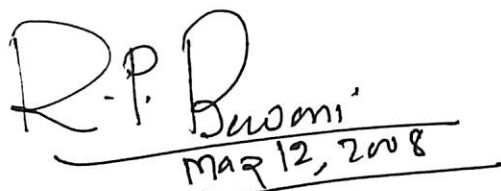
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This is to certify that the work contained in this thesis titled "ISOMERIZATION OF C7+ PARAFFINIC NAPHTHA TO INCREASE ITS OCTANE NUMBER FOR FUTURE FUELS" has been carried out by ASHISH GARG & ASHUTOSH NEGI under my supervision and has not been submitted elsewhere for a degree.


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Isomerization of C7+ Paraffinic Naphtha to Increase Its Octane Number for Future Fuels

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Nomenclature

API	-	American Petroleum Institute
ASTM	-	American society for Testing and materials
DBT	-	Dibenzothiophene
DHDS	-	Diesel Hydrodesuphurization
DMDS	-	Dimethyl disulphide
E_A	-	Activation energy
EP	-	End point
FCCU	-	Fluid catalytic Cracking Unit
HDM	-	Hydrodemetallation
HDN	-	Hydrodenitrogenation
HDO	-	Hydrodeoxygenation
HDS	-	Hydrodesuphurization
HDT	-	Hydrotreating
IBP	-	Initial boiling point
IP	-	Institute of Petroleum
K	-	Reaction rate constant
LCO	-	Light Cycle Oil
LGO	-	Light Gas Oil
LHSV	-	Liquid Hourly Space
LVGO	-	Liquid Vacuum gas Oil
MON	-	Motor Octane Number
MTBE	-	Methyl Tertiary Butyl Ether
n	-	Apparent reaction order
P	-	Reactor pressure
RON	-	Research Octane Number
S_f	-	Sulphur Content in the feedstock, ppmw
S_p	-	Sulphur content in the product
SOR	-	Start of Run
SRGO	-	Straight Run Gas Oil
SRLGO	-	Straight Run Light Gas Oil
T	-	Reactor Temperature
TEL	-	Tetra Ethyl Led
TAME	-	Tertiary Amylmethyl Ether
ULSD	-	Ultra Low Sulphur Diesel
UOP	-	Universal Oil Product



ABSTRACT

Environmental concern and the subsequent legislations on emissions demand the use of high quality fuels. In case of gasoline, the Lead phase out, limitations on aromatics with specific restrictions to benzene left a few options for alternative gasoline blends, where the recently adopted oxygenates such as MTBE too created ambiguity due to its contribution to ground water contamination. At the present scenario of gasoline, branched hydrocarbons gain much importance, as they are the only components left to give high octane without any emission problems.

Abundant availability of naphtha (90-140°C cut) that mainly contains C_{7+} hydrocarbons is a great source for the isomerization reaction. Hydro-isomerization of high sulfur, high olefinic FCC gasoline is also an interesting way to improve gasoline quality without losing any octane. Even in the present refinery configuration, addition of isomerization catalyst in the catalytic reformer can improve the quality of gasoline.

Discovery of a suitable technology and catalysts which could convert the especially the n-paraffins in C_{7+} range into isomers having 90+ RONC without cracking the hydrocarbons would be a boon to refiners and provide eco-friendly gasoline by minimizing olefines and aromatics.

Aim of the project is to develop a zeolite based catalyst for value addition of industrial feeds rich in C_7-C_9 hydrocarbons through isomerization.



CHAPTER 1

INTRODUCTION

Motor gasoline is a key automotive fuel and is likely to occupy the leading edge in the coming decades all over the globe. A common tool to enhance the octane number of gasoline used to be the addition of lead-containing components. Since its discovery in 1922, tetraethyl lead (TEL) has been added in small quantities to improve the quality of gasoline. However, in recent years, in many countries the amount of lead has been decreased by legislation with the target of its complete elimination. Phase out of TEL has been compensated by aromatic rich gasoline that generally obtained by increasing the severity of the reformer. At this juncture, use of oxygenate additives such as methyl tertiary butyl ether (MTBE) and tertiary amylmethyl ether (TAME) is increasingly being used to improve the gasoline quality as well as to control the emissions from gasoline, although they cost more per octane number. However, contribution of oxygenates to environmental pollution is also observed and there has been much debate on their use as gasoline additives.

The existing main processes for high-octane gasoline production are reforming and FCC. Catalytic reforming of S-R naphtha/ FCC naphtha/ cocker naphtha/ hydrocracked heavy naphtha which yields reformate having as high as 95-105 RONC with large percentage of aromatics. Although reformate is high-octane products, they typically contain over 60% aromatics, and their use in reformulated gasoline should therefore be limited. In addition, in order to decrease harmful vehicle emissions, the concentration of benzene in gasoline has also been limited in several countries by government regulations.

Isomerization of paraffins larger than C_6 is one way to improve octane without increasing the aromatic or olefin content. $n-C_7$ has a research octane rating of 0, while 2-methyl hexane and 2,3-dimethyl pentane have research octane ratings of 53 and 93, respectively. C_7 paraffins are



relatively abundant in naphtha, and their isomerization is a natural extension to existing C_5/C_6 isomerization.

Discovery of a suitable technology and catalysts which could convert the especially the n-paraffins in C_7+ range (having RONC < 17) into isomers having 90+ RONC without cracking the hydrocarbons would be a boon to refiners and provide eco-friendly gasoline by minimizing olefines and aromatics.

Abundant availability of light naphtha (90-140°C cut) that mainly contains C_7+ hydrocarbons is a great source for the isomerization reaction.



CHAPTER 2

CONCEPT OF OCTANE NUMBER

The **octane rating** is a measure of the auto ignition resistance of gasoline (petrol) and other fuels used in spark-ignition internal combustion engines.

Knock resistance

Engine knocking is compression detonation of fuel in the power stroke of the engine. Knocking occurs when the air-fuel mixture autoignites all at once (or sometimes perhaps when the flame front goes supersonic because of early ignition timing), before the flame front from spark plug ignition can reach it[11]. The explosive reaction causes combustion to stop before the optimum timing, causing a decrease in performance. A fuel, such as ethanol, with a high auto ignition temperature that burns reasonably fast and thus does not need early ignition timing will most often have high practical value knock resistance.

Definition of octane rating

Octane is measured relative to a mixture of isooctane (2, 2, 4-trimethylpentane, an isomer of octane) and n-heptane. An 87-octane gasoline, for example, has a mixture of 87 vol-% isooctane and 13 vol-% n-heptane. This does not mean, however, that the gasoline actually should contain these chemicals in these proportions. It simply means that it has the same auto ignition resistance as the described mixture.

A high tendency to auto ignite, or low octane rating, is undesirable in a gasoline engine but desirable in a diesel engine. The standard for the combustion quality of diesel fuel is the cetane number. A diesel fuel with a high cetane number has a high tendency to auto ignite, as is preferred.



Measurement methods

The most common type of octane rating worldwide is the **Research Octane Number (RON)**. RON is determined by running the fuel through a specific test engine with a variable compression ratio under controlled conditions, and comparing these results with those for mixtures of isooctane and n-heptane.

There is another type of octane rating, called **Motor Octane Number (MON)** or the aviation lean octane rating, which is a better measure of how the fuel behaves when under load. MON testing uses a similar test engine to that used in RON testing, but with a preheated fuel mixture, a higher engine speed, and variable ignition timing to further stress the fuel's knock resistance. Depending on the composition of the fuel, the MON of a modern gasoline will be about 8 to 10 points lower than the RON. Normally fuel specifications require both a minimum RON and a minimum MON.

	MON	RON
Inlet air temperature	148.9 C	65.6 C
Engine jacket temp	100 C	100 C
Engine RPM	900	600

In most countries (including all of Europe and Australia) the "headline" octane that would be shown on the pump is the RON, but in the United States and some other countries the headline number is the average of the RON and the MON, sometimes called the **Anti-Knock Index (AKI)**, **Road Octane Number (RdON)**, **Pump Octane Number (PON)**, or $(R+M)/2$. Because of the 8 to 10 point difference noted above, this means that the octane in the United States will be about 4 to 5 points lower than the same fuel elsewhere: 87 octane fuel, the "regular" gasoline in the US and Canada, would be 91-95 (regular) in Europe.

The octane rating may also be a "trade name", with the actual figure being higher than the nominal rating.



It is possible for a fuel to have a RON greater than 100, because isooctane is not the most knock-resistant substance available. Racing fuels, straight ethanol, Avgas and liquefied petroleum gas (LPG) typically have octane ratings of 110 or significantly higher - ethanol's RON is 129 (MON 102, AKI 116). Typical "octane booster" additives include tetra-ethyl lead and toluene. Tetra-ethyl lead is easily decomposed to its component radicals, which react with the radicals from the fuel and oxygen that would start the combustion, thereby delaying ignition.

Many high-performance engines are designed to operate with a high maximum compression and thus need a high quality (high energy) fuel usually associated with high octane numbers and thus demand high-octane premium gasoline.

The power output of an engine depends on the energy content of its fuel, and this bears no simple relationship to the octane rating. A common myth amongst petrol consumers is that adding a higher octane fuel to a vehicle's engine will increase its performance and/or lessen its fuel consumption; this is mostly false—engines perform best when using fuel with the octane rating they were designed for and any increase in performance by using a fuel with a different octane rating is minimal.

Using high octane fuel for an engine makes a difference when the engine is producing its maximum power. This will occur when the intake manifold has no air restriction and is running at minimum vacuum. Depending on the engine design, this particular circumstance can be anywhere along the RPM range, but is usually easy to pin-point if you can examine a print-out of the power-output (torque values) of an engine. On a typical high-revving motorcycle engine, for example, the maximum power occurs at a point where the movements of the intake and exhaust valves are timed in such a way to maximize the compression loading of the cylinder; although the cylinder is already rising at the time the intake valve closes, the forward speed of the charge coming into the cylinder is high enough to continue to load the air-fuel mixture in.

When this occurs, if a fuel with below recommended octane is used, then the engine will knock. Modern engines have anti-knock provisions built into the control systems and this is usually achieved by dynamically de-tuning the engine while under load by increasing the fuel-air mixture and retarding the spark. Here is a white paper that gives an example: In this example the engine maximum power is reduced by about 4% with a fuel switch from 93 to 91 octanes (11 hp,



from 291 to 280 hp). If the engine is being run below maximum load then the difference in octane will have even less effect. The example cited does not indicate at what elevation the test is being conducted or what the barometric pressure is. For each 1000 feet of altitude the atmospheric pressure will drop by a little less than 1 in Hg (11 kPa/km). An engine that might require 93 octane at sea level may perform at maximum on a fuel rated at 91 octane if the elevation is over, say, 1000 feet. See also the APC article.

The octane rating was developed by the chemist Russell Marker. The selection of *n*-heptane as the zero point of the scale was due to the availability of very high purity *n*-heptane, not mixed with other isomers of heptane or octane, distilled from the resin of the Jeffrey Pine. Other sources of heptane produced from crude oil contain a mixture of different isomers with greatly differing ratings, which would not give a precise zero point.

4 MON and RON depend on Gasoline Composition

The octane number measured is not an absolute number but rather a relative value based on accepted standards. By definition, *n*-heptane has an octane number (RON and MON) of 0, while iso-octane (2, 2, 4-trimethyl pentane) is 100. Linear combinations of these two components are used to measure the octane number of a particular fuel. A 90%/10% blend of iso-octane/*n*-heptane has an octane value of 90. Any fuel knocking at the same compression ratio as this mixture is said to have an octane number of 90.

In general, RON values are never less than MON, although exceptions to this rule exist. For pure compounds the differences between RON and MON range from 0 to more than 15 numbers. Typical values for gasoline range hydrocarbons having boiling points between 30° and 350° F go from less than 0 to greater than 100 with the extreme values being generated by extrapolation. Table 8 summarizes actual RON and MON values for a variety of pure hydrocarbons.

In practice octane numbers do not blend linearly. To accommodate this, complex blending calculations employing blending octane numbers as opposed to the values for pure hydrocarbons are routinely employed. There is no universal blending program used industry wide. In fact, for a given oil company, blending calculations that are refinery specific are not uncommon. As an improvement over octane numbers of pure compounds, there are tabulations of blending octane



numbers for both RON and MON. Summarized in Table 1, these numbers are measured by blending 20 vol.% of the specific hydrocarbon in 80 vol.% of a 60/40 iso-octane/n-heptane mixture. Although still not exactly indicative of the actual blending octane number for a specific gasoline composition, the blending octane numbers are more representative. In general, the blending octane numbers are greater than the corresponding pure octane number.

2.5 General Rules Regarding Octane Number of Compounds

- Normal (n) paraffins have the least desirable knocking characteristics, and these become progressively worse as the molecular weight increases.
- Iso (i) paraffins and naphthenes have higher octane than corresponding n-paraffins.
- Octane number of i-paraffins increases as the degree of branching of the chain is increased.
- Olefins have markedly higher octane numbers than the corresponding paraffins.
- Aromatics are hydrocarbons with the highest octane number for the same number of carbon atoms.

Thus it is clear that in order to have a large increase in octane number, it is necessary to transform paraffins and naphthenes into aromatics.

In view of strong environmental restrictions on gasoline, the main thrust of technological research has been in the field of finding different options for:

- *Lead phase out and octane enhancement
- *Reduction in sulfur and olefin content
- *Decrease in benzene and aromatic content
- *Reduced tailpipe and evaporation emissions



Table 1: Octane Numbers of pure hydrocarbons

<u>Hydrocarbon</u>	<u>Actual</u>		<u>Blending</u>	
	<u>RON</u>	<u>MON</u>	<u>RON</u>	<u>MON</u>
<u>PARAFFINS</u>				
n-butane	93		113	114
n-pentane	62	62	62	67
2-methylbutane	92	90	99	104
2,2-dimethylpropane	85	80	100	90
n-hexane	25	26	19	22
2,2-dimethylbutane	92	93	89	97
n-heptane	0	0	0	0
2,2-dimethylpentane	93	96	89	93
2,2,3-trimethylbutane	>100	>100	113	113
2,2,3-trimethylpentane	100	100	105	112
2,2,4-trimethylpentane	100	100	100	100
<u>OLEFINS</u>				
1-Pentane	91	77	152	135
2-Methyl-2 butene	97	85	176	141
3-Methyl-2 pentene	97	81	130	118
4-Methyl-2 pentene	99	84	130	128
2,2,4-trimethyl-1 pentene	>100	86	164	153
2,2,4-trimethyl-2 pentene	>100	86	148	139
<u>AROMATICS</u>				
Benzene	>100	>100	99	91
Toluene	>100	>100	124	112
O-Xylene	>100	>100	120	103
M-Xylene	>100	>100	145	124
P-Xylene	>100	98	146	127
Ethylbenzene	>100	>100	124	107
1,3,5-trimethylbenzene	>100	>100	171	137
Propylbenzene	>100	98	127	129
Isopropylbenzene	>100	99	132	124
<u>NAPHTHENES</u>				
Cyclopentane	101	85	141	141
Methylcyclopentane	91	80	107	99
Cyclohexane	83	77	110	97
Methylcyclohexane	75	71	104	84
O-Dimethylcyclohexane	81	79	85	83
M-Dimethylcyclohexane	67	64	67	65
P-Dimethylcyclohexane	68	65	66	63



CHAPTER 3

FEEDSTOCK FOR GASOLINE

3.1 Gasoline

The common name of the gasoline is motor sprit, it is widely used petroleum product. Gasoline is light distillate consist of fraction with boiling ranges of 30 to 180°C. It consist of hydrocarbon ranging from C5 to about C10. The main types are (a) normal or straight chain paraffins (b) iso branched chain paraffins (c) cyclo paraffins (d) aromatics (e) olefins. Of these normal paraffins are major component in straight run naphthas. Iso-paraffins have high octane number followed by cyclo paraffins. Olefins & aromatics have high octane number [27]. A high proportion of olefins are not tolerated in gasoline because of its storage problem i.e. due to gum formation during storage. Gasoline is prepared by various components produced in refining processes such as alkylation, catalytic reforming, hydro cracking, visbreaking, isomerization, polymerization etc. It is usual to incorporate very small quantities of additives to inhibit knocking, pre-ignition, gum formation and icing of carburetor. Catalytic reforming is employed to improve octane number of straight run naphtha.

3.2 Feedstock for Gasoline

The feedstock used for gasoline is Naphtha. Naphtha is a name given to the light hydrocarbons boiling in gasoline range. It is a light distillate obtained from refining of crude oil.

The boiling ranges of different types of naphtha are as follows:-

C5 ----- 85 °C

C5 ----- 110 °C

C5 ----- 140°C

Naphtha is classified as light, heavy & Intermediate Naphtha. Light naphtha fraction boils at 100°C. Heavy naphtha boils at 150 °C [26]. Intermediate boils in between 100 °C & 150 °C. Naphtha is produced by atmospheric distillation of crude oil. This is called straight run Naphtha. It is also produced by several conversion processes such visbreaking, fluid catalytic cracking,



hydrocracking, coking etc. These are called cracked Naphthas. The proper quality Naphtha for petrochemical & fertilizer industry is produced by diagrammatizing by with or without reforming operations. In petrochemical industry C5 - 140°C naphtha is used as feedstock for steam cracker. Catalytic reforming of straight run naphtha yields C6-C8 reformato rich in aromatic hydrocarbons, benzene, toluene, ethylbenzene & xylenes. The use of naphtha as gasoline requires its high anti-knock value or octane number.

The Naphtha has boiling range of 60°C-140°C. For benzene production we need 60°C-90°C naphtha range because of higher C6 precursor in this range. Similarly for Toluene, Xylenes and Gasoline the feedstock range is 90°C-110°C, 110°C-140°C and 90°C-140°C respectively.

3.3 Properties of Gasoline

Octane number:-The octane number of the fuel is defined as volume percentage of iso octane (2, 2, 4-trimethylpentane) in a blend of n-heptane which is equal to test fuel in knock intensity in a standardized and closely controlled conditions of a test in a single cylinder.

Combustion Characteristics:-Combustion in the spark engine is mainly depends on engine design and fuel quality. If there is evenly burning of the fuel and there is no untimely burning of the fuel i.e. knocking. Then fuel is good.

Oxidation Stability:-On prolonged storage gasoline undergo a slow but progressive oxidation deterioration. The result is non volatile gummy residue If it present⁵ in the gasoline it causes multiple trouble such as deposit formation in the carburetor parts, venturi.

Volatility:-The volatility of the fuel is important for rate of warm-up, vapor lock carburetor icing and crankcase dilution. The fuel is sufficiently volatile to give easy starting, rapid warm-up and adequate vaporization for proper distribution between the cylinders.

3.4 Impurities in the Feed:

The catalyst can be inhibited, either temporarily or permanently by poisons contained in the feed.



Table 2: Impurities in feed and their limit

As	5ppb max.
Pb	5ppb max.
Cu	5ppb max.
Fe	5ppb max.
Ni	5ppb max.
Organic Nitrogen	1ppm max.
Halogens (F, Cl)	1ppm max.
Water & Oxygenated Products	4ppm max.
Sulfur	1ppm max.

Nitrogen under NH_3 form affects the acidic function and leads to a fast neutralization of the support. This explains the limitation required for the nitrogen content in the reformer feed.

3.5 Feed Preparation:

The charge to the catalytic reformer is naphtha that has been processed in a feed unit 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 is itself a catalytic unit using a Co-Mo or a Ni-Mo catalyst. Hydrogen is included with the feed to the feed preparation units. These feed preparations units are called hydrodesulphurization (HDS) units, or hydro treaters. After passing over the Co-Mo or Ni-Mo catalyst, the naphtha goes to the stripper or fractionators that remove the hydrogen sulfide, ammonia, water and light hydrocarbons formed in the hydrotreater reactor. The feed stripper could be either is in the tail end of the hydrotreater or on the front end of the reformer.

A number of early reformers were design with a center well in the prefractinator so both initial point and end boiling point were made to specification in one vessel. The reactor feed is by far greatest volume yield off the prefractionator. With a center well, almost all the naphtha must be



vaporized. This requires much more energy than the scheme of yielding, or making, reactor charge off the bottom of the prefractionator.

On the other hand, some refiners like to include a light distillate, such as kerosene or jet fuel, in the feed to the hydrotreater for desulphurization along with the reformer feed. In that case of the center well design provides a means of separating the distillate from the reactor charge.

The reformer charge, pretreated and fractionated to proper initial and end boiling points, is combined with gas stream containing 60-90 mol% hydrogen. Also a chloride chemical representing 0.5-5.0 ppm wt of the reactor charge is injected. In reforming nomenclature, reactor charge means the naphtha feed. Total reactor charge is the naphtha feed plus hydrogen-bearing recycle gas stream[1,29].

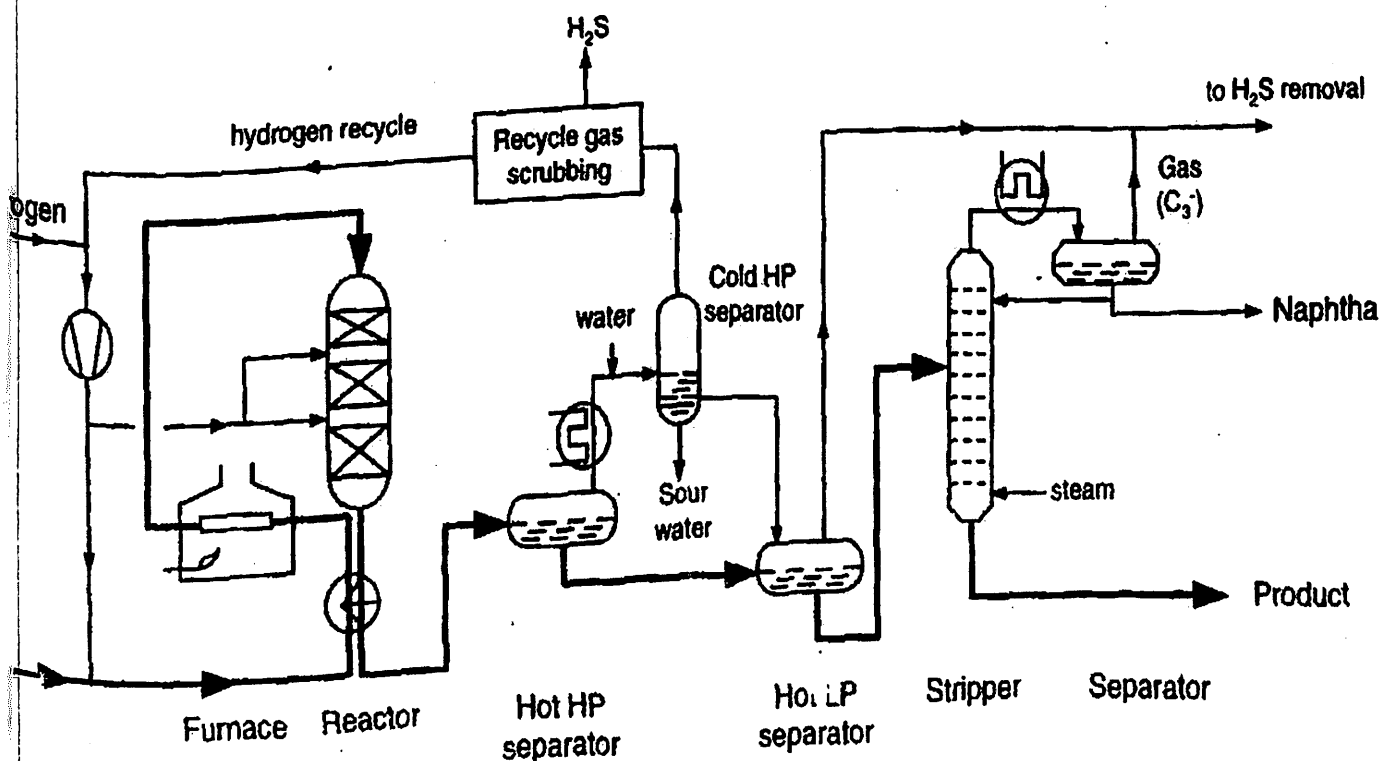


Figure 1: Hydro desulphurization Unit



3.6 GREEN GASOLINE

Motor gasoline is one of the key products obtained from a petroleum (crude oil) refinery. It is a complex mixture of light hydrocarbons containing 5 to 12 carbon atoms and having a boiling range of 40°C to 190°C.

Gasoline pool is a blend of several refinery streams namely Catalytic Reformate, Straight Run Naphtha (SRN), FCC Gasoline, Visbreaker / Coker Naphtha, Isomerate, Alkylate, Oxygenate etc. The product application and customer acceptance set detailed specifications for various gasoline properties, which in turn determine which refinery streams are suitable for a specific blend.

Today most petroleum refineries are facing the challenge of producing motor gasoline having all the desirable properties and also complying with the ever-increasing environmental regulations & health restrictions on automotive emissions. The environmental regulations were created to guard against high levels of aromatics (benzene in particular), olefins, and sulfur in the gasoline. Reduction in volatile organic compounds, toxic and nitrogen oxides (TOx & NOx) in automotive tailpipe emissions, and evaporative and refueling emissions have also assumed high priority. In India, there is an increased awareness of environmental regulations towards maintaining better air quality. Therefore, keeping the health hazards in view, the Indian refiners have also initiated to consider various methodologies for producing cleaner products than what was being produced before. The following major changes are sought in the specifications of motor gasoline for better air quality:

- Reduction in sulfur.
- Reduction in total aromatics and benzene.
- Reduction in RVP.
- Reduction in volatile organic compounds particularly olefins, which react with high atmosphere reactivity leading to ground level ozone formation.



Novel technological options are evolving that will improve the quality of gasoline pool streams. The focus is on the two most important refinery streams: FCC gasoline and catalytic reformat. FCC gasoline is a major contributor of sulfur and olefins while reformat is the main source of benzene and aromatics.

FCC gasoline being the major component of the motor gasoline pool has 1000-2000 ppmw sulfur depending upon the feed VGO used in a FCC unit. Therefore, it is essential to reduce the sulfur content of FCC gasoline either by pretreatment i.e. desulfurization of vacuum gas oil, or by post treatment. Each of these has its merits and demerits depending upon the individual refinery configuration.

3.7 Impact of Gasoline on the Environment

The impact of gasoline on the environment is directly related to its fuel properties and contents. Table-1 gives a brief account of gasoline properties, their desirable impact on engine performance and their undesirable impact on the environment.

"In a nutshell, the global trend is towards making gasoline more environment & human friendly or in other words making gasoline, a really green fuel."

Table 3: Summary of Gasoline Properties

Gasoline Property	Desirable for	Impact on Environment
Octane Number	Avoiding engine knocking; increasing fuel-air mix compression ratio, engine power & efficiency.	<ol style="list-style-type: none"> 1. Benzene is carcinogenic. 2. Aromatics produce more smoke & smog. 3. Olefins form engine fouling gums, more smoke & smog.



<p>Volatility (Reid vapor pressure)</p>	<p>Sufficient light components to give adequate vaporization of fuel air mix for easy engine cold start.</p>	<ol style="list-style-type: none"> 1. Too many light components result in hydrocarbon loss & in atmospheric pollution. 2. Too many heavy components contribute to chamber deposits & spark plug fouling causing release of unburnt hydrocarbons into the atmosphere.
<p>Sulfur Content</p>	<p>Not desirable at all.</p>	<ol style="list-style-type: none"> 1. Sulfur compounds are corrosive, foul smelling, and increase sulfur trioxide emissions. 2. Decrease catalytic converter efficiency and adverse effect on sensor.
<p>Olefins</p>	<p>Desirable for their octane value</p>	<ol style="list-style-type: none"> 1. Leads to deposits and gum formation and increased emissions of ozone forming hydrocarbons and toxic compounds.
<p>Aromatics</p>	<p>Desirable for their octane value</p>	<ol style="list-style-type: none"> 1. Increased engine deposits and tailpipe emissions including carbon dioxide 2. Produces carcinogenic benzene in exhaust



CHAPTER 4

CATALYTIC REFORMING

The catalytic reforming process converts naphthas and heavy straight-run gasoline into high-octane gasoline blending components. The feed and product streams to and from the reformer are composed of four major hydrocarbon groups: paraffins, olefins, naphthenes, and aromatics. Table 4 depicts the change in volume of these hydrocarbon groups as they pass through this unit. During this process, the octane value of the product stream increases with the formation of aromatics.

Table 4: Typical reformer Feed and Make-Up

Chemical Family	Feed (Volume %)	Product (Volume %)
Paraffins	45-55	30-50
Olefins	0-2	0
Naphthenes	30-40	5-10
Aromatics	5-10	45-60

Source: Gary 1984

Rather than combining or breaking down molecules to obtain the desired product, catalytic reforming essentially restructures hydrocarbon molecules that are the right size but have the wrong molecular configuration or structure. Catalytic reforming primarily increases the octane of motor gasoline rather than increasing its yield.

The four major reaction types that take place during reforming include dehydrogenation, dehydrocyclization, isomerization, and hydrocracking. The four reaction types are presented in more detail in Figure 11 with specific reactions that are typical of each type.



Catalytic reforming reactions are promoted by the presence of a metal catalyst, such as platinum on alumina, or bimetallic catalysts, such as platinum-rhenium on alumina. The reformer is typically designed as a series of reactors, as shown in Figure 12, to accommodate various reaction rates and allow for interstage heating. Interstage heaters maintain the hydrocarbon feed stream at a temperature of approximately 950^o F, which is required for the primarily endothermic reactions. Catalytic reforming can be continuous (e.g., cyclic) or semi-regenerative. In continuous processes, the catalysts can be regenerated one reactor at a time without disrupting operation [DOE 1998].

Catalytic reforming is a key process in petroleum refining. It is one process that makes high-octane number, unleaded gasoline a reality. This is the process which converts or reconstructs, without changing carbon numbers in the molecule, gasoline boiling range low-octane hydrocarbons to the high-octane gasoline blending stock. The process is also used to produce rich concentrate of aromatics (BTX) i.e. benzene, toluene and xylenes required in petrochemical industry for producing plastics and fibers. The basic change that takes place in the reforming is the formation of aromatics from paraffins and naphthenes. During the process, some iso-paraffins responsible for high octane are also produced. The units that are designed to produce high-octane motor gasoline are known as octane reformers and those that are operated for production of BTX are called BTX reformers[1,12]. The other products of consequence from catalytic reforming are hydrogen and liquefied petroleum gas (LPG) which makes the process economically more viable. Hydrogen is used in refinery for hydrotreating the middle distillate to premium products. With the fast growing market for aromatic and motor gasoline, catalytic reforming is expected to continue as an important process in refining and petrochemical industry. 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 reformer. The primary product from the reformer is reformate. Because reformer feedstocks contain paraffins, a BTX reformer yields a mixture of paraffins and aromatics. Further processing such a mixture is necessary to recover aromatics of mark able purity. After removal of aromatics from the reformate the remainder is called raffinate.



In some refineries a catalyst reformer may operate part time as a motor fuel unit and part time as a BTX unit.

Until the advent of catalytic reforming, refining processes were unselective (except a few like Alkylation, polymerization and isomerisation) - that's the feedstock was indiscriminately converted or cracked with little attempt to control specific chemical reactions. Catalytic reforming catalyst and operating conditions are designed to promote certain reactions and inhibit others. Reactions most prevalent in catalytic reforming are dehydrogenation, isomerisation, dehydrocyclisation and hydrocracking.

4.1 Development of Reforming

- In the 1930s gasoline octane improved by use of thermal reforming, Mild thermal cracking of naphtha's paraffins to olefins.
- In late 30s & early 40s, alkylation of olefins developed to improve the octane of aviation gasoline.
- By the 50s, high performance automotive engines needed high-octane gasoline
 - » Expanded use of alkylation, reforming, & isomerization.
- Some large refineries had catalytic reforming capacity based on the cyclic process used in World War II
 - » Benzene for styrene
 - » Toluene for TNT
 - » Aromatics for aviation fuel
- Catalyst regeneration cycle was very short & required elaborate cycle controllers — small refineries could not afford Platforming commercialized by UOP in 1949
 - » Platinum catalyst
 - » Could be operated for a year before regeneration was required
- Catalytic reforming became ubiquitous as the smaller refiner quickly adopted it.



4.2 Overview of Reforming

- Produces large amounts of hydrogen that is ultimately used in hydrotreating
 - »Catalytic reforming second only to catalytic cracking in commercial importance to refiners
 - »Almost every refinery in the world has a reformer
- Reformate desirable component for gasoline
 - »High octane number, low vapor pressure, very low sulfur levels, & low olefins concentration
 - »Despite levels of benzene, aromatics, & olefins
- Catalytic reformer contributes the second highest volume to the gasoline pool.

Isomerization 15 vol%

Alkylation 20 vol%

Reformer 30 vol%

FCCU 35 vol%

4.3 PRINCIPAL REACTIONS IN REFORMING:

4.3.1 Dehydrogenation

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

Reaction:

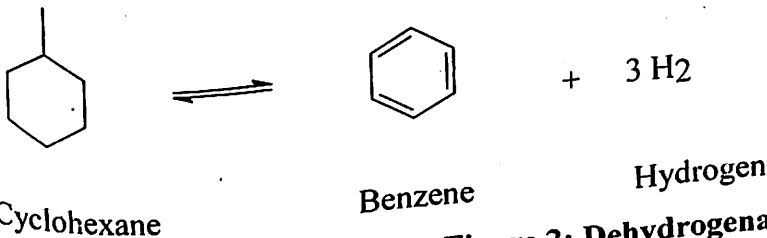


Figure 2: Dehydrogenation Reaction

When naphthene is converted to aromatic octane number is gained at a loss of volume. Some reforming reactions increase octane number with very little change in volume, an example is isomerisation of paraffins.



4.3.2 Isomerization of Paraffins and Naphthenes

Isomerisation of paraffin rearranges the molecule with essentially no change in volume but with a marked increase in octane number. A refinery motor fuel containing just 2 vol % n-hexane would gain about 1.3 RON or 1.5 (R+M)/2 octane rating by isomerisation.

Naphthene hydrocarbons may also isomerize in reformer reactors. When this happens they almost immediately undergo dehydrogenation to an aromatic. A classic example is conversion of Methylcyclopentane (MCP) to benzene.

Reaction:

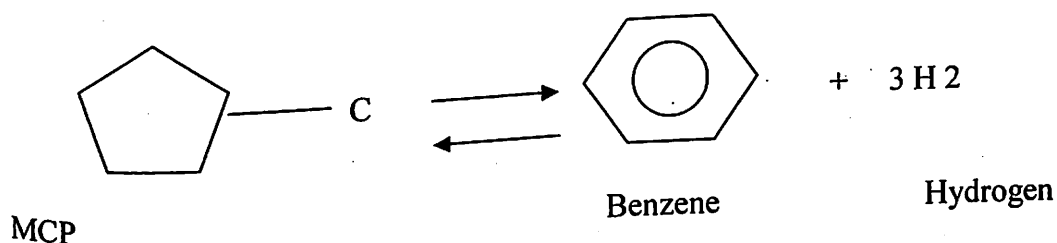


Figure 3: Isomerization Reaction

MCP 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 cyclised to aromatics by what is known as aromatisation.

4.3.3 Dehydrocyclization of Paraffins

It is the most sought for but very difficult reaction in reforming. It is required for production of a satisfactory yield of high-octane number reformates. A typical dehydrocyclization reaction is given below. And also the most difficult reaction to promote is dehydrocyclisation. It is a required reaction for the production of satisfactory yield of high octane number reformat. Most reforming feedstocks contain a substantial quantity of low octane number paraffins. The dehydrogenation and isomerisation reaction of paraffin alone cannot produce enough aromatics



and isoparaffins to yields high octane number reformat of 80 or higher RONO. As with the naphthene isomerisation, there are intermediate steps between the paraffinic and aromatic. The reaction is favored by high temperature and low pressure, it predominately takes place in the last reactor on the train.

For cyclization paraffin with atleast six carbon straight chain is needed. Consequently n-pentane does not cyclize, nor does 2 methyl pentane nor 2, 2 dimethyl pentane [13]. However, n-hexane will cyclize to benzene. The longer straight chain paraffin will dehydrocyclise more readily the shorter chains.

Reaction:

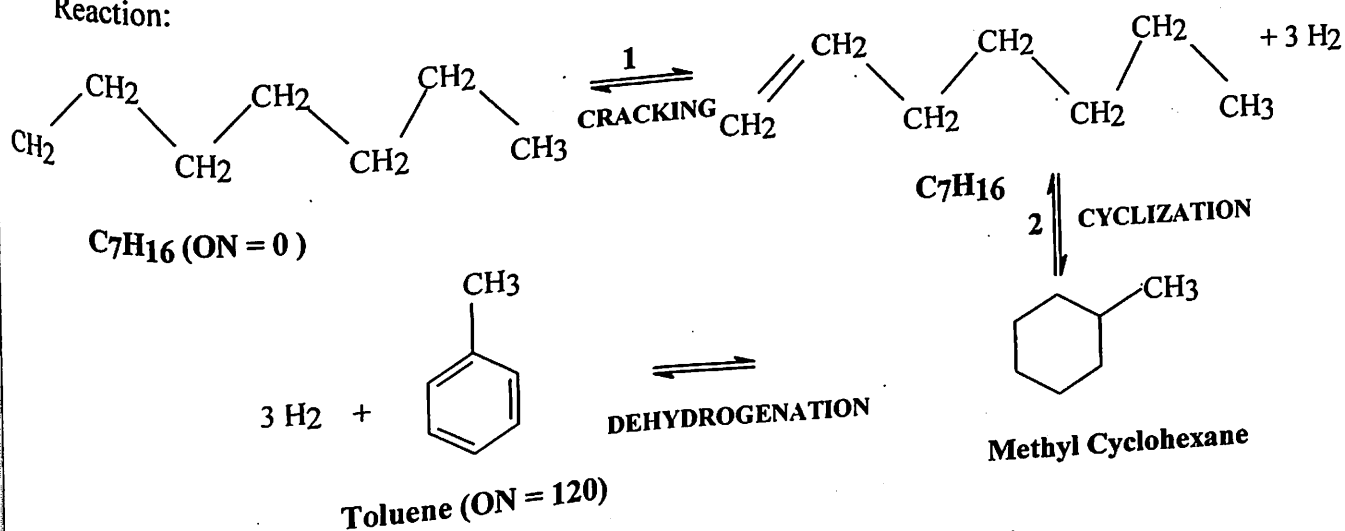


Figure 4: Dehydrocyclisation Reaction

4.3.4 Hydrocracking

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

The sharing of C-C bond initially produces an olefin that is quickly hydrogenated. The C₅+reformat from a reformer contains only about trace of olefins usually less than 0.5 vol%. these olefins are result of hydrocracking close to the outlet of last reactor where no time is left



for hydrogenation. High temperature and high pressure accelerates hydrocracking. It usually takes place on the acidic sites of the catalyst but can also cause pyrolysis. (Chemical decomposition by heat) at temperature above 1,100 F. hydrocracking produces coke or coke precursors that cover active catalyst sites [14].

Hydrocracking is not all bad. For example n-decane can split into n-heptane and propane. The n-heptane can then dehydrocyclise to toluene a high octane number aromatic. Although a reformer like to operate with minimum hydrocracking to maximize c5+ output a reformer can be operated a little at higher than required octane to yield more propanes and butanes. The price of LPG compared with the price of gasoline dictates this mode of operation.

Reaction:

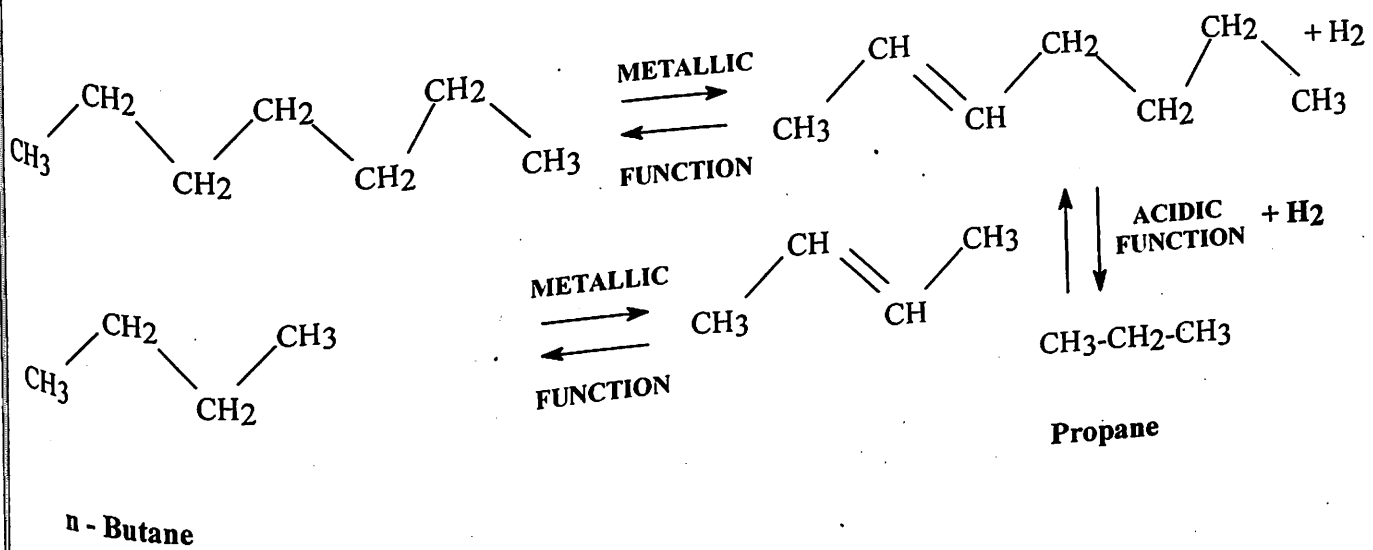


Figure 5 : Hydrocracking Reaction

4.3.5 Other Reactions:

4.3.5.1 Hydrogenolysis Reactions

These lead to formation of C₁ and C₂ and are promoted by metallic function.

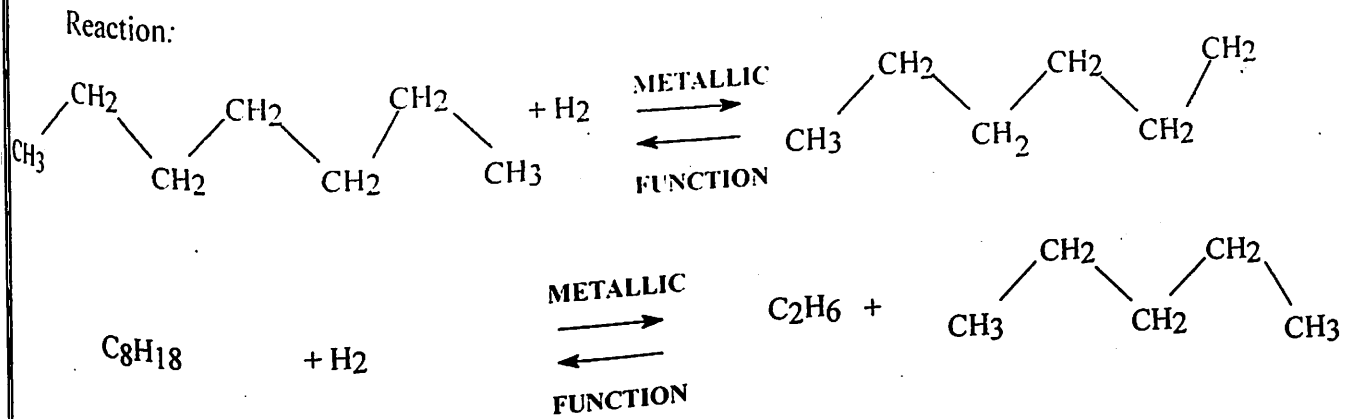


Figure 6 : Hydrogenolysis Reaction

These are highly exothermic and are favored at high pressure and temperature

4.3.5.2 HydroDealkylation

It is the breakage of the branched radical of an aromatic ring.

Reaction:

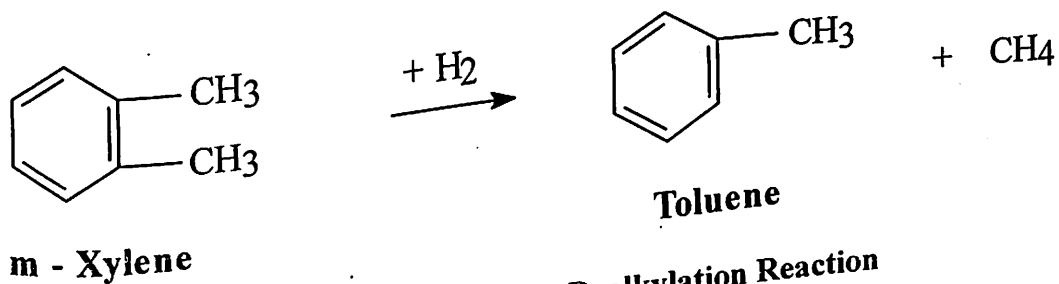


Figure 7 : Hydro Dealkylation Reaction

These reactions consume H₂ and produce CH₄. These are favored at high temperature and high pressure and are promoted by metallic function of the catalyst

4.3.5.3 Demethylation



One more reaction that can occur in the reformer reactors sometime with disastrous results should be mentioned. At very severe conditions of high temperature and high pressure, superactive catalyst and low space velocities, demethylation occurs. One example of demethylation is:

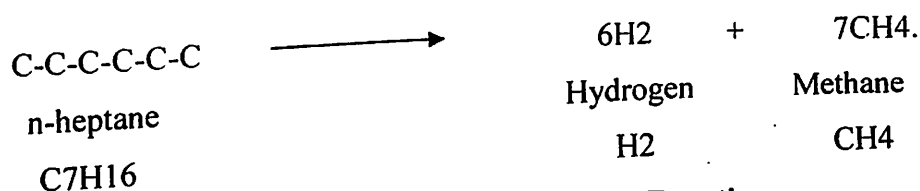


Figure 8: Demethylation Reaction

This reaction is highly exothermic so it releases a great amount of heat. The heat release of the reaction is calculated to be 154,000 BTU/lb mol of n-heptane converted. If it is not rapidly removed the heat further promotes the reaction ultimately melting the catalyst and steel walls of the reactor too.

In early reformer units demethylation seemed more likely to occur during start up with fresh catalyst. The newer generation catalyst, pre sulfiding the catalyst and strict attention to start up procedure have essentially eliminated demethylation during start up. The problem is more likely to occur when reactors are operated over lengthy periods between internal inspections.

4.3.5.4 Coking :

Heavy polyaromatics leading to coke formed by alkylation, dimutation and cyclization reaction. Nevertheless the mechanism of these reactions, responsible for coke deposit on the catalyst, inhibiting its activity, is not well known. High temperature favors these reactions. When dehydrogenation of naphthenes and isomerisation of paraffins have reached equilibrium, the octane number of reformat is only 60-70 RON clear. This number is far below the 90-100 required for unleaded gasoline. Paraffin hydrocracking increases octane number but at the penalty of substantial yield loss. Dehydrocyclisation produces the higher octane number reformates and better yield.



Advances in catalytic reforming technology have emphasized unit design and catalyst developments that promote the dehydrocyclisation reaction.

4.4 Thermodynamic Considerations in Reforming

The dehydrogenation of cyclohexanes and the dehydrocyclization of n-alkanes to aromatic hydrocarbons are strongly endothermic, so that according to Le-Chatelier's principle increasing temperature improves the extent of conversion to aromatic hydrocarbons. From the viewpoint of equilibrium alone, it is advantageous to operate at as high a temperature and as low a H_2 partial pressure as possible to maximize the yield.

However, other considerations, such as coking of catalyst place a practical upper limit on temperature and lower limit on H_2 partial pressure in catalytic reforming operations.

The dehydrogenation of alkanes to alkenes, while not occurring to large extent at typical reforming conditions (equilibrium conversion of n-hexane to 1-hexene is about 0.3%), is nevertheless of considerable importance, since alkenes appear to be intermediates in some of the reactions. The formation of alkenes, similar to the formation of aromatic hydrocarbon, is formed by the combination of high temperature and low hydrogen partial pressure. The thermodynamics of alkene formation can play an important role in those reactions, which proceed via alkene intermediates, since thermodynamics sets an upper limit on the attainable concentrations of alkenes in the system.

The equilibrium for isomerization reaction takes place at much less temperature than the equilibrium for dehydrogenation reactions, since the heat of reaction of the former is relatively small. Other interesting features of the isomerization equilibria are conveniently discussed by considering specific examples involving C_6 alkanes and cycloalkanes. In the equilibrium between methylcyclopentane, thermodynamics favor the former, an illustration of the greater stability of the five-membered ring structure. For the equilibrium between n-hexane and methyl pentanes, 2-methyl pentane is favored isomer over 3-methyl pentane, which is reasonable from



the single statistical considerations that the subsequent methyl group can occupy either of the two equivalent positions in the former molecule as compared to one in the latter. Thermodynamic calculations would indicate the presence of appreciable quantities of dimethyl butanes among the C₆ alkanes at equilibrium (about 30-35% of the total hexane isomers) but the amount of these isomers observed in reforming products are small. Whereas equilibrium tends to be established rather readily in case of n-hexane and the methyl pentanes this does not appear to be true for the dimethylbutanes. This suggests that a strong kinetic barrier resist the rearrangement of singly branched to doubly branched isomers, which apparently does not exist in the case of the rearrangement of the normal structure to the singly branched structures.

At equilibrium, cyclohexanes are substantially converted into aromatics. Equilibrium conversion of six ring naphthenes to aromatics readily takes place. These dehydrogenation reactions are reversible and highly endothermic. The endothermicity decreases with increase in carbon number. Isomerization reactions are reversible and mildly exothermic and equilibrium between normal and iso-paraffins is readily attained. In case of reversible naphthene isomerization equilibrium is favored to cyclopentanes over cyclohexanes[16]. These reactions are also mildly exothermic. Dehydrocyclization of normal paraffins, the most critical of all reforming reactions, are reversible and endothermic. Conversion of paraffins to naphthenes increases with increase in carbon number. Hydrocracking reactions are irreversible and exothermic. Reactivities of paraffins hydrocracking increase with carbon number. The typical equilibrium conversion of C₈ naphthenes to xylene indicates that low pressure and high temperature operations are favorable to obtain high yields of aromatics.



Table 5 : Heat of Reactions

REACTION	ΔH kcal/gmole			
	C ₆	C ₇	C ₈	C ₉
ISOMERISATION				
n-p \longrightarrow i-p	-2.3	-2.3	-1.9	-2
ACP \longrightarrow ACH	-3.8	-4.5	-7.1	-8.8
CYCLISATION				
n-p \longrightarrow ACH+H ₂	10.6	8.4	7.3	5.8
n-p \longrightarrow ACP+H ₂	14.4	13	14.4	14.6
DEHYDROGENATION OF NAPHTHENES				
ACH \longrightarrow AR+3H ₂	52.3	51.5	49.9	51
ACP \longrightarrow AR+3H ₂	48.5	47	42.8	42.2

4.5 TYPES OF CATALYTIC REFORMERS:

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





A catalytic reformer may have three to five reactors in its reaction section. Variations within a unit are necessary but basic flow scheme is still recognizable. Fig shows the basic element of reforming unit for a step by step description of the process.

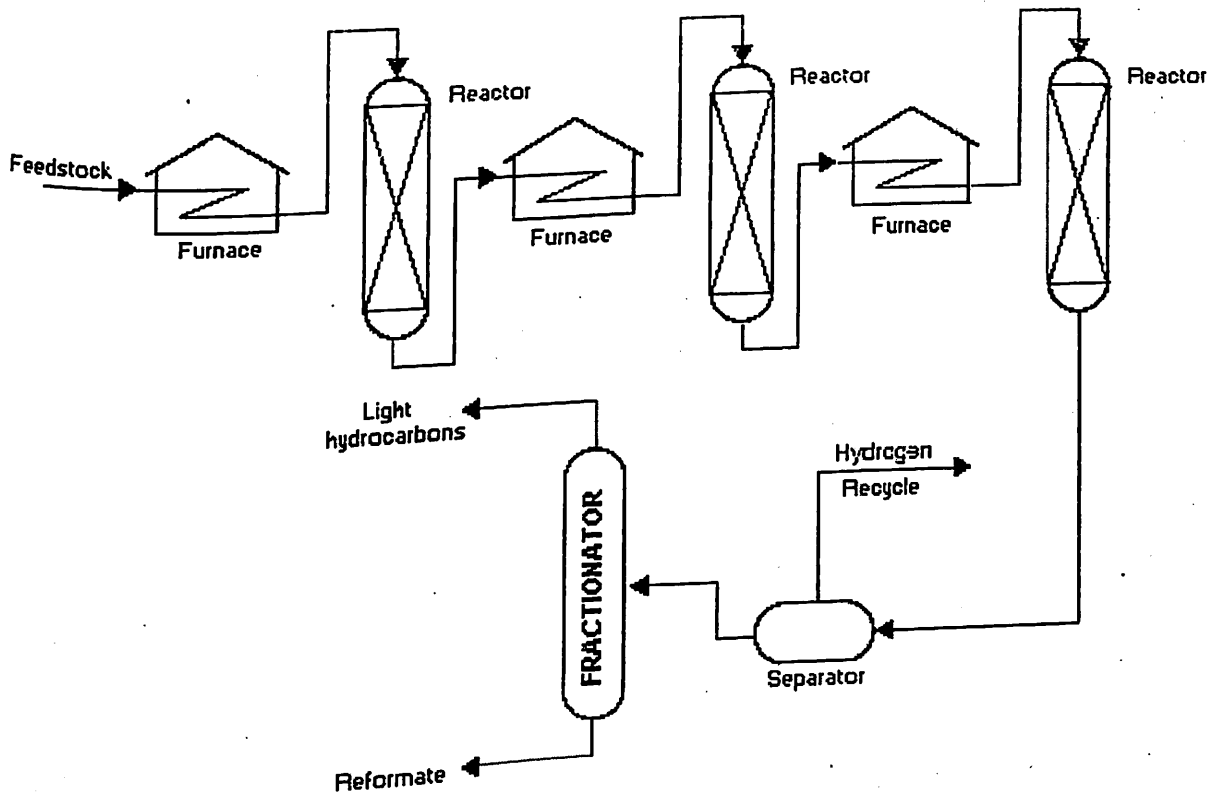


Figure 9: Catalytic Reforming Unit

4.6 Types of Reformers

Reformers can be classified into four types as follows:

4.6.1 Semi-Regenerative:

This means that the reformer processes feedstock for a time and then shuts down for regeneration and rejuvenation of the catalyst. The time between regenerations is called cycle and is expressed in months (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 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 regeneration procedure, which includes rejuvenation, restores the catalyst to fresh-catalyst conditions. The catalyst in Semi Regenerative unit is expected to retain its usefulness over multiple regenerations and to have an ultimate life of 7-10 years..

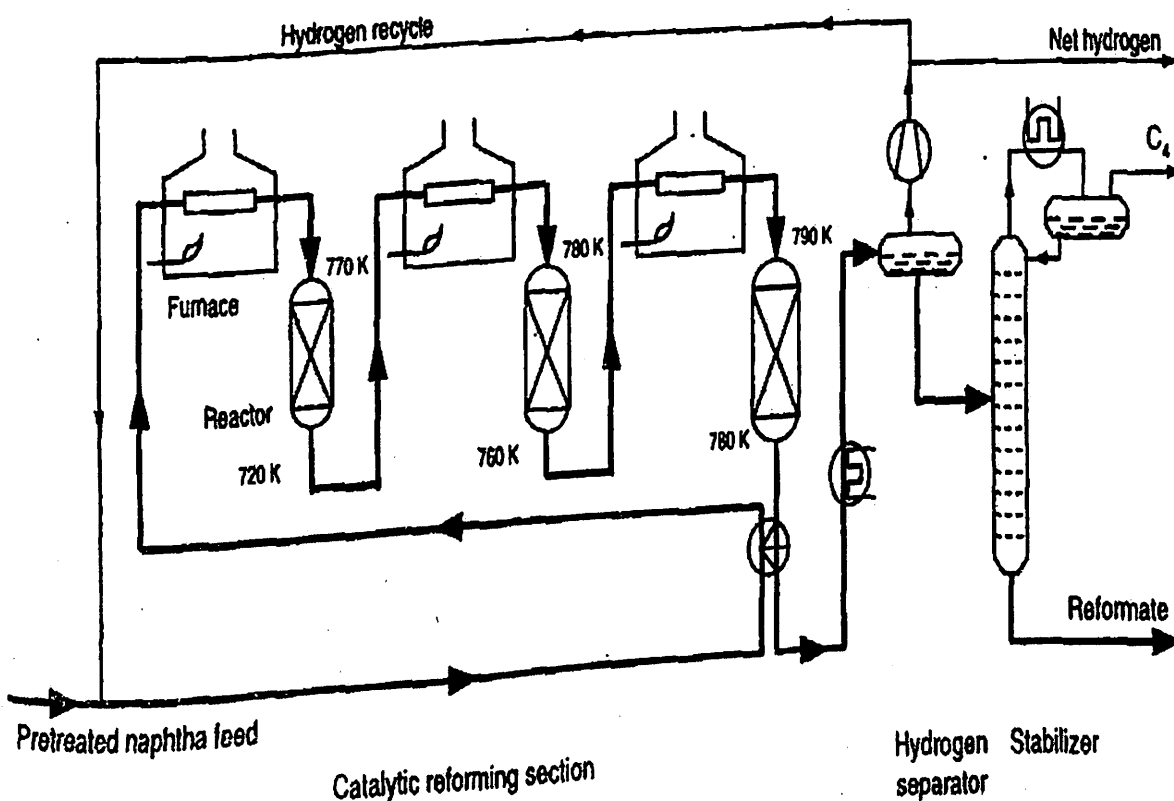


Figure 10: Semi-Regenerative Catalytic Reforming Unit

4.6.2 Non-Regenerative:

Some reformers do not regenerate the catalyst because the cycle is long enough for the refiner to justify replacing-instead of regenerating the catalyst.



4.6.3 Cyclic Reformers:

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 semi regenerative 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 semi regenerative 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 semi regenerative units, even though rapid coking results. The cycles (switching reactors in a cyclic unit) vary from few hours to weeks or months. Although the reactors can be operated in any sequence, the last reactor is usually the one taken offline for regeneration.

4.6.4 Moving Bed Reformers:

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 catalytic cracking unit, the rate of catalyst flow in a reformer is very slow. Whereas FCC catalyst circulation is measured in tonnes per hour, reforming catalyst circulation is a few hundred or few thousand pounds per hour. The moving bed reformer operates in a semi regenerative mode by shutting down the regeneration section. In fact, a number of new units are designed to operate initially as semi regenerative, with the provision that a regeneration section can be added later. The reactors in a moving bed reformers are radial flow and are either separated as in the semi regenerative unit or stacked one above the other. The moving bed unit operates at a lower pressure and a higher temperature (higher severity) than the semi-regenerative units because catalyst can be removed and regenerated before coke buildup seriously affects catalyst performance.

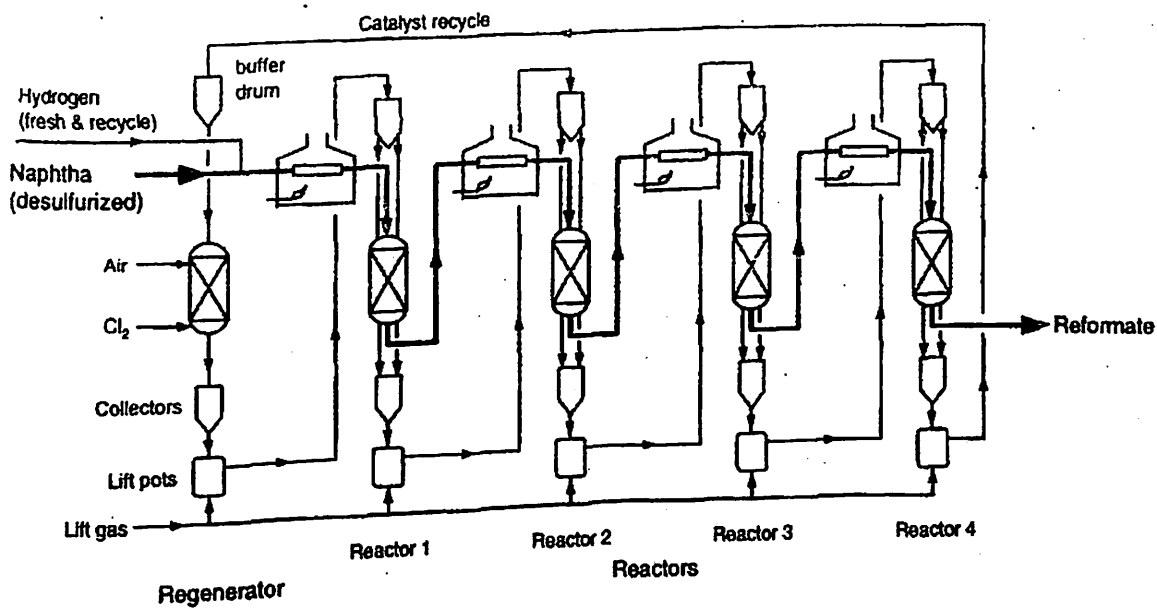


Figure 11: Moving bed Catalytic Reforming Unit

4.7 Commercial Reformers:

4.7.1 IFP Catalytic Reforming:

Process Type : Catalytic reforming of petroleum naphtha, regenerable catalyst through a series of fixed – catalyst- bed reactors

Catalyst : Proprietary catalyst

Developed by : Institut francais du petrole

1. The entire sequence of operation including withdrawal and circulation of catalyst is programmed on real time computer.
2. Catalyst is transferred from one unit to a by means of gas lift system. Gas tight valves open but never close on the catalyst.
3. The regeneration sequence is automatic.
4. A small fraction of the total catalyst is regenerated at a time.



4.7.2 Magnaforming

Process type : Catalytic reforming of petroleum naphtha, through a series of fixed catalyst- bed reactors

Catalyst : Proprietary catalyst

Developed by : Engelhard Industries Div.

1. Controlling the temperature and hydrogen partial pressure at the front end of the reactor system to reduce hydrocracking of naphthenes and to increase dehydrogenation of aromatics. The front end reactors are relatively small and operating temperature is relatively low. These conditions permit the reactor to operate at reduced H: HC ratios. The first two reactors are held at fixed and ascending temperatures say 88-900 F throughout a cycle.
2. The hydrogen ring gas stream is divided into two streams. One part joins the reactor charge to the first reactor. The other portion secondary recycle is added between the second and third reactors. In this mode the hydrogen partial pressure is lower in the two front end reactors for the benefit of naphthenes dehydrogenation and is higher in the last two reactors for the protection of the catalyst at higher temperatures and lower space velocities. Divided recycle gas can be achieved either by two compressors or by a single side take off machine.
3. Ascending reactor temperature profile is used with the lowest temperature in lead reactor and highest temperature in the terminal reactor. An increase in the reformat yield and catalyst cycle life for ascending reactor temperature profile and skewed catalyst loading is reported.
4. Sulfur guard technology is also offered.
5. Typically the process is semi regenerative but it can be designed for semi cyclic regenerative operation.

4.7.3 Platforming:

Process type : Catalytic reforming of petroleum naphtha with platinum containing catalyst through a series of fixed catalyst bed reactors.

Catalyst : Alumina with platinum and halogen in 1/8 - inch pellets.

Developed by : Universal Oil Product Co.

Date of process announced: March 1949.



1. The reactors are stacked on top of other which requires less plot plan space with minimum piping. This facilitates the transfer of catalysts from one reactor to another by gravity flow. Reactors internals are generally similar to those of conventional reformers, that is radial flow with an annular screen and a centre pipe. The catalyst move is essentially plug flow. The rate of flow is determined by the rate of catalyst withdrawal. The combined feed exchanger the reactor section pipe sizes and the plot plan layout are designs for economically beneficial low pressure operation.
2. The catalyst regeneration requires five basic operation:
 - a. Burning of coke.
 - b. Oxidizing metal promoters.
 - c. Adjusting chloride balance.
 - d. Drying of excess moisture.
 - e. Reducing the metal promoters.
3. The reactor and regenerative process can be isolated from another. The reactor system can continue to operate leaving the regeneration system available for inspection and maintenance.
4. The reactor system can operate as regenerative unit with in-situ catalyst regeneration.

4.7.4 Powerforming

Process type : Catalytic reforming of petroleum naphtha through a series of fixed catalyst bed reactors.

Developed by : Exxon Research and Engineering.

1. The semi regenerative unit is taken off stream for about a week at interval varying from 6 to 24 months, while all the catalyst bed are regenerated. off all the modern catalytic reformers, the semi regenerative type requires the least investment and has lowest operating cost.
2. The cyclic process employs the additional (swing) reactor and a regeneration system that permits regeneration of any individual reactor without taking the unit off stream. Regeneration of one reactor each 24-48 hours is typical but the frequency can be varied to meet changing process objectives.



3. Flexibility is inherent in cyclic design. The swing reactor permits a wide choice of operation between cyclic and semi regenerative. A cyclic unit can operate at very high severity without shutting down and thus attain long periods of on-stream time.
4. Powerformers can be designed and built for initial operation as semi regenerative units with provision of later conversion to cyclic units by addition of regeneration system.
5. The purpose of recycle gas dryer is to remove moisture and to thus control the moisture in the feed to the reactors. The addition of hydrogen sulfide absorbent to the desiccant prevents recirculation of feed sulfur and of sulfur introduced during catalyst regeneration.

4.7.5 Rheniforming:

Process type : Catalytic reforming of petroleum naphtha with platinum -rhenium containing, regenerable catalyst through a series of fixed - catalyst- bed reactors.

Catalyst : Alumina with bimetallic platinum and rhenium

Developed by : Chevron Research Co.

1. Rheniformers have few moving parts and no large high temperature valves or complete manifolding. New designed units employ vertical single pass, low pressure drop heat exchangers and low hydrogen to recycle gas ratio to minimize utility requirements.
2. Proprietary operating technology has been developed to assure operation within optimum ranges of the proprietary catalyst and recycle gas properties.
3. Rheniforming catalyst has undergone a number of developments since catalyst A was introduced in 1967. Rheniforming F catalyst introduced in 1978, has a run length 1.4 times that of catalyst A, despite having half platinum.
4. Regeneration technique ensures complete recovery of catalyst activity and performance after each regeneration.
5. It includes sulfur control of reactor feed for optimum catalyst performance. Chevron's information on the relationship between hydrogen sulfide content of the recycle gas and feed sulfur control.



4.7.6 Ultraforming:

Process type : Catalytic reforming of petroleum naphtha with platinum containing, regenerable catalyst through a series of fixed - catalyst- bed reactors

Catalyst : 0.6% platinum on an alumina support.

Developed by : Standard Oil Co. (Indiana)

Date of process announced: Nov. 1953

1. The design includes a swing reactor which can replace any of the reactors during regeneration. Regeneration is carried out while the units remain on-stream without interrupting process flow or reducing feed rate or octane number. The unit can operate at low pressure and high severity and still remain on stream for long periods.
2. Ultraformers use a proprietary catalyst that has been proven in commercial process. After hundreds of regenerations this catalyst is restored to fresh catalyst performance level.
3. Ultraformers are designed for operating flexibility. The unit can function in the cyclic or in the semi regenerative mode. The unit can be designed for initial operation as semi regenerative type and later converted to cyclic type by addition of swing reactor and regeneration system.
4. These units have a vent and block-valve system. This system allows isolation and shutdown of any reactor of regeneration, skimming of catalyst, dumping and screening of catalyst or repair of reactor internals without shutting down of the unit.

4.8 Reforming in India

Presently there are fifteen reforming plants operating in various refineries and petrochemical units having a total installed capacity of 4.91 MMT/Y. The location of these reformers, their capacities, duties and present catalysts along with their supplier names are stated in Table-4. Among them nine are of semi regenerative type. All of them are now using bimetallic reforming catalyst. Duty wise eight are for octane mode and rest are for BTX mode. Seeing the growing demand of product, one new reformer M/s. Essar Refineries Ltd. of CCR type having designed capacity of 0.9 MMT/Y is under advance stage of construction.



Table 6 : Reforming in India

S. No.	Location	Capacity 103 T/A	Duty	Type	Present Catalyst	Catalyst Supplier
1.	BPCL, Bombay	210	Benzene	S.R.	RG-482	Procatalyse, France
2.	BRPL, Bongaingaoan	110	Xylenes	S.R.	RG-451	--do--
3.	CRL, Cochin	240	Benzene	S.R.	PR-9	Criterion, Singapore
4.	IOC, Vadodara	330	B.T.X.	S.R.	CK-433	Cynamide, Katazen
5.	IOC, Haldia	196	Octane	S.R.	RG-482	Procatalys, France
6.	IPCL, Vadodra	110	Xylenes	S.R.	IPR-2001	IIP-IPCL*
7.	CPCL, Chennai	90	Octane	S.R.	IPR-2001	IIP-IPCL*
8.	Reliance, Patalganga	233	Xylenes	CCR	R-32	UOP
9.	IOC, Digboi	90	Octane	S.R.	RG-482	Procatalys, France
10.	IOC, Barauni	300	Octane	S.R.	RG-482	--do--



11.	IOC, Mathura	500	Octane	CCR	CR-201	--do--
12.	IOC, Karnal	500	Octane	CCR	CR-201	--do--
13.	MRPL, Mangalore	300 + 300	Octane	CCR	R-134	UOP
14.	Reliance Petroleum, Jamnagar	1400	Xylenes	CCR	R-134	--do--
	Total	4909				

***Indigenous catalysts and process technology developed at Indian Institute of Petroleum, Dehradun**

IIP along with IFP has licensed all catalytic reforming processes and diesel Hydrodesulfurization (DHDS) units in India. IIP renders pre-startup, start up, regeneration and trouble shooting services to reformer plants in India based on the expertise.

4.9 REFORMING CATALYST

The first catalyst to be used in catalytic reforming was 9-10% chromium oxide or molybdenum oxides on alumina to catalyze hydrogenation and dehydrogenation reactions to produce high-octane gasoline. In 1949, UOP first introduced platinum on alumina in catalytic reforming (Platforming) and since then till today almost all research is carried out on and around platinum. Subsequently efforts were made to improve the functioning of the platinum catalyst.[17] Some of them are as follows:

- ✓ High purity alumina gives longer life (stability).
- ✓ Improved procedure developed for re dispersion of platinum for reforming catalyst activity and selectivity to that of fresh catalyst.



- ✓ Incorporation of other metals (Ir, Re, Sn, Ge etc.) to promote the performance of platinum catalyst (bimetallic) build up.

4.9.1 Properties of Reforming catalyst

A reforming catalyst like all other catalyst must possess the following properties:

Activity:

Activity generally means how well a catalyst does its job with respect to reaction rate, temperature or space velocity. When considering a specific reaction, activity may be related to temperature or space velocity. The higher the reaction rate the higher the activity of the catalyst. For motor fuel reforming, activity is generally represented by the temperature required to produce a given octane number reformat. The lower the temperature, the more active the catalyst.

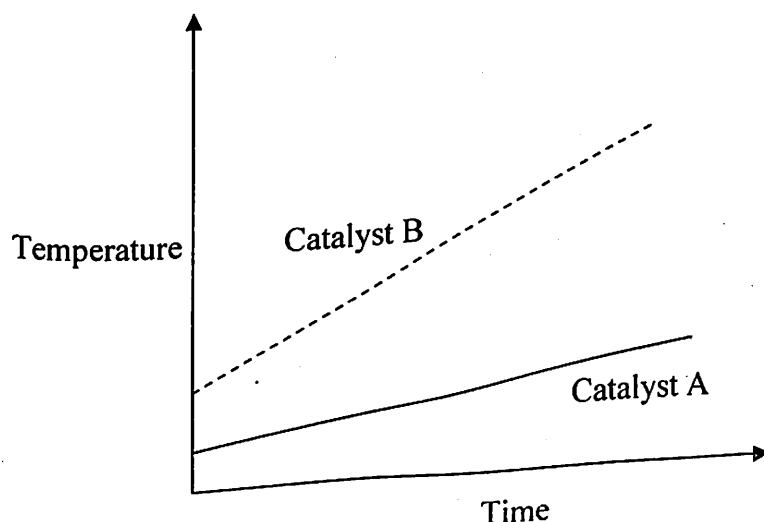


Figure 12 Relative Catalyst Activity

Figure-37 represents two catalysts reforming the same feedstock at the same pressure and space velocity. As the run progresses, temperature is increased to maintain a constant octane number of the reformat. Catalyst A has higher activity than catalyst B, because A requires a lower temperature to produce the same octane number reformat. Catalyst A also maintains higher activity than catalyst B. Both catalysts deactivate as the run progresses. Some refiners prefer to



use space velocity instead of temperature to compare catalyst activities. The higher the space velocity, the more active the catalyst.

Selectivity

In catalytic reforming, selectivity of the catalyst means the percent of desired product yielded from the feedstock. In motor fuel reforming, a high yield of reformate at the desired octane number is good selectivity. In BTX reforming, a high yield of total aromatics or of a desired specific aromatic yield is good selectivity.

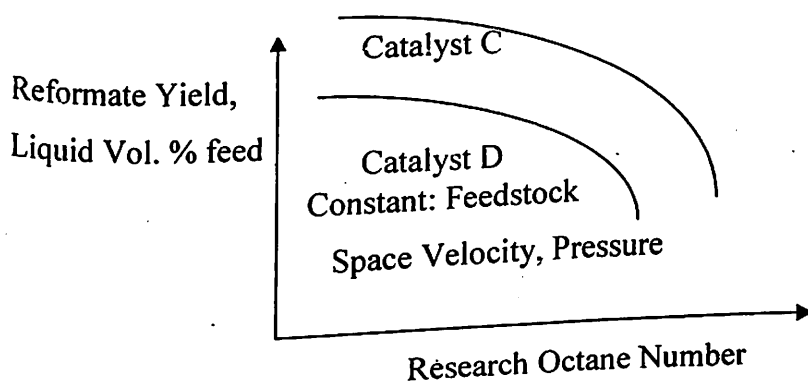


Figure 13: Relative Selectivity of Reforming Catalyst

For example, in figure-38, pilot unit data for reformate yield-octane number from two different catalyst are shown. Catalyst C has better selectivity than catalyst D because on the same feedstock and the same operating conditions (Except reactor temperature) catalyst C yielded 1-1.2 liquid vol.% more reformate of the same octane number than did catalyst D[18].

Stability

A catalyst may have very high activity and excellent selectivity, but unless it also has stability it will be of no use to a refiner. Stability is the ability of a catalyst to maintain its activity and selectivity over a reasonable period. A catalyst that operates for a long time with little or no loss in activity and selectivity has good stability. A catalyst that quickly loses its activity or selectivity has poor stability. A catalyst with good stability has a long cycle life between regenerations in a commercial unit.



Regenerability

After a period of time due to coke deposition and catalyst poisoning the catalyst may tend to deactivate i.e. lose its activity and selectivity. Hence to restore the activity and selectivity of the catalyst to fresh catalyst conditions regeneration of the catalyst is carried out. Regenerability of the catalyst is defined as the extent upto which the activity, selectivity and stability can be restored after regeneration. In addition to above mentioned properties a catalyst should also possess high regenerability in order to make the process economically more viable.

4.9.2 Function of a Reforming Catalyst

An outstanding feature of reforming catalysts, 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 multi functional.

Reforming reactions require atleast two different functions. One is a metal to catalyze the dehydrogenation of naphthenes to aromatics and to hydrogenate olefins formed by the dehydrogenation 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 reforming reactions is still not well understood.

4.9.3 Catalyst Characterization

There are many reasons for catalyst characterization. Characterization is an integral part of any worthwhile catalytic research and development program. The characterization of a catalyst provides information on three distinct but related sorts. These are chemical composition and chemical structure, texture and mechanical properties and chemical activity.

Chemical composition and structure refers to matters such as elemental composition; the composition, structure and proportions of individual phases which may be present; surface



composition, the nature and composition of functional groups which may be present on the surface.

The texture of the catalyst refers to its geometric structure and morphology, ranging from the grossest macro scale down to the finest micro scale. This deals with the shape and size of individual units, pore structure. Total surface area, the way in which individual phases are arranged relative to one another. The mechanical properties refer to those, which are important to the integrity of the catalyst in an industrial application. This refers to abrasion or attrition resistance, strength and thermal shock resistance. The characterization of a catalyst is a quantitative measure of the ability of a catalyst to carry out a particular chemical transformation under specified conditions.

Table 7: Catalyst characteristics and Characterization Techniques

S.No.	Characteristic	Characterization Technique
1.	Surface Area	BET Equation.
2.	Metal Dispersion	By selective hydrogen or oxygen chemisorption
3.	Pore Volume	Porosimeter Instrument
4.	Pore Size Distribution	Porosimeter Instrument
5.	Acidity	By Calorimeter or ammonia adsorption/desorption Technique or TPD
6.	Acid Strength Distribution	By Calorimeter or ammonia adsorption/desorption Technique or TPD
7.	Temperature Programming Reduction	Using micro reactor under hydrogen reduction behavior.

4.9.4 Catalyst Poisons

Catalyst contaminants are classified in two categories:



4.9.4.1 Temporary Poisons

They are those which can be removed from the catalyst without a shut down. the activity and selectivity of the catalysis restored once the poison disappears. Namely

- Sulphur 0.5 –1.0
- nitrogen 0.5 –1.0
- chlorine 0.5
- water 5.0

4.9.4.2 Permanent poison

Are those which induce a loss of activity which cannot be recovered even with regeneration and is so severe that catalyst needs replacement.

- * Arsenic
- * Lead
- * Copper
- * Iron
- * Sodium
- * Nickel
- * Chromium
- * Mercury
- * Potassium

Too much chloride increases the acid function of the catalyst beyond the optimum required for balanced catalytic 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 that fluoride is very difficult to strip from the catalyst and makes controlling the acid catalyzed hydrocracking reaction more difficult.

4.9.4.3 Water

Water 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 chlorine injection.



4.9.4.4 Metals

Trace quantities of metals such as arsenic or lead can enter a reformer along with the reactor charge. The metals deposit nearly quantitatively on the catalyst and deactivate the metal (Pt) function of the catalyst. The effect is irreversible; the arsenic or 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 is necessary to bring unit performance upto its proper level

4.10 OPERATING PARAMETERS:

Catalytic reformers are designed for flexibility in operation whether for motor fuel reforming or for aromatics (BTX) production. The changes in operation which affects reformat yield and quality are termed process variables. The process variables having the greatest effects on reforming are:-

- ii. Pressure
- iii. Temperature
- iv. Space Velocity
- v. Hydrogen to Hydrocarbon Ratio
- vi. Feed Quality
- vii. Catalyst Type

4.10.1 Pressure:

Theoretically, lower the pressure, the higher the reformat yield and hydrogen purity- for a given space velocity-and feed characteristics. However there is little flexibility since the unit and the recycle compressor are designed for a given pressure. Lowering the operating pressure below the design pressure results in higher-pressure drop and is limited by the recycle compressor design driver power. The low pressure, which favors high yield, favors also coke build up.

4.10.2 Temperature :

Temperature, together with space velocity (see hereafter) is the most important and most used operating parameter. By simply raising or lowering reactor inlet temperature operators can raise



or lower the octane number of the product. Since all reactor inlet temperatures are not necessarily identical it is commonly accepted to consider the weight average inlet temperature (WAIT) as representative of the reactor temperatures.

The WAIT is defined as follows:

$$\text{WAIT} = \frac{\{(\text{Wt. Of catalyst R1} \cdot \text{Ti1}) + (\text{Wt. Of catalyst R2} \cdot \text{Ti2}) + (\text{Wt. Of catalyst R3} \cdot \text{Ti3})\}}{\text{Total Wt. of the catalyst}}$$

Ti1, Ti2, Ti3 etc. Are the Inlet temperatures to reactors R1, R2 and R3.

An increase of temperature has the following effects, assuming the space velocity and feed characteristics stay unchanged:

- *Increases octane.
- *Decreases the yield (of C5+ fraction).
- *Decreases the hydrogen purity.
- *Increases the coke deposit.

At constant WAIT, the coke deposit and the ageing of the catalyst (caused by the regenerations, the possible metal deposit and the unavoidable upsets) results in a slight but steady loss of activity (i.e. of octane). An increased temperature through the cycle makes up for this activity loss.

Larger and temporary changes in temperature are required for the following:

- To change octane at constant feed quality and quantity.
- To change feed quantity and still maintain octane.
- To change feed quality and still maintain octane.

4.10.3 Space Velocity:

Space velocity is defined as the amount of liquid (expressed in weight or in volume) which is processed per hour divided by the amount of catalyst (in weight or in volume). The inverse of the space velocity is linked to the residence time in the reactors.

Knowing the liquid flow rate (or the space velocity), plus the recycle flow and the reactor's operating conditions enables to calculate the actual flow in the reactor, hence the contact time.



Lower the space velocity (i.e. higher the contact time), the higher the severity, assuming all other conditions unchanged. Lowering the space velocity has then the same effects as increasing the temperature i.e.

- 1) Increases the octane.
- 2) Decreases the product yield.
- 3) Decreases the hydrogen purity.
- 4) Increases the coke deposit.

If temperature increase is limited (by heater design duty or anything else) lowering space velocity (i.e. decreasing flow rate) can give an additional boost to octane.. It is heuristic that when liquid feed rate is changed a temperature correction must also be applied if the octane is to be maintained. When feed is increased, temperature must be raised and conversely, when the feed is reduced temperature must be lowered. An important rule when changing feed rate is

FOR FEED INCREASE: Increase feed first, then adjust temperature increase to meet octane.

FOR FEED REDUCTION: Lower temperature first, then adjust feed reduction to meet the octane.

4.10.4 Hydrogen to Hydrocarbon Ratio:

The H_2/HC ratio is the ratio of pure hydrogen in the recycle (mole per hour) to the feed flow rate (mole per hour). The H_2/HC ratio is calculated as follows:

$$H_2/HC = \frac{\{ (R/M) * Y \}}{\{ F/m \}}$$

Where

R is the recycle flow in kg. /hr.

M is the recycle gas molecular weight.

F is the feed rate in kg. /hr.

m is the feed molecular weight

Y is the volume fraction of hydrogen in the recycle gas.



The recycle gas molecular weight (m) is obtained by chromatographic analysis as well as the volume fraction (Y) of the hydrogen in the recycle gas. The H_2/HC ratio can be changed by lowering or increasing the recycle compressor flow. The H_2/HC ratio has no obvious impact on the product quality or yield but an increased H_2/HC ratio reduces coke. Catalyst is the heart of the catalytic reforming process. The catalyst in the reactor promotes the desired reforming reactions. And makes catalytic reforming a commercially feasible process. Reforming catalyst are a marvel in their performance in commercial units and are getting better. They promote desired reactions and suppress undesirable reactions. These catalysts function efficiently with a wide range of feedstock composition. They can survive a variety of operating upsets and continue to reform in an acceptable manner. Finally when their performance is no longer economically *satisfactory* they can be regenerated, rejuvenated and restored to fresh-catalyst condition, ready for another operating cycle.

4.10.5 Feed Quality

Mainly naphtha as a feed is used in the catalytic reforming process.

4.10.6 Catalyst

Platinum on alumina or platinum on rhenium are mainly used now a days.

Table 8 : Effects of Temperature and Pressure on different reactions

Reaction	Pressure	Temperature
Isomerization of naphthenes	Indeterminate	Indeterminate
Dehydrocyclization of paraffins to naphthenes	Low pressure	High temperature
Dehydrogenation of naphthenes to aromatics	Low pressure	High temperature
Isomerization of normal paraffins to isoparaffins	Slight dependence	Slight dependence
Hydrocracking	High pressure	High temperature



CHAPTER 5

ISOMERISATION

Catalytic isomerization process is used to convert n-paraffin to isoparaffin, which may be alkylated to liquid hydrocarbons in the boiling range of motor gasoline. This process is also used to convert relatively low octane number paraffins contained in light straight run naphtha and raffinate into the more desirable isoparaffins which may have higher octane number. Isoparaffins provide high octane components in the lower boiling end of motor gasoline.

Isomerization reaction is mildly exothermic. It is a reversible first order reaction. It requires catalyst to obtain significant yield of isomers. The role of catalyst in isomerization is extremely important, since the equilibrium concentrations of branched isomers in the reaction products increases at lower temperatures. The intensity of unwanted side reactions diminishes at lower temperatures. For that reason, isomerizing catalysts must ensure the optimal rate of reactions at as low temperature as possible. To prevent coke deposition on catalyst, isomerization is carried out at an elevated pressure in a hydrogen atmosphere.

The isomerisation process involves the transformation of one molecular structure into another (isomer) whose component atoms are the same but arranged in a different geometrical structure. Since isomers may differ greatly in physical and chemical properties, isomerisation offers the possibility of converting less desirable compounds into isomers with desirable properties, in particular to convert n-paraffins into iso-paraffins, thereby increasing the octane of the hydrocarbon stream. The main fields of application of isomerisation are:

- ISOMERISATION of normal butane into isobutane
- ISOMERISATION of pentanes and hexanes into higher- branched isomers

Since branched isomers have a higher antiknock quality than the corresponding linear paraffins, this form of isomerisation is important for the production of motor fuels.

Though butane isomerisation has maintained its importance, present day interest in isomerisation is specially focussed on the upgrading of fractions containing C5 Pentane and C6 Hexane for use as motor gasoline components. This application has been prompted by the world drive to remove



the lead additives gradually from motor gasoline in order to reduce air pollution. The octane loss caused by the removal or reduction of lead antiknock additives can be compensated for by isomerisation of pentane/hexane paraffin fraction of the light gasoline fractions.

Isomerisation technology has also improved substantially due to the hard work of many technologists. In order to achieve the low temperature necessary to obtain an acceptable yield of isomers, the Catalyst systems used in the early units were based on aluminium chloride in some form. These catalyst systems, however, had the drawback of being highly corrosive and difficult to handle. In recent years, catalyst of a different type have come in use. These are solid catalysts consisting of a support having an acidic carrier and a hydrogenation function, frequently a noble metal. Modern isomerisation units utilise these dual- function catalysts and operate in the vapour phase and the presence of hydrogen. For these reasons, these processes are called hydro-isomerisation processes.

The first hydro- isomerisation unit was introduced in 1953 by UOP, followed in 1965 by the first BP one, while in 1970 the first Shell hydro-isomerisation (HYSOMER) unit was started up.

At present the following hydro-isomerisation processes are commercially available:

- UOP BUTAMER for butane isomerisation
- UOP PENEX for pentane/hexane isomerisation
- BP C₄ isomerisation for butane isomerisation
- BP C₅/C₆ isomerisation for pentane/hexane isomerisation
- SHELL Hysomer for pentane/hexane isomerisation

All these processes take place in the vapour phase on a fixed bed catalyst containing platinum on a solid carrier.

As an example, the Shell Hysomer process will be briefly described. The liquid feedstock is pentane/hexane from light naphtha. Naphtha splitters are widely used to split naphtha into light naphtha, heavy naphtha and also LPG. The light naphtha (C₅/C₆) is combined with the recycle gas/ fresh gas mixture. The resultant combined reactor feed is routed to a feed/ effluent heat exchanger, where it is heated and completely vaporised by the effluent of the reactor. The vapourised combined reactor feed is further heated to the desired reactor inlet temperature in the

reactor charge heater. The hot charge enters the Hysomer reactor at the top and flows downwards through the catalyst bed, where a portion of normal and mono- branched paraffins is converted into higher branched (high octane) components. Temperature rise from the heat of reaction release is controlled by a cold quench gas injection into the reactor. Reactor effluent is cooled and subsequently separated in the product separator into two streams: a liquid product (isomerate) and a recycle gas stream returning to the reactor via the recycle gas compressor.

The catalyst is a dual function catalyst consisting of platinum on a zeolite basis, highly stable and regenerable. Temperatures and pressure vary in a range of 230 - 285 °C and 13-30 bar, C₅/C₆ content in product relative to that in feed is 97% or better, and octane upgrading ranges between 8 and 10 points, depending on feedstock quality. The Hysomer process can be integrated with catalytic reformer, resulting in substantial equipment savings, or with iso-normal separation processes which allows for a complete conversion of pentane/hexane mixtures into isoparaffin mixtures.

5.1 Thermodynamics of Isomerisation

Isomerization of paraffins is limited by thermodynamics. Low temperatures are therefore favored. High activity catalysts approach equilibrium conversion at lower temperature, leading to higher iso-paraffin yields.

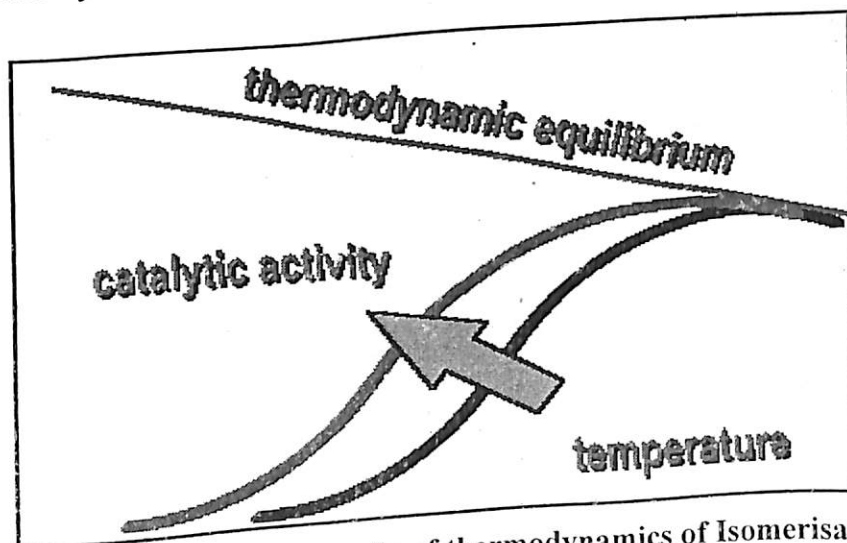
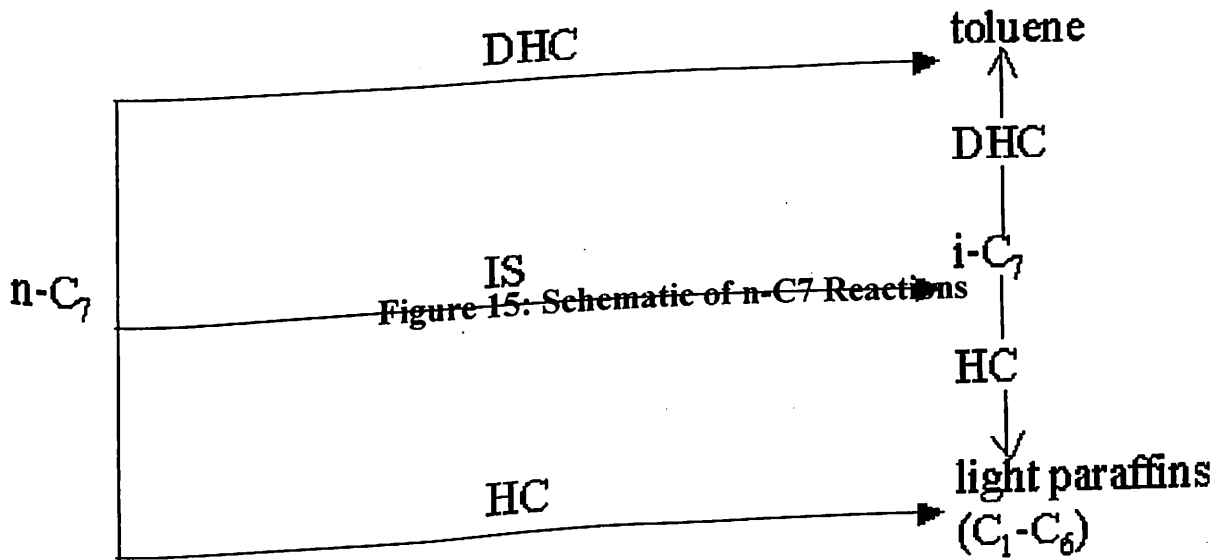


Figure 14 : Schematic of thermodynamics of Isomerisation



Nowadays many refiners are looking into the isomerisation processes to add potential extra value and complimentary to the platforming process. Directly both the platforming and isomerisation process work hand in hand in several ways. C5 paraffins tend to crack away in the platformer, but give high upgrading in the isomerisation unit. C6 components convert nicely to benzene in the platformer, but nowadays the specs on aromatics and benzene are tightening, which makes conversion of these components to C6 isomers preferred. Furthermore, benzene is hydrogenated in the isomerisation unit. C7 paraffin cracks into light paraffin and also give high end toluene and C7 isomers.



By adjusting the cutpoint between the light and heavy naphtha, i.e. the cutpoint between the feed to the isomerisation feed and the platformer feed, the refiner has the flexibility to control the benzene content of its gasoline pool. Catalytic hydro-isomerization of paraffines takes place under medium pressure (typically 30 bar) in a hydrogen atmosphere.



CHAPTER 6

PROJECT OBJECTIVE

To develop a catalyst for isomerization of C_7 - C_9 paraffins for the preparation of high-octane gasoline blending stock with low aromatics and benzene.

The proposed research work is aimed to isomerize C_7+ normal paraffins to high-octane isoparaffins with controlled cracking. Similarly C_7+ cyclo paraffins also would be converted to corresponding isoparaffins via ring opening isomerization. The process is thus aimed to take care of paraffins and naphthenes in the C_7+ hydrocarbon feed to yield environ-friendly gasoline by minimizing benzene and total aromatics.

6.1 Background of the Proposed Project

Motor gasoline is a key automotive fuel and is likely to occupy the leading edge in the coming decades all over the globe. A common tool to enhance the octane number of gasoline used to be the addition of lead-containing components. Since its discovery in 1922, tetraethyl lead (TEL) has been added in small quantities to improve the quality of gasoline. However, in recent years, in many countries the amount of lead has been decreased by legislation with the target of its complete elimination. Phase out of TEL has been compensated by aromatic rich gasoline that generally obtained by increasing the severity of the reformer.

Worldwide fuel charter specifies various categories of gasoline. The category 4, lists the fuel quality recommendations to be provided to the end users to control the emissions. The maximum recommended limits for sulfur, olefins, aromatics and benzene are given in Table-1 below.

Though the quality of Indian gasoline pool is not as strictly regulated as in the West, soon its quality is also expected to become similar to those in developed nations.



Table 9: Limitations of various hydrocarbon components in gasoline

Component	Limit
Sulfur (ppm)	5 -10
Olefins (vol. %)	10
Aromatic content (vol.%)	35
Benzene (vol.%)	1.0

Table 10: Gasoline Standards

Property	India		Europe	
	2000-05	Beyond 2005	Euro I and II	Euro III
Sulphur (% m/m)	0.10-0.05	0.02	0.05	0.015
Maximum lead content (g/l)	0.013	0.005	0.013	0.005
Maximum benzene content (% v/v)	5-3	2-1	5	1
Octane number				
▪ Research octane number	87-91	91, 95	95 (min)	95 (min)
▪ Motor octane number	82	82, 85	85 (min)	85 (min)
Hydrocarbon composition (% v/v)				
▪ Aromatics	45-40	<35	--	42
▪ Olefins	30-20	20-10	--	18
Distillation - E100 (% v)	50-65	50-65	40-70	40-70
Reid vapour pressure (kilo Pascal)	35-60	45-60	35-100	35-100



Density at 15 °C (kg/m³) 700-750 715-770 725-780 725-780

At this juncture, use of oxygenate additives such as methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME) are increasingly used to improve the gasoline quality as well as to control the emissions from gasoline, although they cost more per octane number. However, contribution of oxygenates to environmental pollution is also observed and there has been much debate on their use as gasoline additives.

The existing main processes for high-octane gasoline production are reforming and FCC. Larger paraffins present in streams used for catalytic reforming. Catalytic reforming of S-R naphtha/ FCC naphtha/ cocker naphtha/ hydrocracked heavy naphtha which yields reformat having as high as 95-105 RONC with large percentage of aromatics. Although reformat is high-octane products, they typically contain over 55-60 wt % aromatics, and their use in reformulated gasoline should therefore be limited. In addition, in order to decrease harmful vehicle emissions, the concentration of benzene in gasoline has also been limited in several countries by government regulations.

Discovery of a suitable technology and catalysts which could convert the especially the *n*-paraffins in C₇⁺ range (having RONC <40) into isomers having 90⁺ RONC with mild cracking the hydrocarbons would be a boon to refiners and provide eco-friendly gasoline by minimizing the aromatics.

Another point in paraffin chemistry that needs to be taken care is the crackability of the *n*-paraffins, where the crackability of the *n*-paraffins increases with increasing chain length of the *n*-paraffins. Selective isomerization of a mixed paraffin feed is made more difficult by the increased ease of conversion and cracking as carbon number increases. For example, reaction conditions that selectively isomerize *n*-C₆ over mordenite almost exclusively crack *n*-C₈. A recent study evaluated a series of zeolite catalysts for the isomerization C₅-C₇ paraffins. A Pt/BEA zeolite catalyst was found to be effective, although the selectivity to isomers for C₇ was much lower than for C₅ and C₆. Thus, the isomerization catalyst developed for the isomerization



of short chain alkanes such as pentane and hexane need not be a good catalyst for C_7+ isomerization, as the crackability of the C_7+ is more.

Another challenge in isomerization of any realistic naphtha cut is the presence of cyclic compounds. Inhibition of catalyst activity by cyclic compounds has been observed over Pt/mordenite catalysts.

Yet another point that is to be considered in catalyst development is the hydrogenolysis function of the noble metal particle, that gives unwanted cracking products. In order to suppress the hydrogenolysis activity of the noble metal, addition of another metal is generally used to modify the electronic properties of the first metal. However, achieving homogeneously dispersed bi-metallic sites and the stability of such sites against metal agglomeration at the reaction conditions needs again expertise on the catalyst development.

6.2 Catalyst Preparation

The catalyst system aimed to develop is of bi-functional nature where acidity and Nobel metal function work together for isomerization reaction. The catalyst development can be carried out in two steps, namely, acidity modification and noble metal incorporation for above mentioned purpose. The following steps may be involved in catalyst development

1. Preparation of bi-metallic mordenite based catalyst
2. Screening of catalysts using n-hexane isomerization as model reaction

Zeolite Modification

Commercial mordenite in powder form was used and modified by acid extraction/hydrothermal treatment to achieve desired acidity as based material. The Si/Al ratios of the samples were varied to alter the acidity and the support was impregnated with Pt and Pd metals by incipient wet impregnation method. The sequential steps involved in catalyst preparation are given below.



Extrudate Preparation

The parent mordenite as well as the four acid treated mordenite samples in the powder form were taken along with alpha – alumina binder in 60:40 mordenite: binder ratio to prepare extrudates for catalyst activity evaluation. In a typical procedure the physical mixture of mordenite and binder material was thoroughly mixed and ground, followed by the drop wise addition of 3 vol% glacial acetic acid as peptizing agent and allowed for Peptization for 2 hours. The resultant paste was extruded using 1mm diameter pore and the extrudates were dried at room temperature overnight, followed by heating at 100°C for 10 hours. All the extrudates were calcinated at 500°C for 4 hours, before using them for metal impregnation.

Need for Metal incorporation

In the initial stage of isomerization reactions, acid sites alone were applied for facilitating the reaction. These are called mono functional catalysts. In advanced stages of catalyst development, the need of a noble metal component such as Pt, Pd were identified that can be improve not only isomerization reaction but also the amount and nature of coke with better stability in activity of the catalyst.

In principle, there are two types of catalysts for skeletal isomerization of paraffin, monofunctional acidic catalysts and bifunctional acid metal catalysts that combine the acidic function with the hydrogenation/dehydrogenation function of a metal. Depending on the active functionality of the catalyst involved in the reaction, the mechanisms of the isomerization also vary. In case of pure acid based mono functional catalyst, the reaction occurs through the formation of carbonium ion and over the bifunctional acid-metal catalyst it occurs via carbenium ion as intermediate.

Impregnation of Pt Salt

Incipient wet impregnation method was used for impregnation of Pt, where tetra amine platinum (II) chloride hydrate (98% Aldrich) salt equivalent to 0.3 wt% of Pt on the basis of final catalyst was dissolved in distill water equivalent to the total pore volume of the catalyst and resultant solution was added to the extrudates drop wise and allowed for adsorption at room temperature



over night, followed by drying at 100 °C for 10 hours, and the oxide form of metal was obtained by calcinations of the above mentioned dry mixture at 500°C temperature for 4 hours. All the above samples were treated with hydrogen flow in reactor for reduction of metal ion. before they were using for the hydro isomerization reaction.

SEQUENTIAL STEPS INVOLVED IN CATALYST PREPARATION

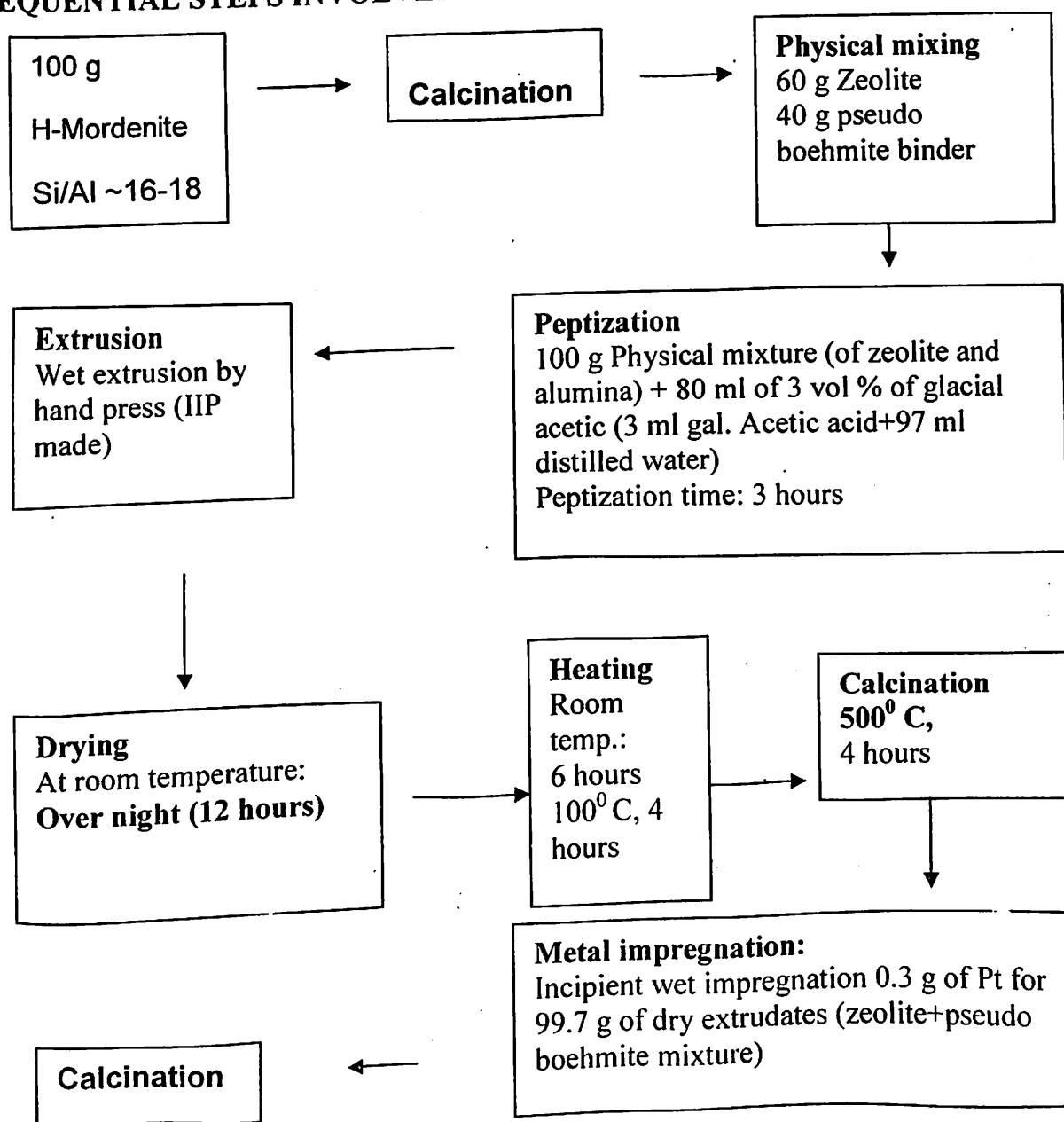


Figure 15:- SEQUENTIAL STEPS INVOLVED IN CATALYST PREPARATION

6.3 Pilot Plant Description

This unit is capable of handling a variety of feedstocks can operate at various temperatures, pressure and flow rate of feedstocks and gases. Computer interfacing maintains system temperatures, pressures and flow rates while storing equipment data, maximum operating temperature is 550⁰C. maximum pressure is 100 bar, feedstock flow rate is 250ml/hr, H₂ flow rate is 500ml/hr. It has a reactor volume of 0.705 l. Heated volume of 0.615 l., total length 1320 mm and heated length 1000 mm, O.D. 42 + 0.2 mm.

The whole unit has been divided into 3 major sections as shown in the figure below

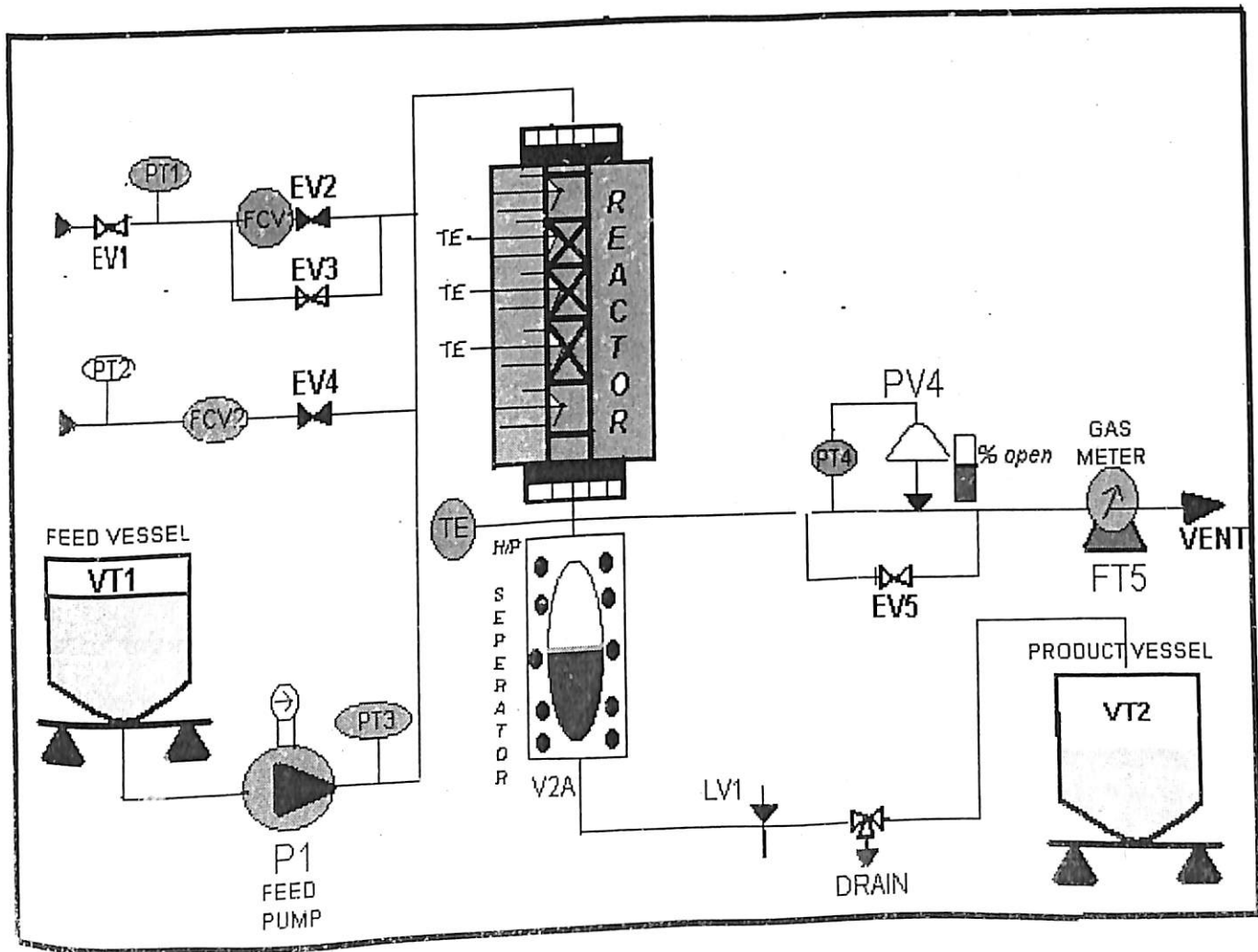


Figure 16: Schematic of the Pilot Plant



1. Feed supply and conditioning section

It comprises feed and gas section. Liquid feed section consists of one feed vessel for naphtha mounted on weight balance. Feed pump is provided to feed naphtha at high pressure. Gas feed section has feed lines for N_2 and H_2 controlled with mass flow controllers. Gaseous and liquid feed are dried in molecular sieve dryers.

2. Reaction zone section

Reactor had five heated zones with five furnaces. Top and bottom zones serve as pre and post heat zones respectively and three middle zones as main reactor zone. Temperatures are monitored at five points both at skin and heart of the reactor separately with thermocouples. Inlet and outlet flanges are also insulated.

3. Product separation section

Process fluid leaving the reactor is immediately quenched by a water cooler and then goes through separator, which have level gauge and external water-cooling arrangement. Gas is recycled by recycle compressor through a catcher cooled by water. Excess gas generated is discharged to atmosphere through wet gas meter. Liquid separated in separators is collected in a product vessel mounted over a weight balance to monitor product weight. Vega Controller maintains level in separator. Gas samples can be collected any time from the recycle loop and from combined recycle and product vessel overhead stream.

6.4 Catalyst Loading

20 gms of the catalyst ISO-1 was loaded in the reactor of Pilot Plant with 120 gms of alpha-Alumina in the dilution ratio of 1:6. The total length of reactor was 115.5 cms. The reactor was divided into five different zones: the top and the bottom zone comprised of beads, the beads were of 7.5 cm height at the top and 8.0 cms at the bottom of the reactor. The next zone of alpha-alumina had a height of 38.0 cms in the upper zone and 40.0 cms in the bottom lower zone. In

the middle zone of the reactor length, a combination of alpha-alumina and catalyst was loaded, 22 cms in length, as shown in the figure:

Wt. of catalyst = 20 gms
 α -Alumina = 120 gms
 α -Alumina dilution ratio 1:6

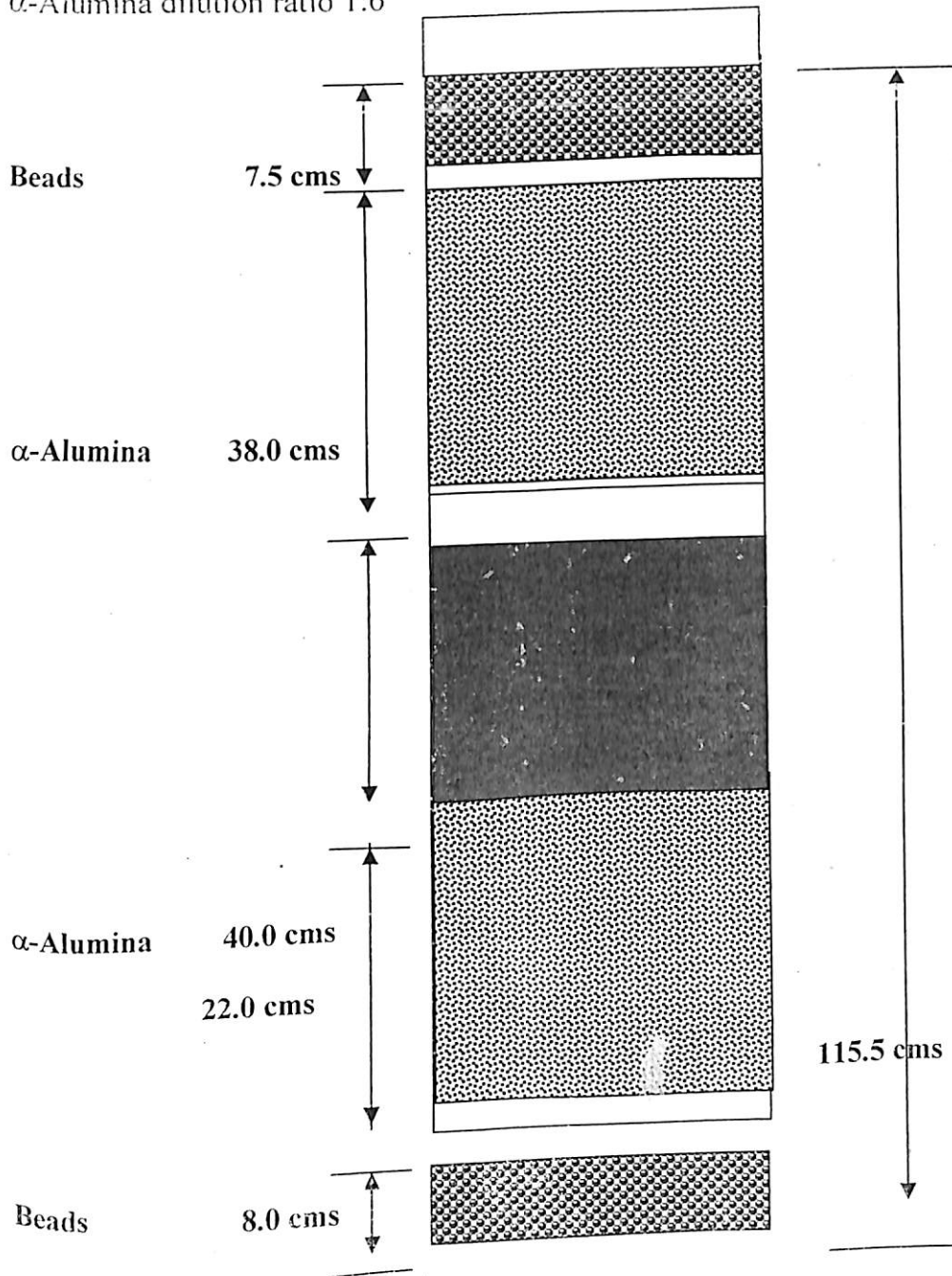


Figure 17 : Schematic of reactor showing various zones



6.5 Pre Start up Activity

After loading the catalyst in the reactor, the system was pressurized and depressurized with ultra hi-purity Nitrogen three times to completely remove air from the system. The unit was pressurized upto 35kg/cm² and checked for the leakage.

After pressure check, the total system was again pressurized and depressurized with the ultra high purity Hydrogen to create Hydrogen atmosphere in the system.

Reduction of the Catalyst

The recycle compressor was started keeping the flow rate 10lt/hr. The unit pressure was maintained at 10kg/cm² and the reactor was heated to 300°C temperature keeping the heating rate at 50°C/hr. This condition was maintained for 2hrs.

The temperature of the reactor was further increased to 520°C, keeping the same heating rate. This condition was maintained for 8 hours. Then the reactor temperature were reduced by stopping the heating and increasing the hydrogen flowrate.

CATALYST EVALUATION RUN

6.6 ACTIVITY TEST WITH MODEL COMPOUNDS

FEED CHARACTERISTICS

Compound	=	n-hexane
Sulphur level	=	< 4 ppm
RONC	=	19

CATALYST CHARACTERISTICS

Name	=	ISO-1
Type	=	bi-metallic
Metals	=	Pt-Pd
Base	=	H-Modernite

**OPERATING CONDITIONS:****PRODUCT ANALYSIS**

RONC = 45

CONVERSION = 49.6 %

Group	Wt%	RON
Aromatics	0.0	0.0
Naphthenes	0.6	0.4
Iso-paraffins	35.5	30.3
Olefins	0.0	0.0
Paraffins	63.8	12.7

FEED CHARACTERISTICS

Compound = n-heptane

Sulphur level = < 4 ppm

RONC = 0

CATALYST CHARACTERISTICS

Name = ISO-1

Type = bi-metallic

Metals = Pt-Pd

Base = H-Modernite



OPERATING CONDITIONS:

Temperature = 320 C
 Pressure = 20 bars
 WHSV = 2
 H₂ / HC = 4

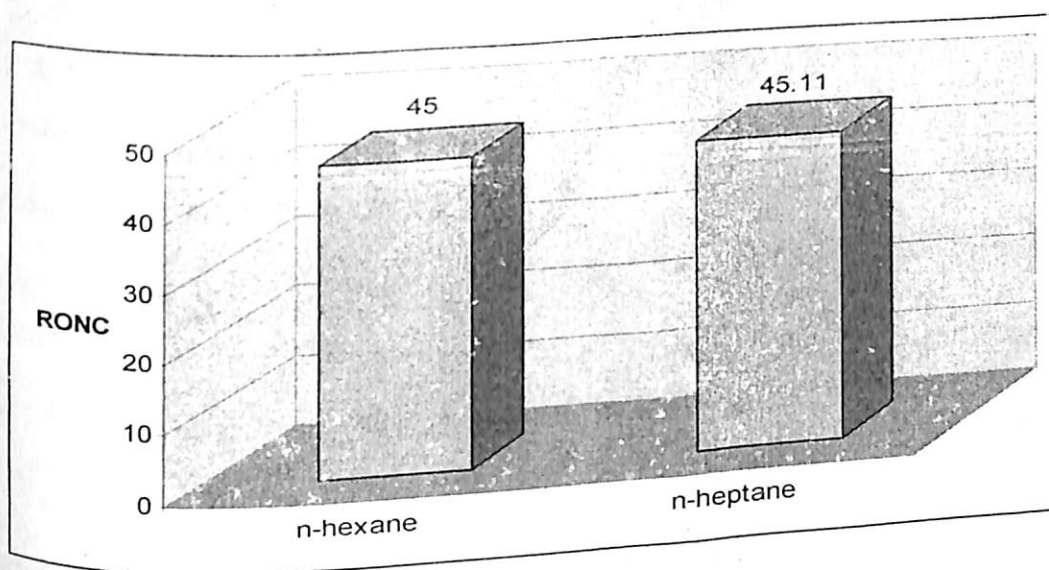
PRODUCT ANALYSIS

RONC = 45.11
 CONVERSION = 58.42 %

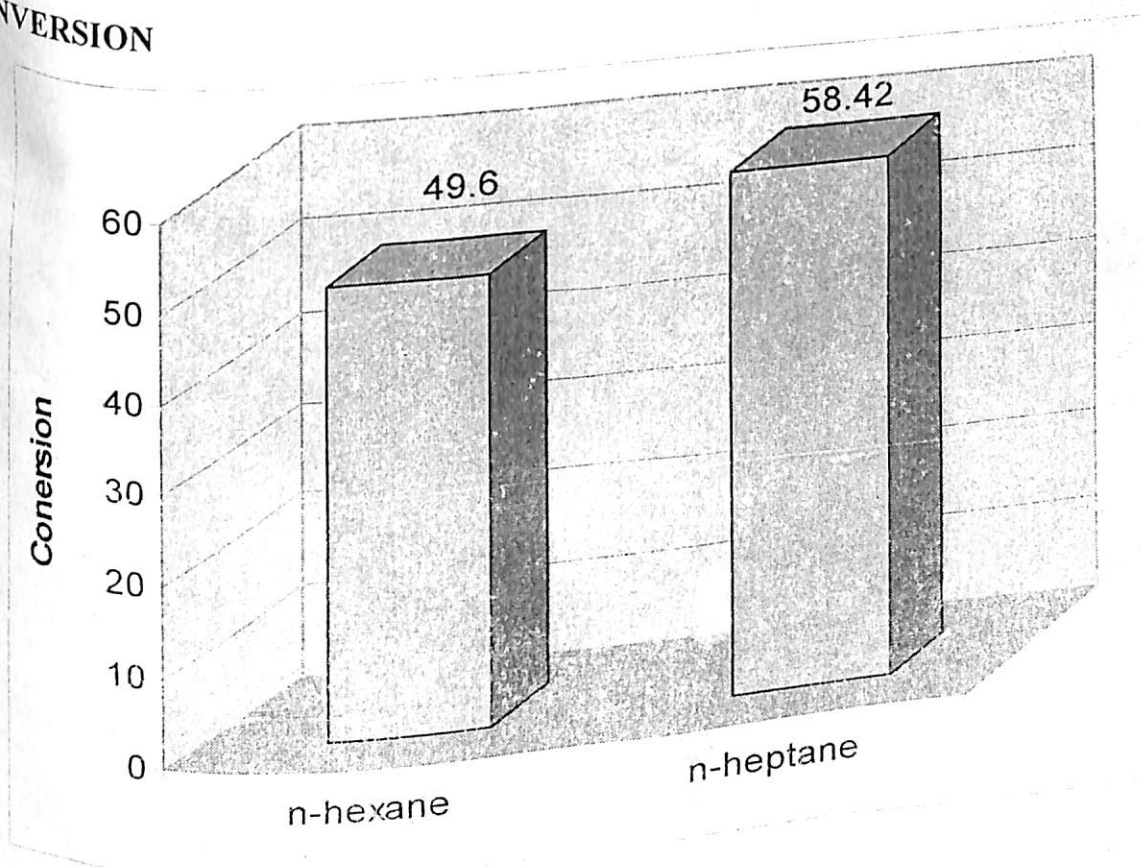
Group	Wt%	RON
Aromatics	1.688	1.62
Naphthenes	8.573	5.95
Iso-paraffins	33.565	25.54
Olefins	0.018	0.02
Paraffins	55.912	11.99
Unidentified	0.244	-

COMPARASION OF N-HEXANE AND N-HEPTANE MODEL COMPOUNDS

1).RONC



2). CONVERSION





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