Chemical Technology
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Module - 6
Petroleum Refinery
Lecture - 6
Catalytic Reforming

We are discussing organic chemical technology course and in which we are discussing the module 6 regarding the petroleum refinery. And we have discussed 5 lectures on different aspects of petroleum refinery starting from the introduction to petroleum refinery industry. Then it was the evolution of the crude oil, distillation of the crude oil. Then the, some of the processes, which are being used for improving the octane number and to use the residue, which we are getting from the atmospheric and vacuum column. So, for in that case we discuss about the thermal and catalytic cracking.

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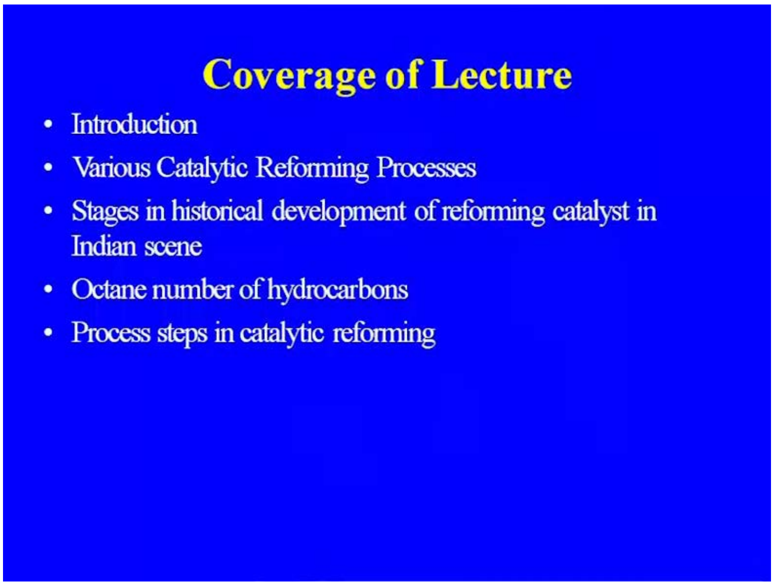

Coverage of Lecture

- Introduction
- Various Catalytic Reforming Processes
- Stages in historical development of reforming catalyst in Indian scene
- Octane number of hydrocarbons
- Process steps in catalytic reforming

Now, we will be discussing in lecture 6 about the catalytic reforming process, which is one of the very important process that is being used in the refinery not only in the refinery, but also in the petro chemical complexities were there making the polyester or the purified diethylic acid or DMT, because parazylene; that is the basic raw material. So, here we will be more concerning about the catalytic reforming with respect to refinery. And while discussing the petro chemical, we will be discussing about the catalytic reforming for aromatic production.

Coverage of the lecture that will be introduction various catalytic reforming processes, because there is a continuous development in the catalytic reforming processes from continuous semi continuous or the batch. And then the stages in the historical development as in happened in case of the catalyst also, stages in the historical development of the catalyst and also the Indian scene, octane number of hydrocarbons, process step in the catalytic reforming.

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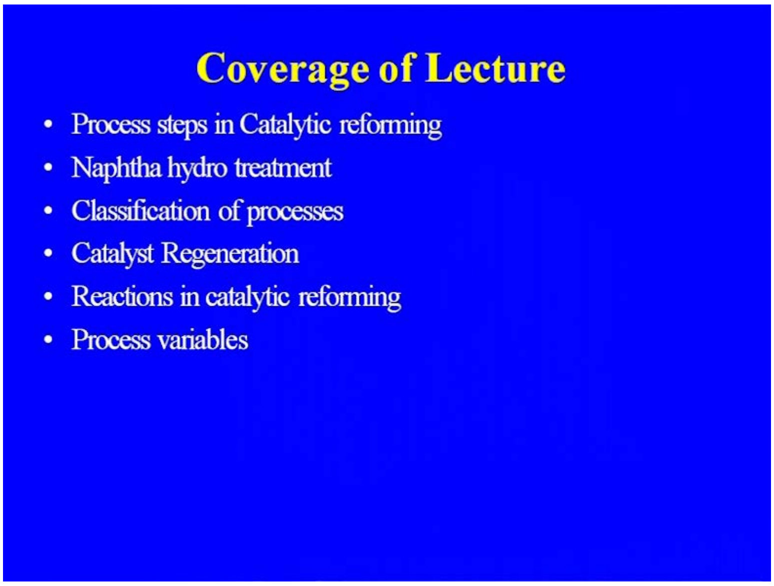

Coverage of Lecture

- Process steps in Catalytic reforming
- Naphtha hydro treatment
- Classification of processes
- Catalyst Regeneration
- Reactions in catalytic reforming
- Process variables

Naphtha hydro treatment, because these are the some of the naphtha hydro treatment, that is the integral part of the catalytic reforming for improving for the reducing the sulphur content of and the other impurities which are present in the naphtha. Classification of the processes, catalyst regeneration which is part of the, your catalytic reforming process, reactions in the catalytic reforming then we will be discussing in detail about the, what are the process variables in catalytic reforming.

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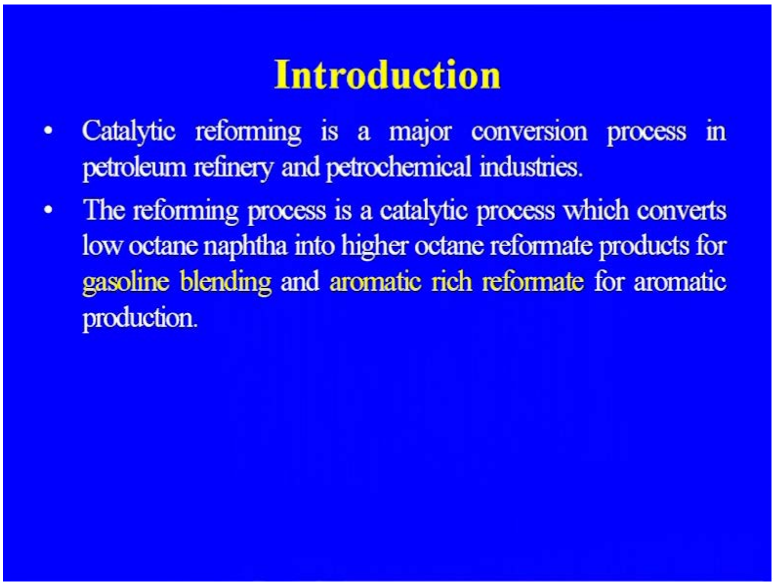

Introduction

- Catalytic reforming is a major conversion process in petroleum refinery and petrochemical industries.
- The reforming process is a catalytic process which converts low octane naphtha into higher octane reformate products for gasoline blending and aromatic rich reformate for aromatic production.

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As I told you that the catalytic reforming is a major conversion process in the petroleum refinery and petrochemical industry. You cannot imagine the refinery without a catalytic reforming, because what happened in the initial stage of the refinery when there was no catalytic reforming many of the refineries. Then at that time lot of the naphtha that was surplus, it happened in India also during the initial stage if in the barony refinery which by Indian Oil Corporation is even not having the catalytic reforming Assam oil company they were not having the catalytic reforming. So, lot of surplus naphtha was available at that time and that naphtha was made available to the fertilizer plant, but with the coming of the petro chemical complex, naphtha cracker and at the same time aromatic production requirement of the parazylic.

Now, we are performing the catalytic reforming for the production of the aromatics also. The reforming process is a catalytic process which converts low octane naphtha into higher octane reformate products for gasoline blending and aromatic rich reformate for aromatic production. By product is LPG and hydrogen in the catalytic reforming process.

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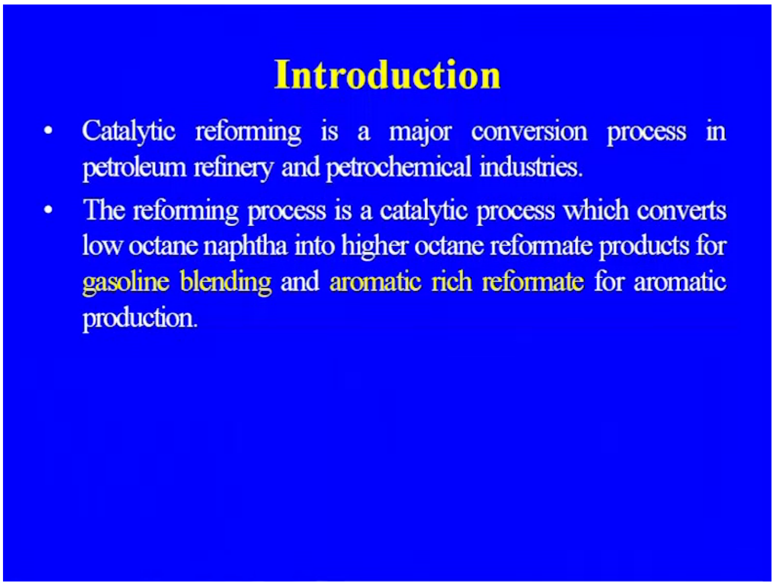

Introduction

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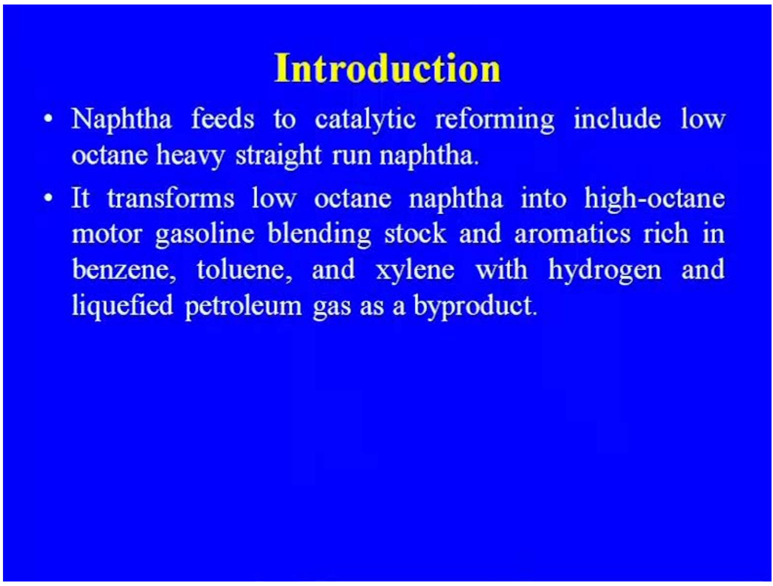

Introduction

- Naphtha feeds to catalytic reforming include low octane heavy straight run naphtha.
- It transforms low octane naphtha into high-octane motor gasoline blending stock and aromatics rich in benzene, toluene, and xylene with hydrogen and liquefied petroleum gas as a byproduct.

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Naphtha feed to catalytic reforming include low octane heavy straight run naphtha, because the naphtha light naphtha which is having higher octane number sometimes we call it the gasoline also that is going to the gasoline pool that is what we call as the straight run gasoline. But medium and the heavy naphtha that is going to the catalytic reforming process, or now we are going for the isomerization of the naphtha also. So, low octane heavy straight run naphtha is the feed for the catalytic reforming process, it transform low octane number into high octane motor gasoline blending stock. And the aromatic rich in benzene, toluene and xylene with hydrogen and liquefied petroleum gas as a byproduct.

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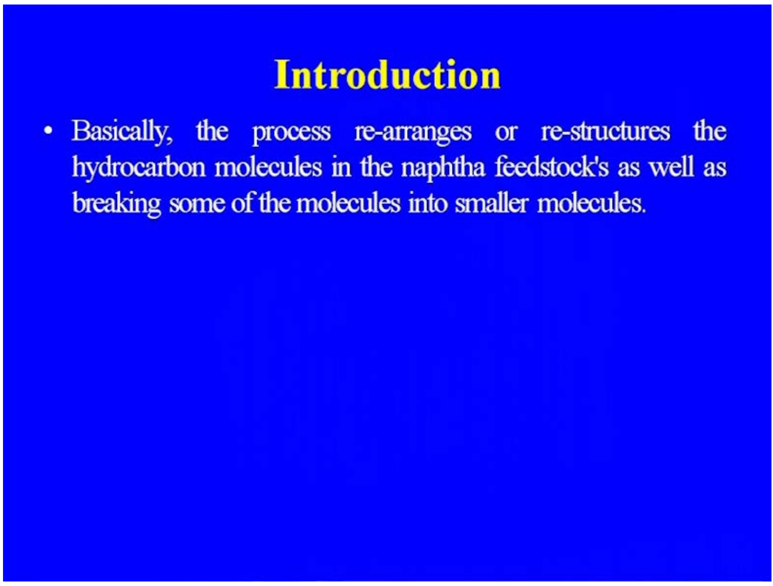

Introduction

- Basically, the process re-arranges or re-structures the hydrocarbon molecules in the naphtha feedstock's as well as breaking some of the molecules into smaller molecules.

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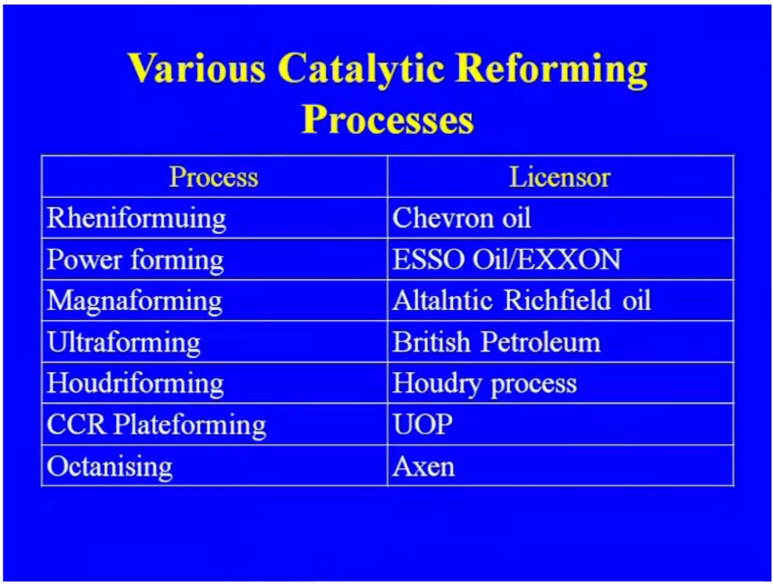

Various Catalytic Reforming Processes

Process	Licensor
Rheniformuing	Chevron oil
Power forming	ESSO Oil/EXXON
Magnaforming	Altalntic Richfield oil
Ultraforming	British Petroleum
Houdriforming	Houdry process
CCR Plateforming	UOP
Octanising	Axen

Basically, the process rearranges or restructures the hydrocarbon molecule in the naphtha feed stock as well as breaking some of the molecules into the smaller molecules. And at the same time during the process some coke formation is also there, because of the hydro cracking another reaction which are undesirable reaction. These are the some of the processes catalytic reforming process which has been licensed. And the various development that has taking place as I told you the in the catalytic reforming reactant based on that these are the some of the technology that is available.

And the process, licensor; rheniforming, powerforming, magnaforming, ultraforming, houdriforming, CCR plateforming, continuous catalytic reforming, octanising these are the some of the process that is available and the various type of the catalytic reformer we are using in this process. Status of the catalytic reforming units in India, as I told you the India lead stage in many of the refineries were not having the even catalytic reforming or FCC. It was the only thermal cracking process or it was the fixed bed catalytic cracking. Similarly, in case of the catalytic reforming that was not there, but now as I told you we cannot imagine a refinery without catalytic reforming.

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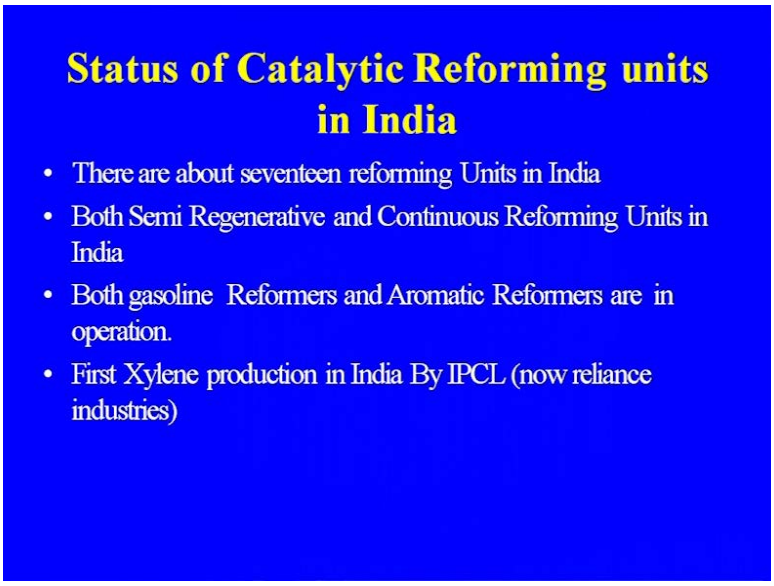

Status of Catalytic Reforming units in India

- There are about seventeen reforming Units in India
- Both Semi Regenerative and Continuous Reforming Units in India
- Both gasoline Reformers and Aromatic Reformers are in operation.
- First Xylene production in India By IPCL (now reliance industries)

So, there are about 17 reforming units in India, both semi regenerative and continuous reforming units are there. Both gasoline reformers and aromatic reformers, because some of the refinery like BPCL IOC Vadodara, Chennai, cochin refinery, aldeer refinery. They are all producing the both the or the even in case of BRPL bongaigaon refinery and petrochemicals.

They are producing gasoline as well as aromatics also they are separating for the various end users which is going as a chemical feed stock for production of large amount of the chemicals just like benzene. We discussed about the L A B so benzene that is going for linear alkyl benzene, toluene for various other products that may be there, or toluene.

Further it is converted to more valuated product more useful product which has got more use like benzene and xylene. First xylene production in India was by the IPCL.

Now, it is by reliance it is in the reliance industry IPCL, Vadodara that is one of the largest integrated petrochemical complex. Octane number of the hydrocarbon; why we need the catalytic reforming? Because you see the low octane naphtha which is not suitable for blending in the gasoline, we will have to improve the octane number and octane number requirement of the fuel that is also changing. And so the octane number as you know that we discussed while discussing the evolution of crude oil the importance of the octane number in case of the gasoline and the CTA number in case of the integer.

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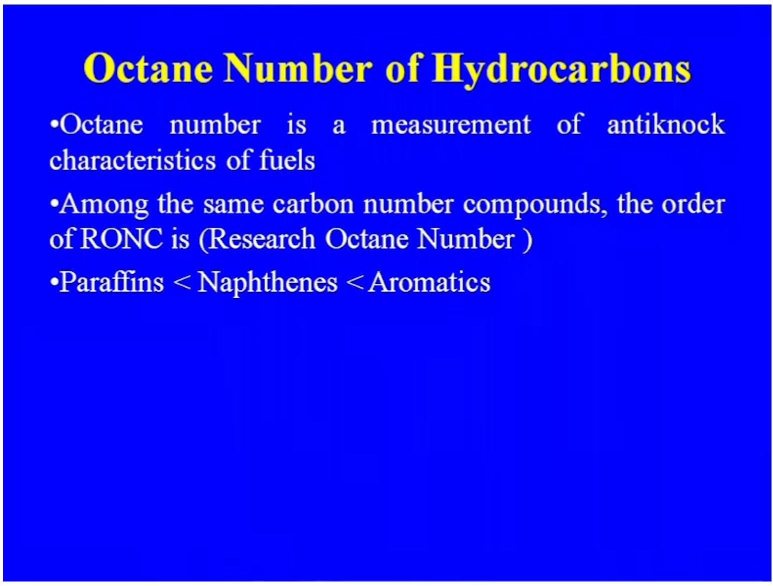

Octane Number of Hydrocarbons

- Octane number is a measurement of antiknock characteristics of fuels
- Among the same carbon number compounds, the order of RONC is (Research Octane Number)
- Paraffins < Naphthenes < Aromatics

So, octane number is a measurement of the antiknock characteristic of the fuels. Among the same carbon compounds, the order of research octane number, paraffins and aromatics. Paraffin will have the lower octane number then it is naphthenic and the highest is in the case of the aromatic. So, this is the order and so that is why for the production of the high octane gasoline or aromatics, we do not for the more paraffinic feed stock, because we, it will more naphtha with less aromatic. And so that will be more suitable for the isomerization, purposes just like in case of the some of the refinery in Assam. We are having in molecular refining, we are having the isoerization section also.

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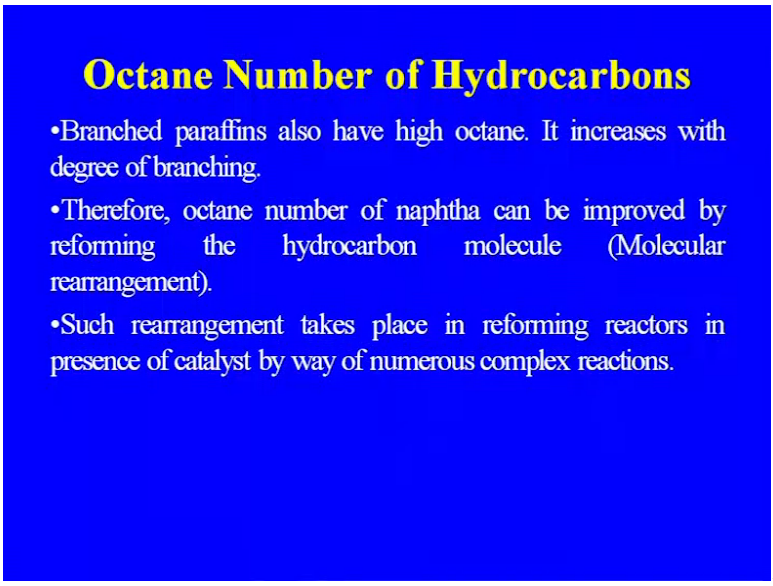

Octane Number of Hydrocarbons

- •Branched paraffins also have high octane. It increases with degree of branching.
- •Therefore, octane number of naphtha can be improved by reforming the hydrocarbon molecule (Molecular rearrangement).
- •Such rearrangement takes place in reforming reactors in presence of catalyst by way of numerous complex reactions.

Branch paraffin also have high octane number it increases with the degree of branching. So, that is why were straight run straight change to more branch change that is required in case of the paraffin. And this is the, what happening in some of the reaction they are that is we are converting the linear to the branching. Therefore, octane number of naphtha can be improved by reforming the hydrocarbon molecules that is the molecule rearrangement, the various constituents which are present in the naphtha. Such rearrangement takes place in reforming reactors in presence of catalyst by way of a numerous, numerous complex reaction, because it is large amount the reaction that is taking place during the catalytic reforming process. So, this I was telling about the octane number here you see the octane is 100 and then we compare with the octane.

Normal butane, iso butane is higher than the normal butane and pentane 61 and iso pentane 93. Similarly, in case of the toluene that is 119, so the higher if the your branching, branch paraffin’s are there or the aromatics are there then the octane number that will be high. Let us now discuss the, what are the various steps involved in the catalytic reforming process.

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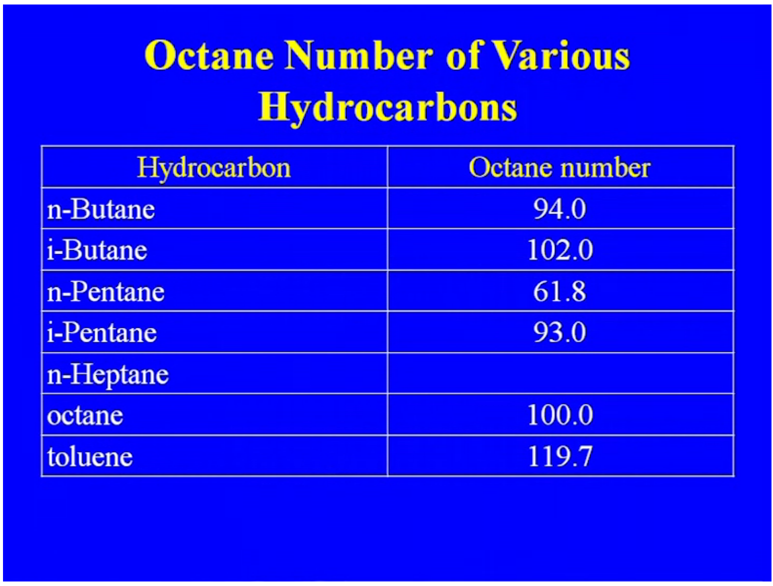

Octane Number of Various Hydrocarbons

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

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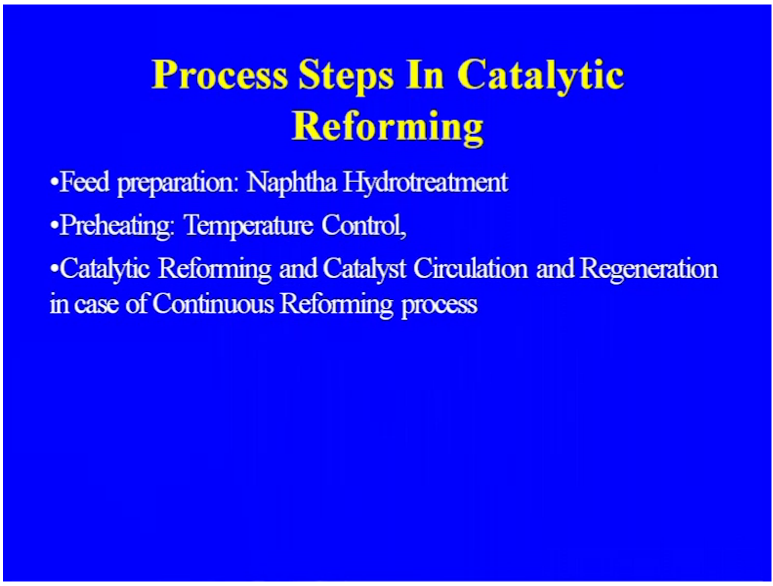

Process Steps In Catalytic Reforming

- Feed preparation: Naphtha Hydrotreatment
- Preheating: Temperature Control,
- Catalytic Reforming and Catalyst Circulation and Regeneration in case of Continuous Reforming process

First thing is the feed preparation naphtha hydro treatment, because what is happening in case of the naphtha, because lot of the impurities present especially the sulphur compound, nitrogenous compound. And the some of the meters which are catalyst poisons. So, the some of the catalyst poisons that may be temporary and other may be permanent that is the need of the requirement of the process that the initial stage of refinery itself we are removing the maximum meters which is present during the desalting process.

And then whatever the sulphur compounds, but what is happening in case of the, because of the use of more and more heavier crude, the sulphur compounds they are coming in the naphtha. And other product which we are getting from the crude oil evaluation and so the treatment pretreatment of the feed before it is going to the catalytic reforming that is very important.

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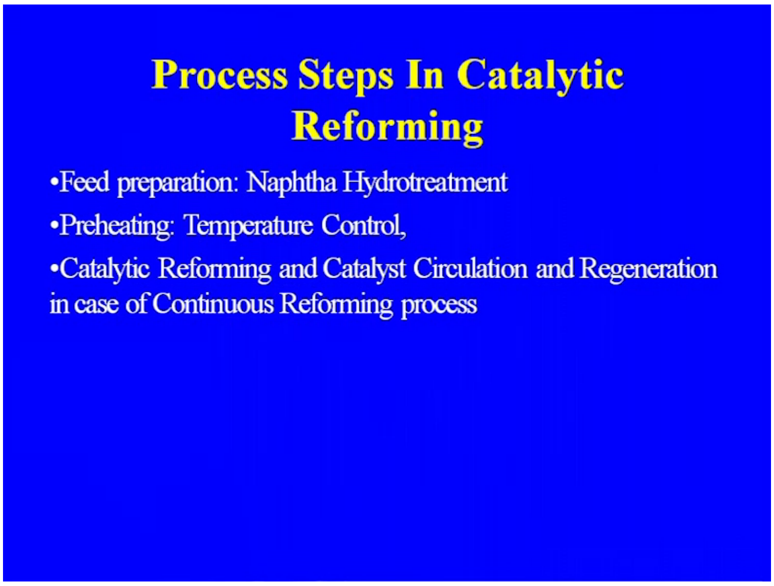

Process Steps In Catalytic Reforming

- Feed preparation: Naphtha Hydrotreatment
- Preheating: Temperature Control,
- Catalytic Reforming and Catalyst Circulation and Regeneration in case of Continuous Reforming process

Another important step that is the, because preheat temperature control, because the major reaction which is taking place the reaction in case of the catalytic reforming that is endothermic, so you will have to provide heat. And so for that the temperature in each stage we are having the interstate heaters, catalytic reforming then the final in the catalytic reforming reaction as taking place in the reactor. And then the catalyst circulation and regeneration in case of the continuous thing, because now we are having the continuous reforming process also, extra creators are there, the catalyst removing it is going the, for regeneration. And then we have, it is coming to the catalytic reforming reactor.

Then comes the product separation removal of the gases, because light component will be there. And that is always associated whenever you are having the item pressure means the either you are going for the catalytic cracking or the catalytic reforming some gases that will be always formed. And then so removal of the gases that is very important.

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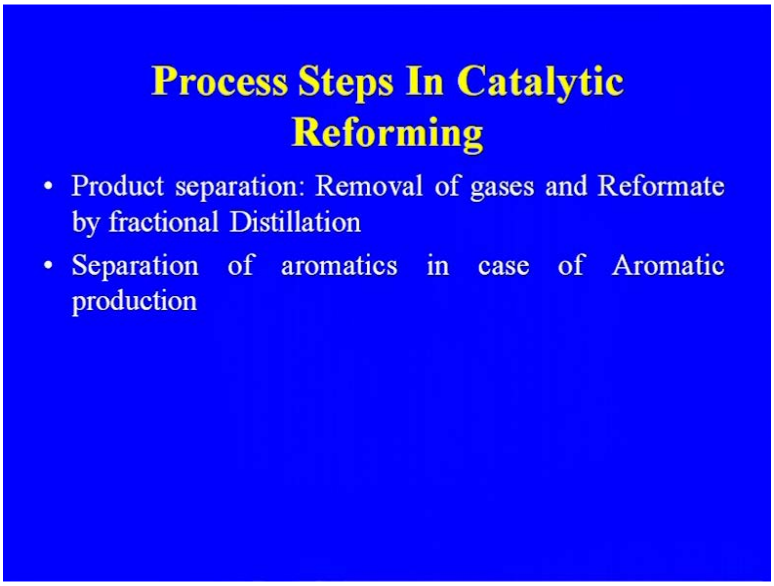

Process Steps In Catalytic Reforming

- Product separation: Removal of gases and Reformate by fractional Distillation
- Separation of aromatics in case of Aromatic production

So, the product separation that includes removal of the gases and reformate by fractional distillation. So, the gases that will contain hydrogen that will contain the, your LPG and hydrogen, that is recycling the process so for that you will have to have the proper separation, separation of the aromatic in case of the aromatic that will be discussing, while discussing the aromatic production in case in the module 7 of the petrochemical part. Let us now discuss about the naphtha hydro treatment. What are the various steps involved in case of the naphtha.

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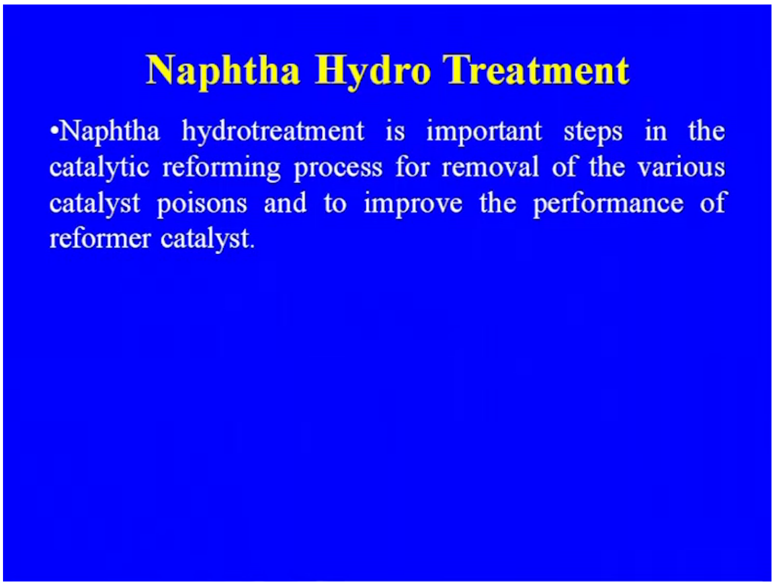

Naphtha Hydro Treatment

•Naphtha hydrotreatment is important steps in the catalytic reforming process for removal of the various catalyst poisons and to improve the performance of reformer catalyst.

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Naphtha hydro treatment is the important step in the catalytic reforming process for removal of the various catalyst poisons and to improve the performance of the reformer catalyst. Because the, if the activity is going down if the life is going down if it is not stable, because of the impurities. Then definitely you will have to use more and more catalyst that will reduce the conversion and so and that will upset whole economy of the process. So, the removal of this catalyst is poisonous which may poison the catalyst is very important. So, what is happening in case of the naphtha hydro treatment when we are doing the naphtha hydro treatment?

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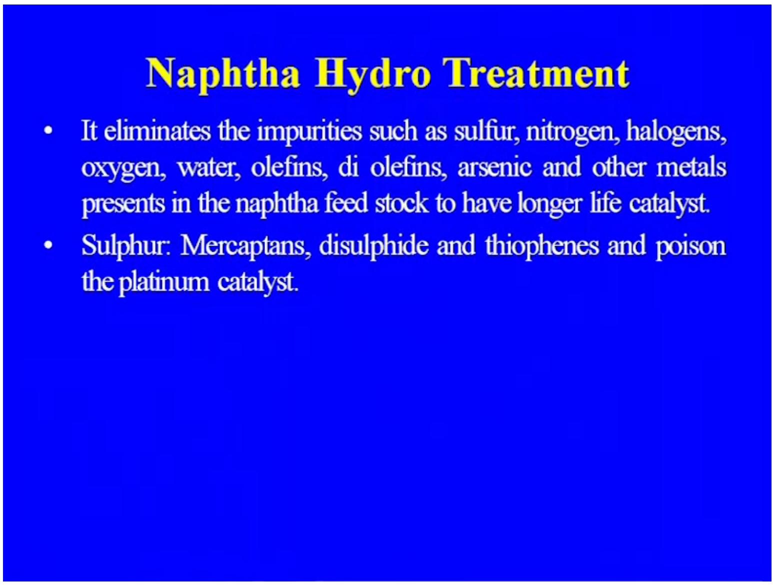

Naphtha Hydro Treatment

- It eliminates the impurities such as sulfur, nitrogen, halogens, oxygen, water, olefins, di olefins, arsenic and other metals presents in the naphtha feed stock to have longer life catalyst.
- Sulphur: Mercaptans, disulphide and thiophenes and poison the platinum catalyst.

It eliminates the impurity such as sulphur, nitrogen, halogens, oxygen, water, olefins, di olefins, arsenic and other metal present in the naphtha feed stock to have longer life catalyst. Sulphur; as I discussed earlier the sulphur that may be in the form of mercaptan and disulphide thiophenes all these sulphur compounds will poison the platinum catalyst.

The sulphur content may be as high as 500 ppm, depending upon the type of the crude oil which we are processing with the heavier crude oil is there. So, sulphur content that will be high if you are having the low sulphur crude oil then the definitely the sulphur content. But in any case we will have to, because our requirement in case of the sulphur content in the final naphtha which is going to the catalytic reformer is 0.5 ppm or less and water content less than 4. So these are the various section in case of the naphtha hydro treatment.

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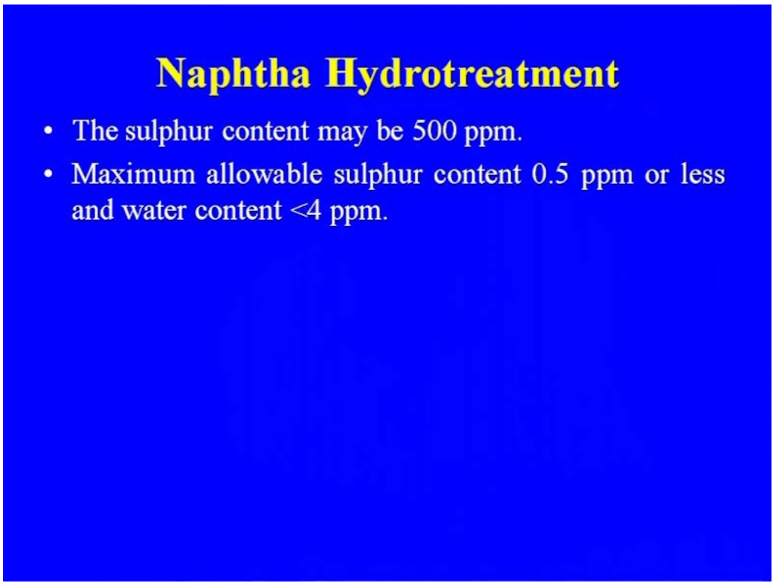

Naphtha Hydrotreatment

- The sulphur content may be 500 ppm.
- Maximum allowable sulphur content 0.5 ppm or less and water content <4 ppm.

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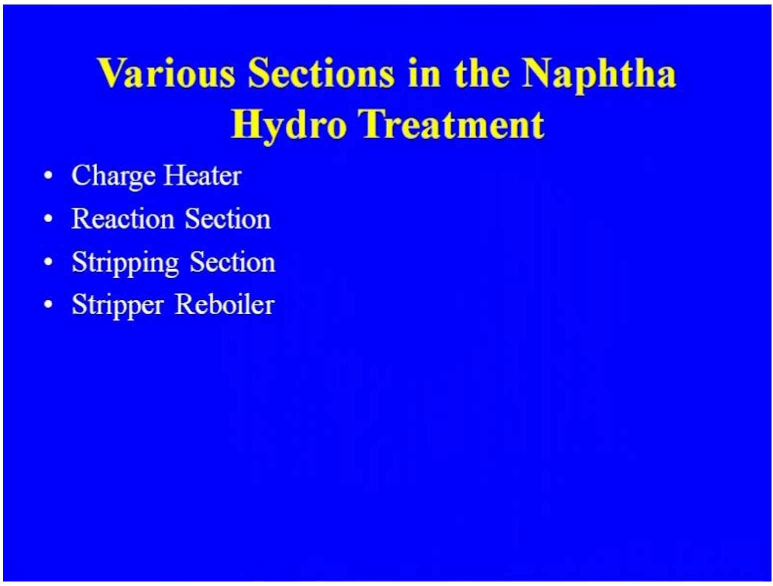

Various Sections in the Naphtha Hydro Treatment

- Charge Heater
- Reaction Section
- Stripping Section
- Stripper Reboiler

Charge Heater, reaction section that is the main reaction stripping section, and the stripper boiler, reboiler. Fixed bed reactor containing a nickel molybdenum catalyst where both the hydro de sulphurisation reaction and hydro de nitrification reaction takes place. So, these are the actually the, as in case of the also when we are using the naphtha the natural gas which is going to the synthesis gas manufacturing.

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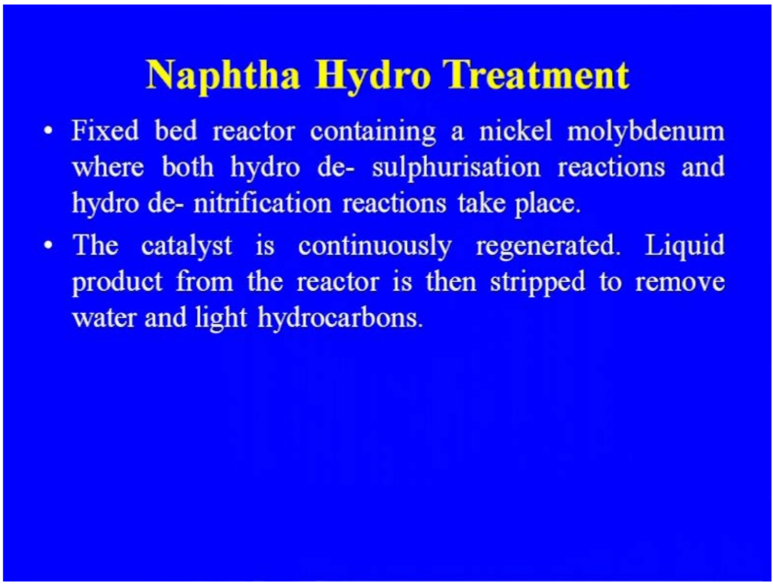

Naphtha Hydro Treatment

- Fixed bed reactor containing a nickel molybdenum where both hydro de- sulphurisation reactions and hydro de- nitrification reactions take place.
- The catalyst is continuously regenerated. Liquid product from the reactor is then stripped to remove water and light hydrocarbons.

There also you are using the same way here also the sulphur that is by de hydro de sulphurisation is taking place that is removal of the nitrogenous compound is also taking place. The catalyst is continuously regenerated liquid product form the reactor is then stripped to remove the water and light hydrocarbon. This is about the de sulphurisation already discussed.

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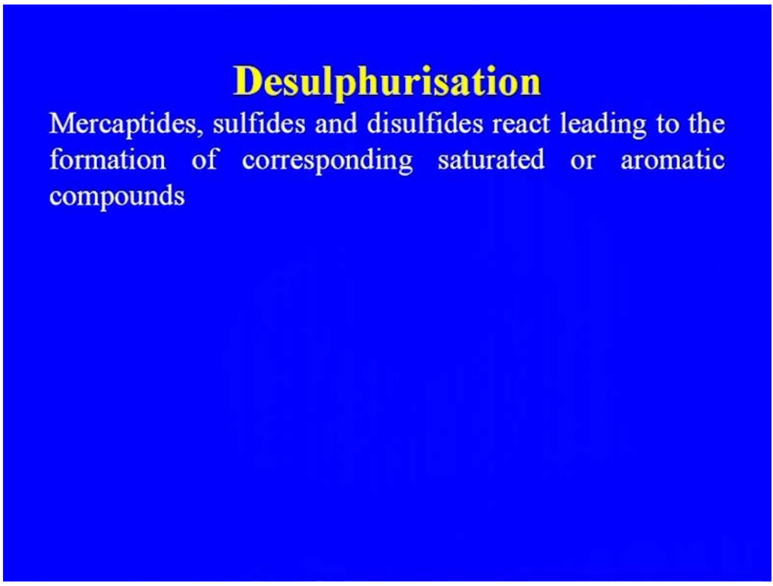

Desulphurisation

Mercaptides, sulfides and disulfides react leading to the formation of corresponding saturated or aromatic compounds

These are the sulphur mercaptides, sulfides and disulfides react leading to the formation of the corresponding saturated or aromatic compounds.

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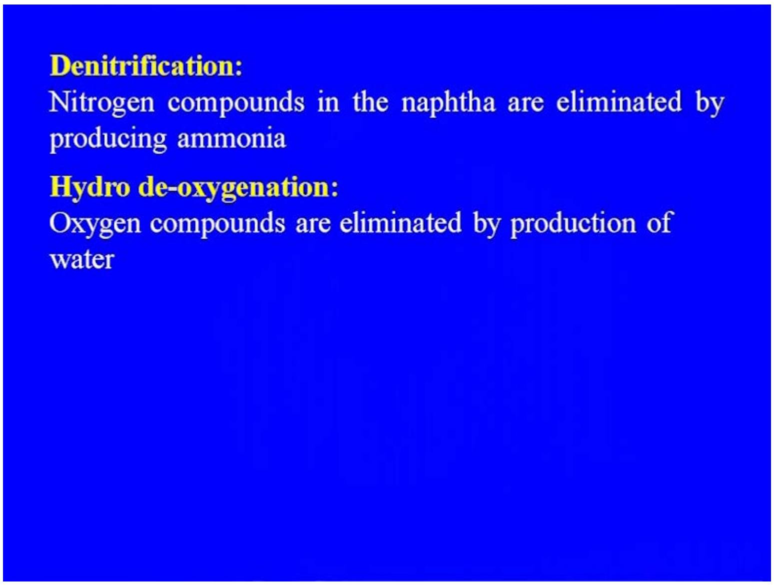

Denitrification:
Nitrogen compounds in the naphtha are eliminated by producing ammonia

Hydro de-oxygenation:
Oxygen compounds are eliminated by production of water

This is the reaction that is taking place de nitrification nitrogen compound in the naphtha are eliminated by producing ammonia, oxygen compounds are eliminated by production of water with the process hydro de oxygenation.

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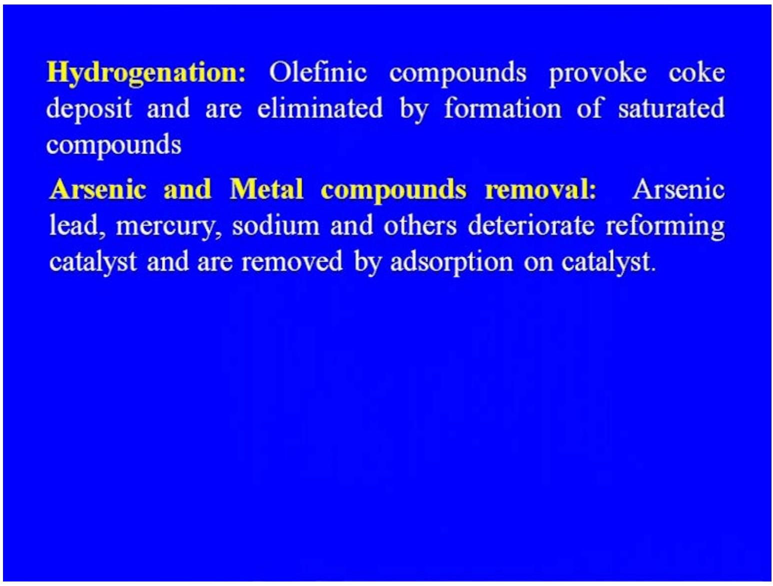

Hydrogenation: Olefinic compounds provoke coke deposit and are eliminated by formation of saturated compounds

Arsenic and Metal compounds removal: Arsenic lead, mercury, sodium and others deteriorate reforming catalyst and are removed by adsorption on catalyst.

Hydrogenation of olefinic compounds, provoke coke deposit and are eliminated by formation of the saturated compound. Arsenic and metal compounds removal; arsenic lead, mercury, sodium and other heavy metals which are present they deteriorate the reforming catalyst and are removed by adsorption on the catalyst.

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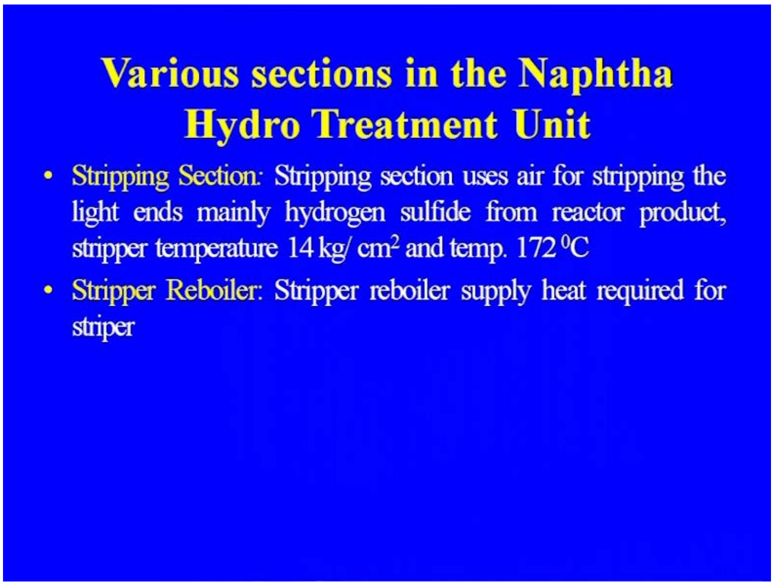

Various sections in the Naphtha Hydro Treatment Unit

- **Stripping Section:** Stripping section uses air for stripping the light ends mainly hydrogen sulfide from reactor product, stripper temperature 14 kg/ cm^2 and temp. 172 ^{0}C
- **Stripper Reboiler:** Stripper reboiler supply heat required for striper

Stripping section; stripping section uses air for stripping the light ends mainly hydrogen sulfide from the reactor product. And then the hydrogen sulfide is further going for the further removal from the gas steam and then it is going to the (()) and other section. The stripper temperature that is the temperature and pressure that we maintaining stripper re boiler stripper usually supply heat required for striper.

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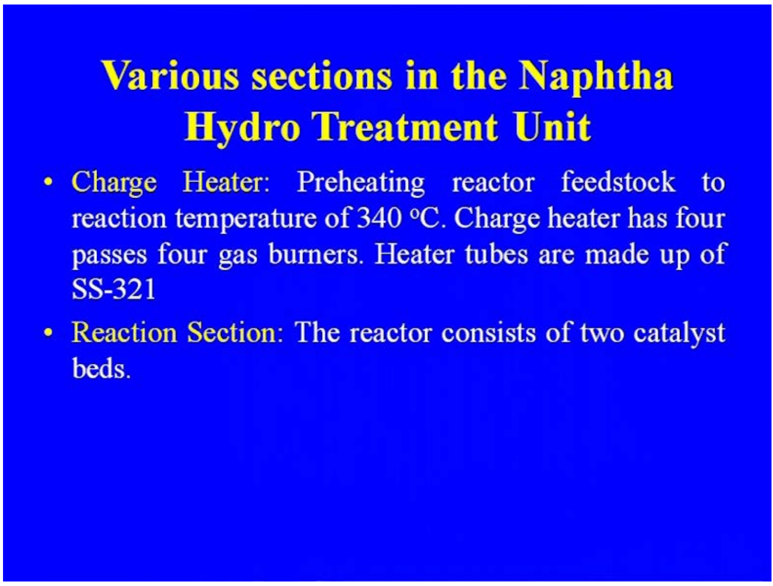

Various sections in the Naphtha Hydro Treatment Unit

- **Charge Heater:** Preheating reactor feedstock to reaction temperature of 340 ^{o}C. Charge heater has four passes four gas burners. Heater tubes are made up of SS-321
- **Reaction Section:** The reactor consists of two catalyst beds.

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Charge heater; preheating reactor feedstock to reaction temperature 340 degree centigrade. A charge heater has 4 passes, 4 gas burners, heater tubes are made of stainless steel 321.

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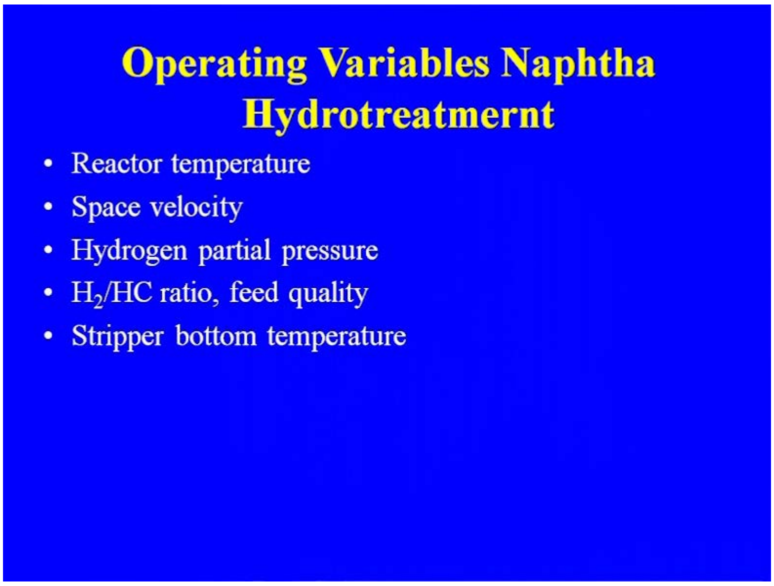

Operating Variables Naphtha Hydrotreatmernt

- Reactor temperature
- Space velocity
- Hydrogen partial pressure
- H_2/HC ratio, feed quality
- Stripper bottom temperature

Operating variables in the naphtha hydro treatment; reactor temperature, space velocity, hydrogen partial pressure, hydrogen to hydrogen carbon ratio, feed quality and the stripper bottom temperature.

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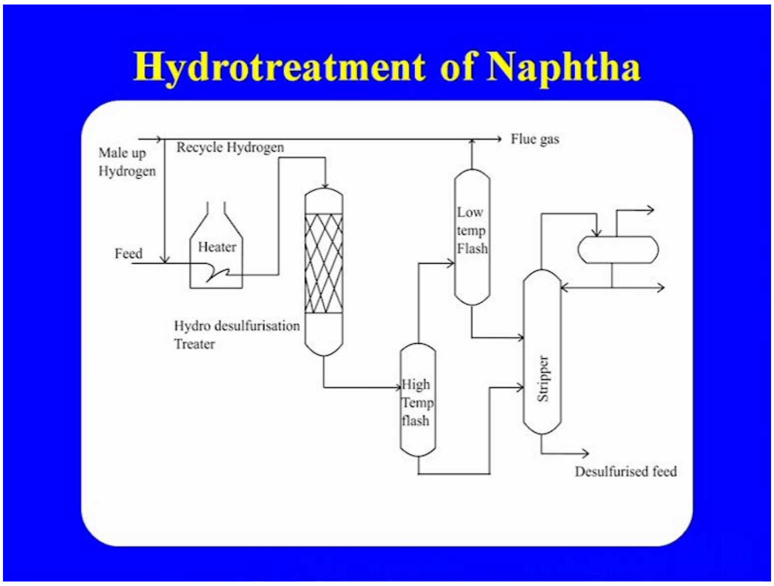

Hydrotreatment of Naphtha

This is the hydro treatment of the naphtha feed is going to the heat heater from the heater, it is going to the main reactor where the hydro desulphurisation. And other reaction that is taking place we are having the catalyst bed and after that the, because the temperature here is high it is going to the higher temperature flash section and the low temperature flash. And then it is going to the stripper section, here the gases which are separated hydrogen that is going excess, because here the in the process we need the hydrogen. And after the stripper the desulphurized feed that is going to the catalytic reforming unit. So, this is the process which we are using in case of the naphtha hydro treatment. Now let us go to the catalytic reforming part.

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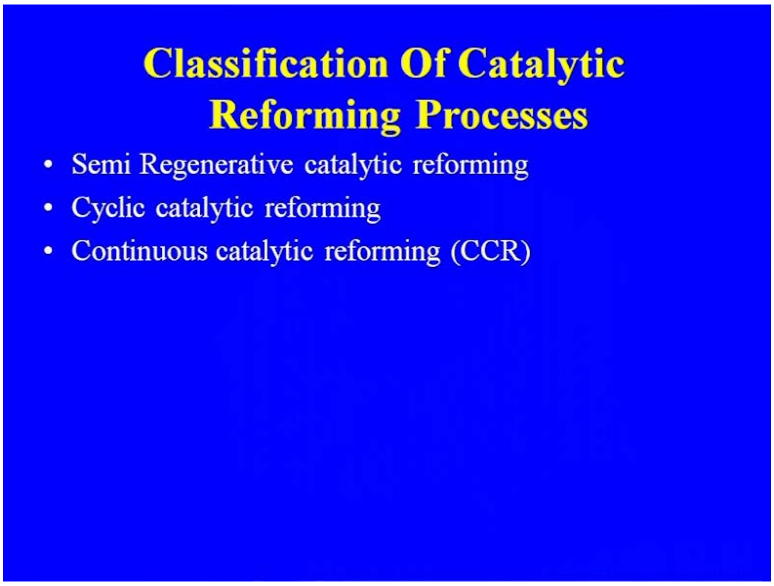

Classification Of Catalytic Reforming Processes

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

The classification of the catalytic reforming process; semi regenerative catalytic reforming, cyclic catalytic reforming means you are doing the catalytic reforming one reactor that will be by pass, continuous catalytic reforming by the catalyst where the catalytic reforming is continuous. And at the same time regeneration of the catalyst is also continuous and then it is being recycled.

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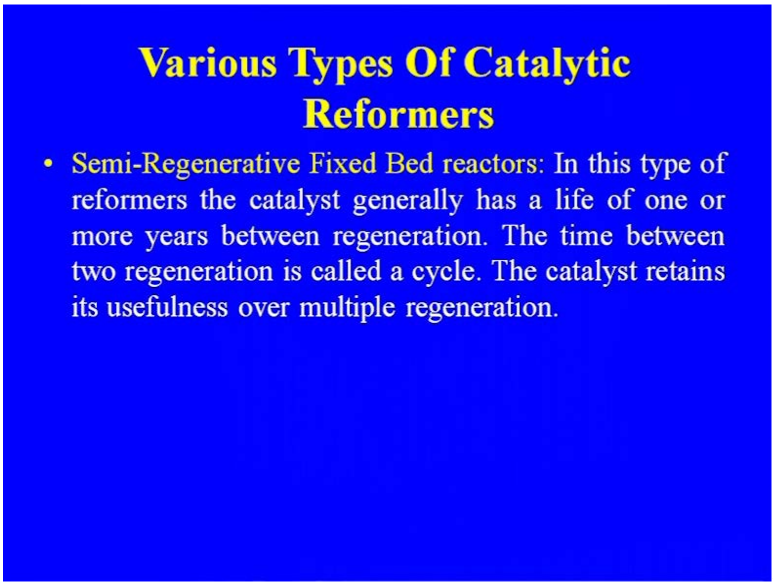

Various Types Of Catalytic Reformers

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

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Semi regenerative fixed bed reactor: in this type of the reformer the catalyst generally has a life of one or more years between regeneration. The time between two regeneration is called a cycle of the reactor. And the catalyst retains its uses usefulness over multiple regeneration, but there is definitely some loss during the regeneration process.

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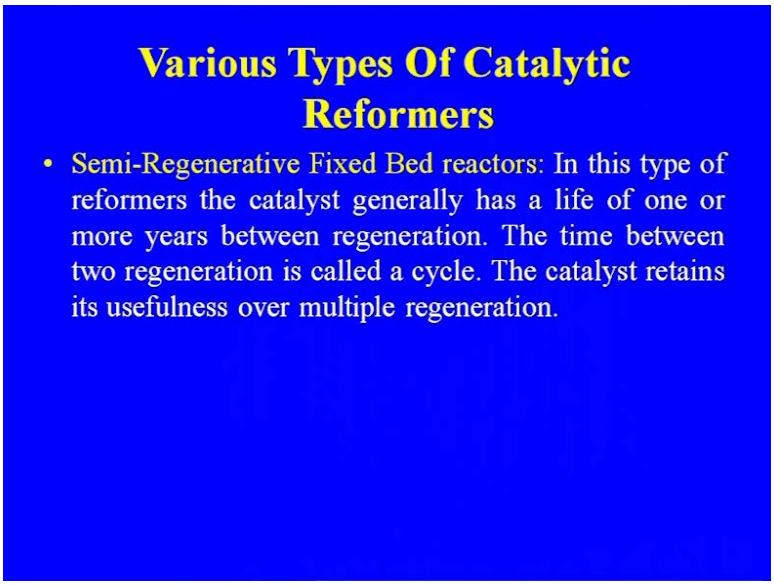

Various Types Of Catalytic Reformers

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

Cyclic fixed bed reactor; cyclic reformers run under more severe operating condition for improved octane number and yields. Individual reactors are taken off offline by a special valving and manifold system and regenerated while the other reformer units are running continuously. And so this is the how the cyclic fixed bed reformers they are working.

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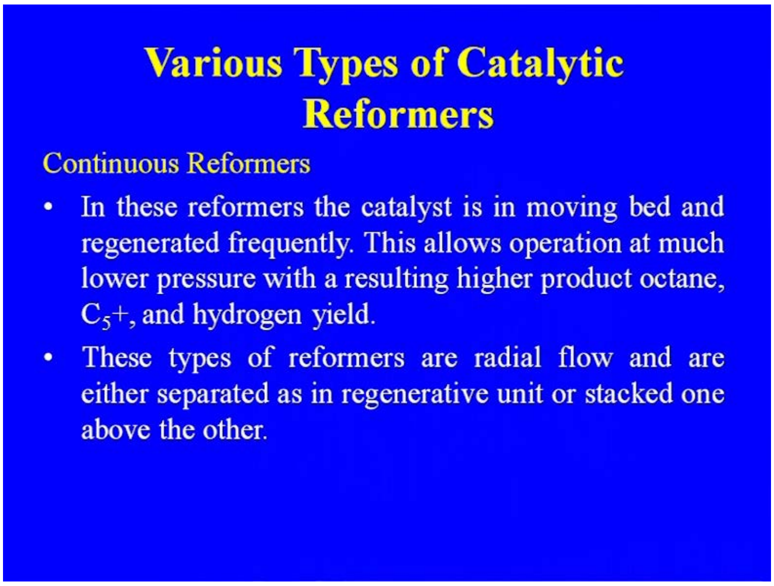

Various Types of Catalytic Reformers

Continuous Reformers

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

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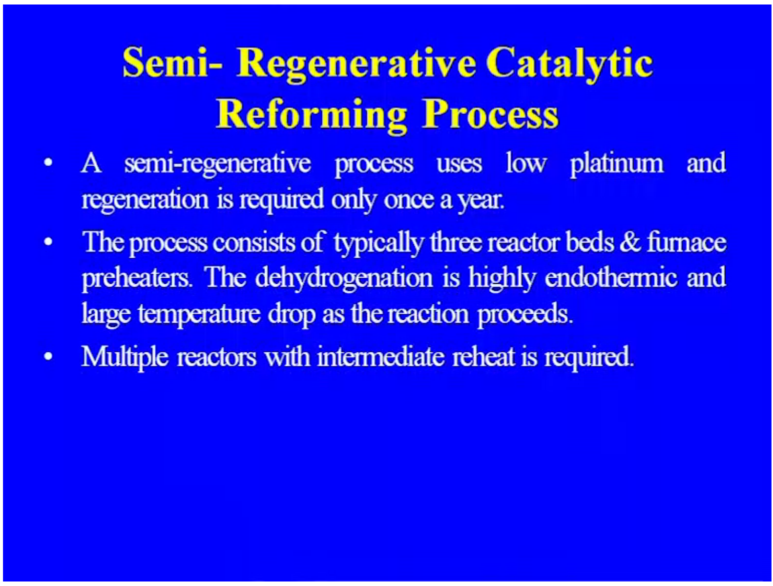

Semi- Regenerative Catalytic Reforming Process

- A semi-regenerative process uses low platinum and regeneration is required only once a year.
- The process consists of typically three reactor beds & furnace preheaters. The dehydrogenation is highly endothermic and large temperature drop as the reaction proceeds.
- Multiple reactors with intermediate reheat is required.

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Continuous reformers; in these reformers the catalyst is in moving bed and regenerated not frequently. But continuously you can say this allows operation at much lower pressure with a resulting higher product of octane C 5 plus and hydrogen yield. These types of reformers are radial flow, because we are having the reactor axial or radial. So, here the reformer is the radial flow and are either separated as in regenerative unit or stacked one, one above one. Because some of the refinery they are having these stacked reactor, reactor 1, reactor 2, reactor 3 and like that. So the in each reactor he your catalyst the pre heaters are there, regeneration of the catalyst is there.

Semi regenerative process is a low platinum and regeneration is required only once a year. The process consists of typically 3 reactor bed and furnace pre heaters. In each stage because normally the 3 stage reactor, 3 reactors are running in series. And so they continuously the from 1 reactor to another, another to third reactor that is going the product from 1 reactor that is going to second, second to third. And in between the, we are having the iterator; the de hydrozination is highly endothermic or this is the main reaction which is taking place in case of the catalytic reforming which is highly endothermic and large temperature drop as the reaction proceed.

So, that is the reason why we need the preheating of the naphtha feed which is coming from one stage to another stage after reforming. I am saying the naphtha the reformate of one number, one di-ester that will go for preheating second. Again it will go for preheating just to maintain the temperature around 500 degree centigrade which is the requirement. Because too low or the too high temperature that is also going to affect the operation of the catalytic reforming process that will be discussing while discussing the process variables..

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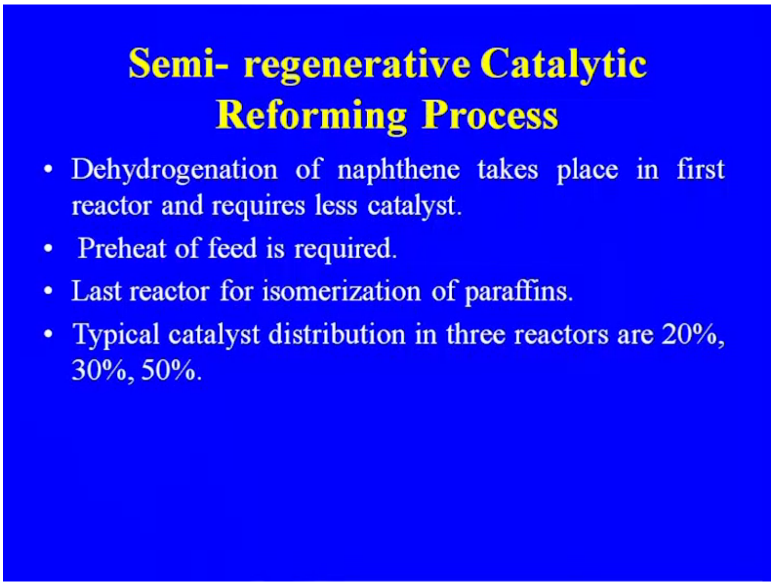

Semi- regenerative Catalytic Reforming Process

- Dehydrogenation of naphthene takes place in first reactor and requires less catalyst.
- Preheat of feed is required.
- Last reactor for isomerization of paraffins.
- Typical catalyst distribution in three reactors are 20%, 30%, 50%.

Dehydrogenation of the naphthenes takes place in the first reactor that is the how the, because we are having the three, some reaction is taking place in the first reactor, second reactor and third like that. So, dehydrogenation of the naphthenes takes place in the first reactor and require less catalyst, preheat of the feed is required. Last reactor for isomerization of the paraffins, typical catalyst distribution in 3 reactors is 20 30 and 50. Catalyst regeneration; why we need the catalyst regeneration?

Because that is in all cases when we are having the, either the catalytic cracking or the catalytic reforming, because the temperature is around 500 some coke formation is there that you can minimize, but you cannot avoid completely, so what has happened? Now, the catalyst in all the cracking process or the catalytic reforming which are which has been developed, now they are having the more resistance towards the coke, so the coke formation and the coke formation also that can be reduced.

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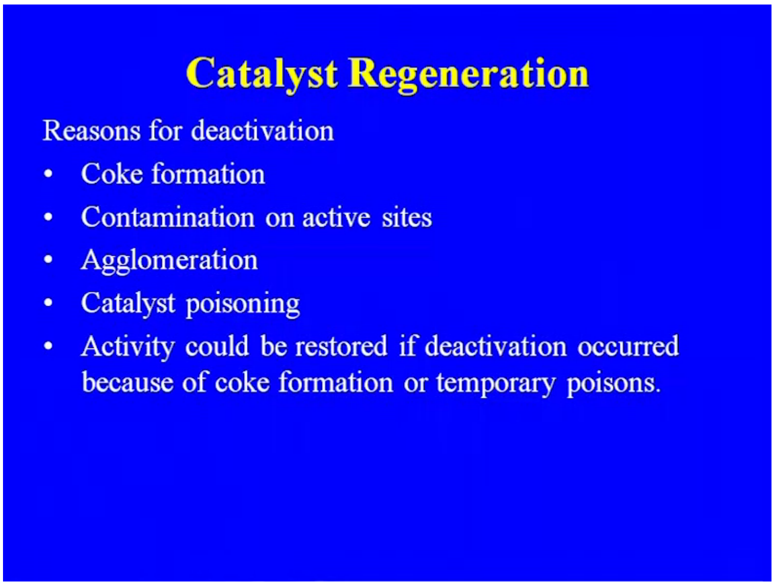

Catalyst Regeneration

Reasons for deactivation

- Coke formation
- Contamination on active sites
- Agglomeration
- Catalyst poisoning
- Activity could be restored if deactivation occurred because of coke formation or temporary poisons.

So, coke formation, contamination on active site, agglomeration, catalyst poisoning, catalyst could be restored if the deactivation occurred, because of the coke formation or the temporary poisons. So, this is the problem in case of the, why we need the catalyst regeneration? Because again the regeneration or the catalyst life that will be totally dependent upon the type of the feed stock. The efficiency of the pretreatment processes which we are doing this naphtha hydro treatment process, because the impurity removal to the required limit which is required for the catalytic reforming that is very important.

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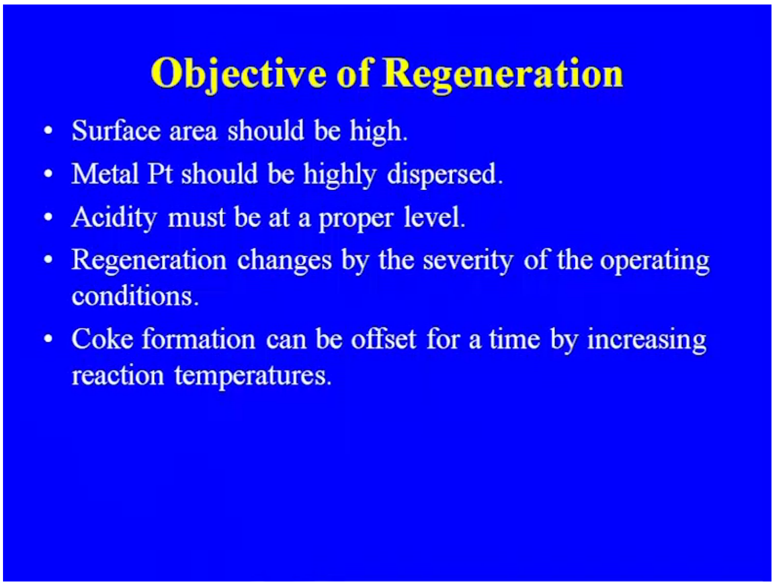

Objective of Regeneration

- Surface area should be high.
- Metal Pt should be highly dispersed.
- Acidity must be at a proper level.
- Regeneration changes by the severity of the operating conditions.
- Coke formation can be offset for a time by increasing reaction temperatures.

Objective of the regeneration surface area should be high, because that is the basic requirement in case of the catalytic reforming or any catalyst, because the coke fine coke that need deposit on the surface. And so that it is in the surface area as well as they will poison the catalyst also. Metal platinum should be highly dispersed, acidity must be at a proper level. Regeneration changes by the severity of the operating condition, coke formation can be offset for a time by increasing the reaction temperature.

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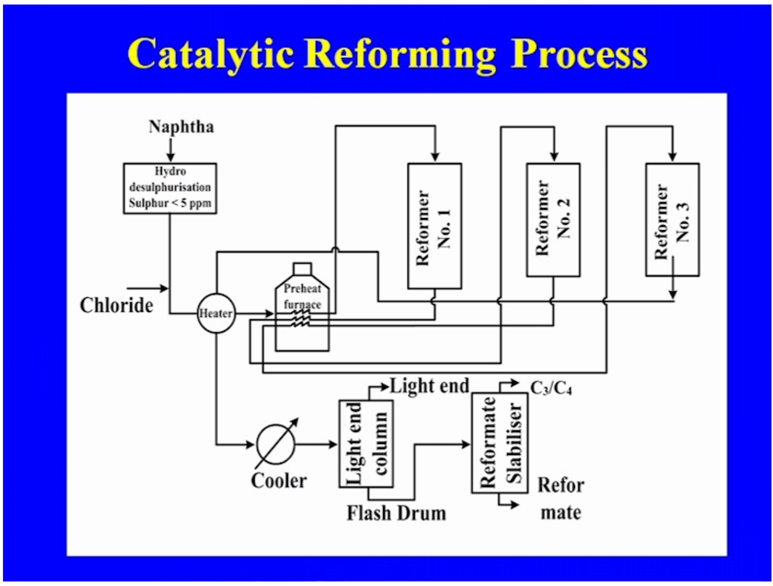

Catalytic Reforming Process

This is I was telling about the catalytic reforming process. Here the naphtha after the pretreatment that is the pretreatment section, naphtha pretreatment section is having the pre heating than the pretreatment of the naphtha than the other units also there. So, that we have already discussed then the chloride hydration is also there, importance of the chloride is also there, excess chloride is also not desirable.

So, after naphtha pretreatment that is going to the heater And from the heater it is going to reactor one from the reactor one the product again it is being preheated and the heater And then it is going to the second after the preheating, again in the from the reformer of the product that will go to the reformer number 2 after the preheating. And like that the all the in the 3 stages we are having the here preheat furnace have some only one.

But this is all the 3 furnaces you are having and after the reformer 3, the final product which you are getting that will go to the, because the heat of this all the reactor that we are utilizing here for preheating. And so the after the cooler it will go to the light end column again as I told you, the, during the process we are getting hydrogen and LPG also. That will be actually again that will depend upon the your operating condition whether the light ends are more or less it will depend upon the temperature. Then the flash drum and flash drum to the formally the, your it is going for the reformate stabilizer where the C 3 C 4 component light, lighter component that will be separated and the reformate the finally, which you are getting that will be use for RFG reformatted gasoline or it may go for the separation of the aromatics in the aromatic plant.

So, the choice of the feed stock also will be decided whether we are going for the reformate or the gasoline pool or it will go for the aromatic production. So, I think the old diagram the flow diagram of a catalytic reforming what is happening in case of the stack reactor? I was not so near, but the stack reactor is one bottom reactor number 1 is at top number 2, number 3 reactors.

So, stack reactors are there in case of the catalytic reforming continuous, catalytic reforming process. So, reactions; what are the reactions that is taking place in case of the catalytic reforming? Desirable reactions, because in case of the catalytic reforming any reaction always there is some, some side reactions which are not desired. But that is taking place so here also in case of the catalytic reforming we are having the 2 types of the reaction which is taking place one is the desirable part and the non desirable part.

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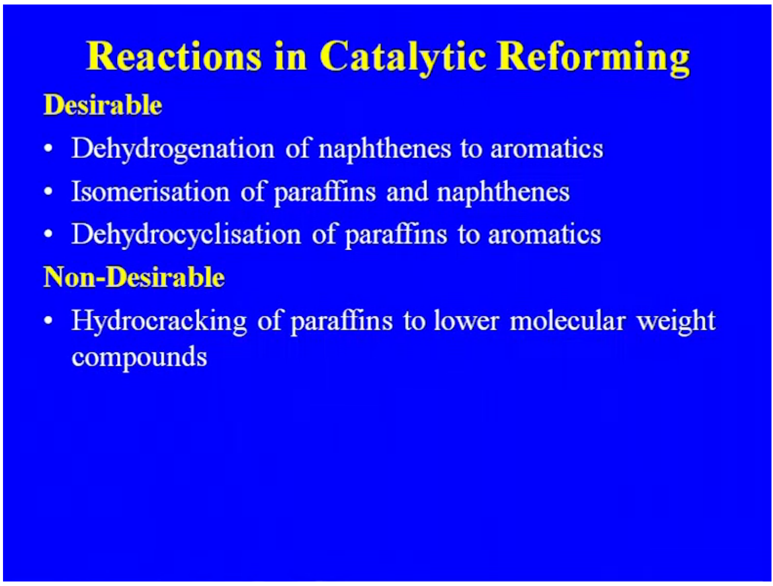

Reactions in Catalytic Reforming

Desirable

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

Non-Desirable

- Hydrocracking of paraffins to lower molecular weight compounds

So, desirable reaction; dehydrogenation of naphthenes to aromatics this is the one of the very important reaction in case of the catalytic reforming process. And this is endothermic and that is the reason why we need the pre heater in each stage in case of the catalytic reforming process and the isomerization of the paraffins and naphthenes. These are the again very important because you need the, you need more branch paraffins, so that the octane number is increase de hydro cyclisation of the paraffins to aromatic.

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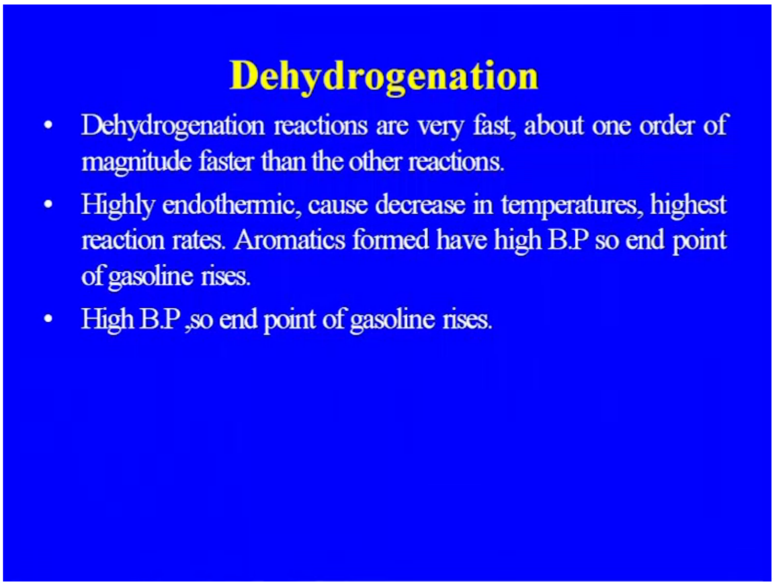

Dehydrogenation

- Dehydrogenation reactions are very fast, about one order of magnitude faster than the other reactions.
- Highly endothermic, cause decrease in temperatures, highest reaction rates. Aromatics formed have high B.P so end point of gasoline rises.
- High B.P ,so end point of gasoline rises.

Some of the non-desirable reaction which will be the only you can reduce the extent of these non-desirable reaction. That is the hydro cracking of the paraffin to lower molecular weight compounds then the formation of coke that will also result. And so let us discuss in detail about the de hydrogenation reaction.

De hydrogenation reaction are very fast, about one order of the magnitude faster than the other reactions. Highly and this is the reason you see the catalyst distribution in the first reactor that is less second higher than the one. And the third is the, your much higher catalyst that we are using. So, the reaction is highly endothermic cause decrease in the temperature highest reaction rates aromatic form have high boiling point. So, end point of the gasoline rises, high boiling point that may be required, because the less you vapor pressure that will affect the vapor pressure of the gasoline.

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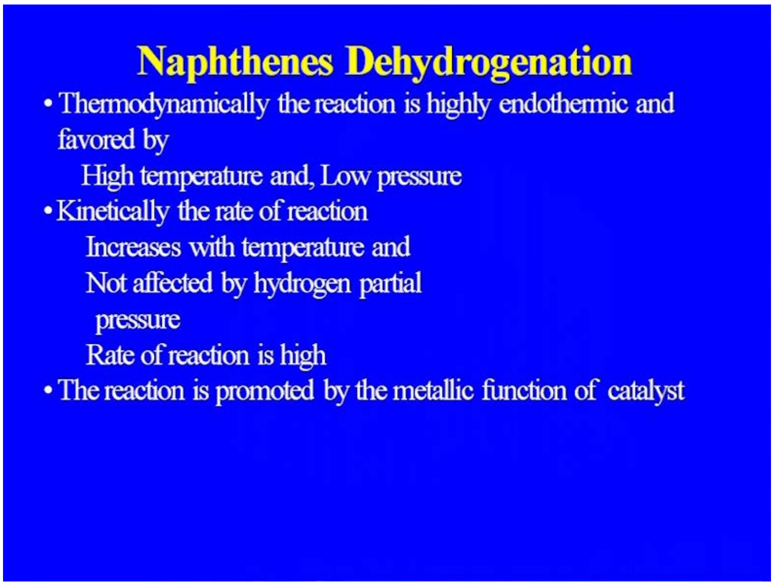

Naphthenes Dehydrogenation

- Thermodynamically the reaction is highly endothermic and favored by
  High temperature and, Low pressure
- Kinetically the rate of reaction
  Increases with temperature and
  Not affected by hydrogen partial pressure
  Rate of reaction is high
- The reaction is promoted by the metallic function of catalyst

Naphthenes de-hydrogenation the reaction is highly endothermic and favored by high temperature, low pressure so will have to have the optimum condition. Kinetically the rate of the reaction in increase with the temperature, not affected by the hydrogen partial pressure, rate of reaction is high. The reaction is promoted by the metallic function of the catalyst, because now the will be discussing about the detail about the catalytic the catalyst are the bio metrical metal function and the acid function catalyst.

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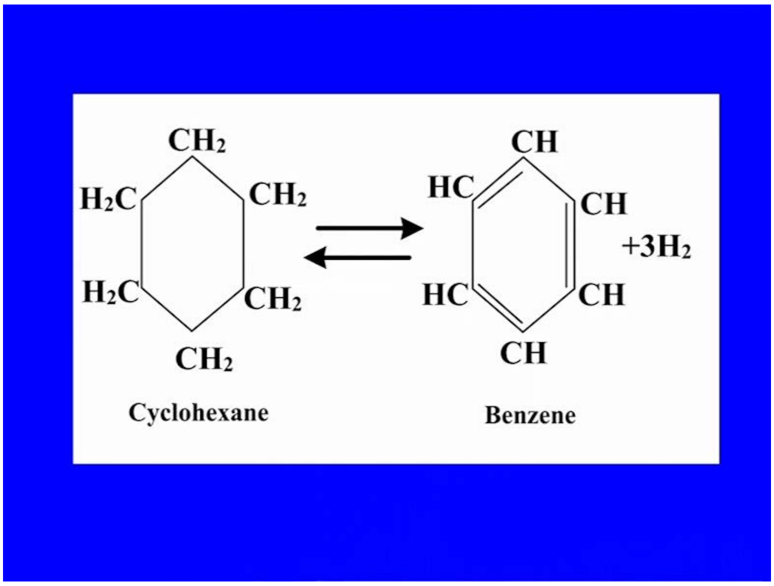

This is the reaction that is taking place here actually cyclohexane that is converted to the benzene.

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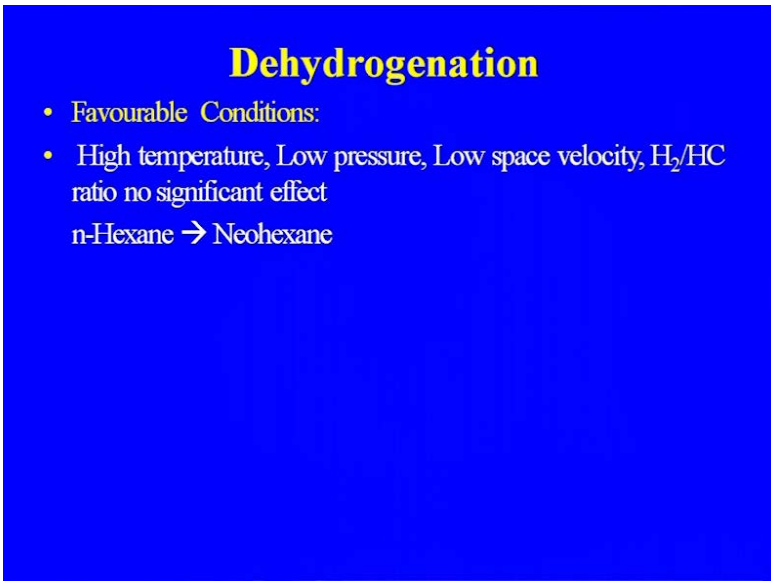

Dehydrogenation

- Favourable Conditions:
- High temperature, Low pressure, Low space velocity, H_2/HC ratio no significant effect
  n-Hexane → Neohexane

Dehydrogenation favorable conditions, already we discuss high temperature low pressure, low space velocity, hydrogen 2, carbon hydrocarbon ratio as it will do that is not having significant effect. And this is the another reaction that is taking place in the de hydrogenation. Paraffins dehydrocyclisation; this is also one of the, that is the multiple step process involved, de hydrogenation of the normal paraffins or the iso paraffins, this is the de hydrocyclization

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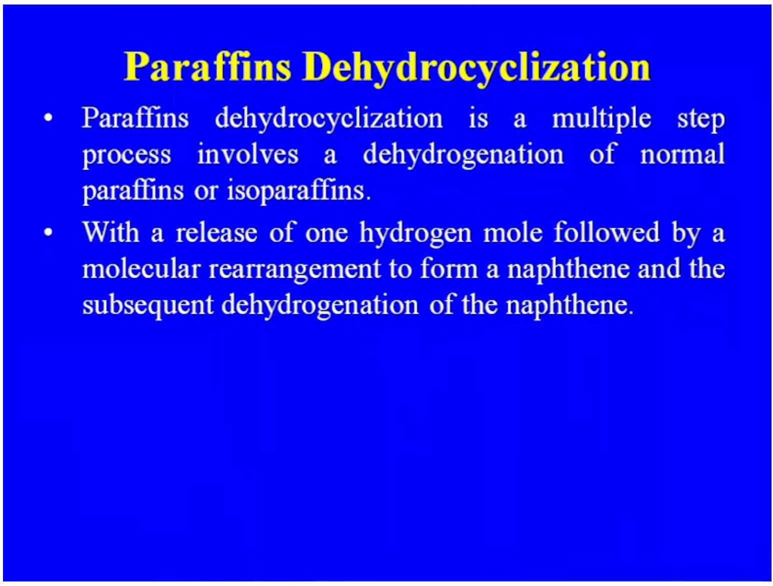

Paraffins Dehydrocyclization

- Paraffins dehydrocyclization is a multiple step process involves a dehydrogenation of normal paraffins or isoparaffins.
- With a release of one hydrogen mole followed by a molecular rearrangement to form a naphthene and the subsequent dehydrogenation of the naphthene.

With a release of one hydrogen mole followed by a molecular rearrangement to form an naphthene and the subsequent dehydrogenation of the naphthene.

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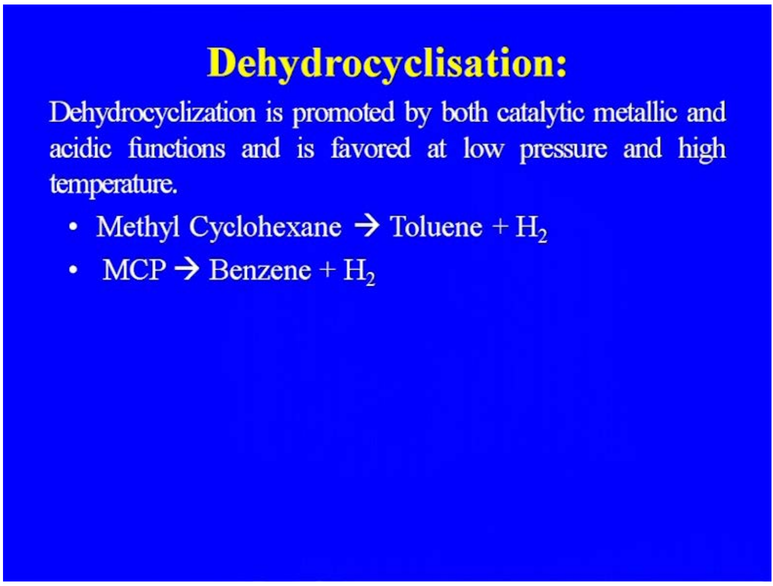

Dehydrocyclisation:

Dehydrocyclization is promoted by both catalytic metallic and acidic functions and is favored at low pressure and high temperature.

- Methyl Cyclohexane → Toluene + H_2
- MCP → Benzene + H_2

De hydrocyclisation is promoted by both catalytic and the metallic function, metallic and acidic function and is favor at low pressure and high temperature.

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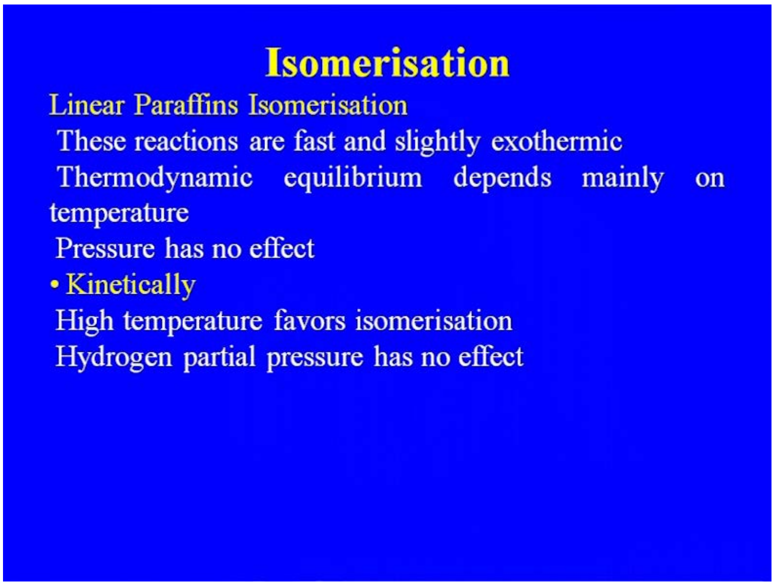

Isomerisation

Linear Paraffins Isomerisation

These reactions are fast and slightly exothermic

Thermodynamic equilibrium depends mainly on temperature

Pressure has no effect

- Kinetically

High temperature favors isomerisation

Hydrogen partial pressure has no effect

.

Isomerization; linear paraffins isomerization, these reactions are fast and slightly exothermic, thermodynamic equilibrium depends mainly on temperature, pressure has no effect high temperature favors isomerization. In case of the isomerization, branch isomers increase octane rating that is why we are having the isomerization And we are producing more branch paraffins

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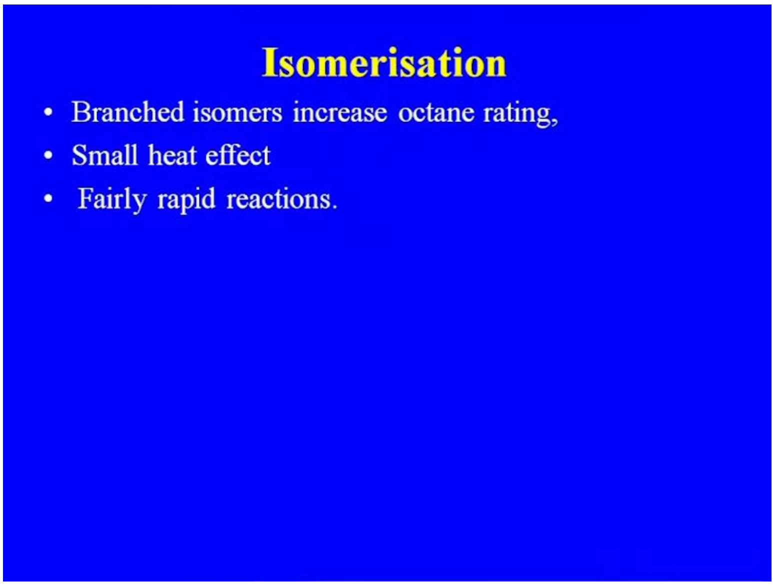

Isomerisation

- Branched isomers increase octane rating,
- Small heat effect
- Fairly rapid reactions.

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A small heat effect fairly rapid reactions is there. Already we discuss about the dehydrocyclisation.

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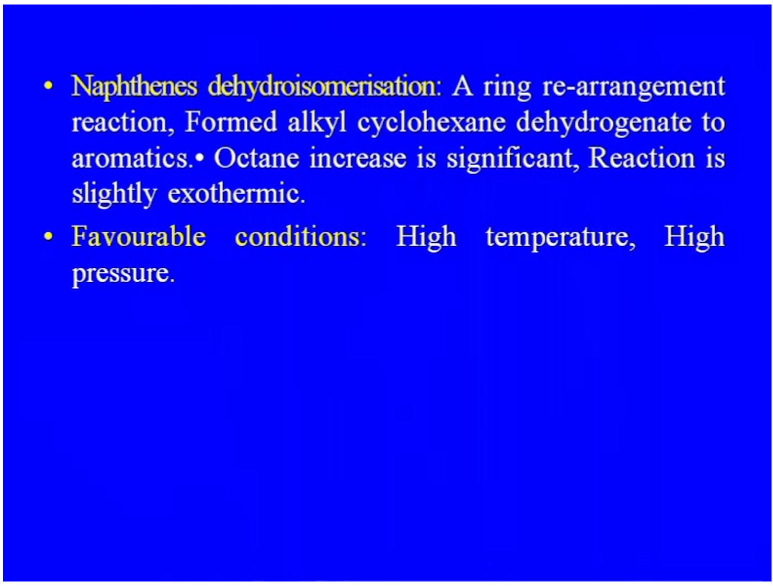

- **Naphthenes dehydroisomerisation:** A ring re-arrangement reaction, Formed alkyl cyclohexane dehydrogenate to aromatics.• Octane increase is significant, Reaction is slightly exothermic.
- **Favourable conditions:** High temperature, High pressure.

.

Naphthenes, de hydro isomerization; a ring re-arrangement reaction, formed alkyl cyclohexane dehydrogenate to aromatics. Octane increase is significant reaction is slightly exothermic. Favorable to favorable conditions high temperature high pressure here you see the high pressure somebody know the low pressure. So, that is this is the optimum condition that has to be maintained in case of the catalytic reforming process. These were the some of the desirable reaction which is taking place in improving the octane number of the.

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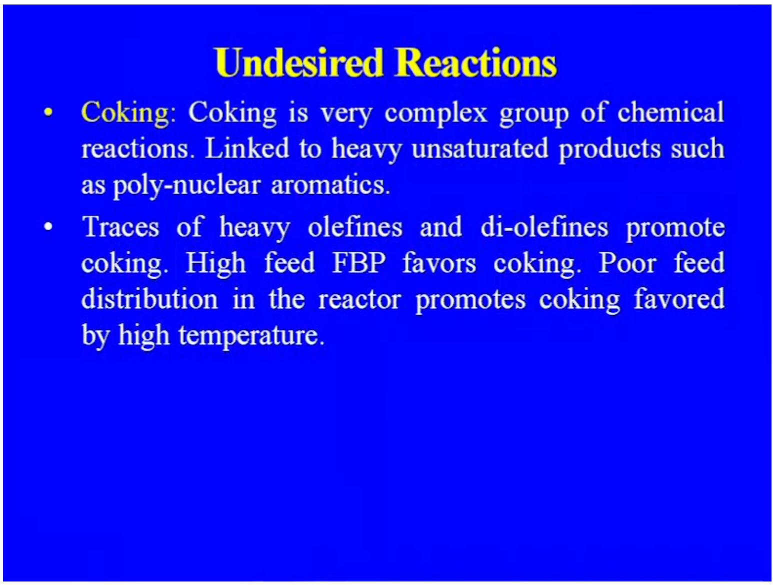

Undesired Reactions

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

.

Now, let us discuss, what are the undesired reaction? First undesired reaction that is taking place that is the coking the formation of the coke, because of the cracking process that is taking place in the process.

So, coking is very complex group of chemical reaction linked to heavy unsaturated products such as the poly-nuclear aromatics, because that was the contents polymerization from to the coke formation that is taking place. So, traces of heavy olefins and di olefins promote coking. High feed, boiling point favors coking poor feed distribution in the reactor promotes coking favored by high temperature.

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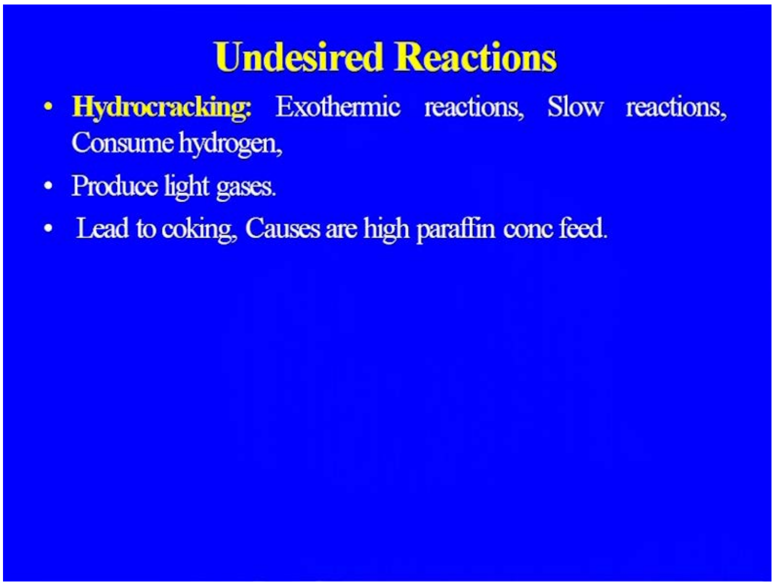

Undesired Reactions

- **Hydrocracking:** Exothermic reactions, Slow reactions, Consume hydrogen,
- Produce light gases.
- Lead to coking, Causes are high paraffin conc feed.

Hydro cracking; exothermic reaction, slow reaction, consume hydrogen, produce light gases, because normal in case of the hydro cracking the lighter gas, so will be losing the reformers. So, that is the, our interest is not in the lighter process our interest in the more reformate. This will be use as a gasoline or for the aromatic plant, produce light gases lead to the coking cause high paraffin concentration effect. This is the cause, because the more paraffins the chances of the coke formation that will be more. Hydro cracking as I told you this is the exothermic reaction.

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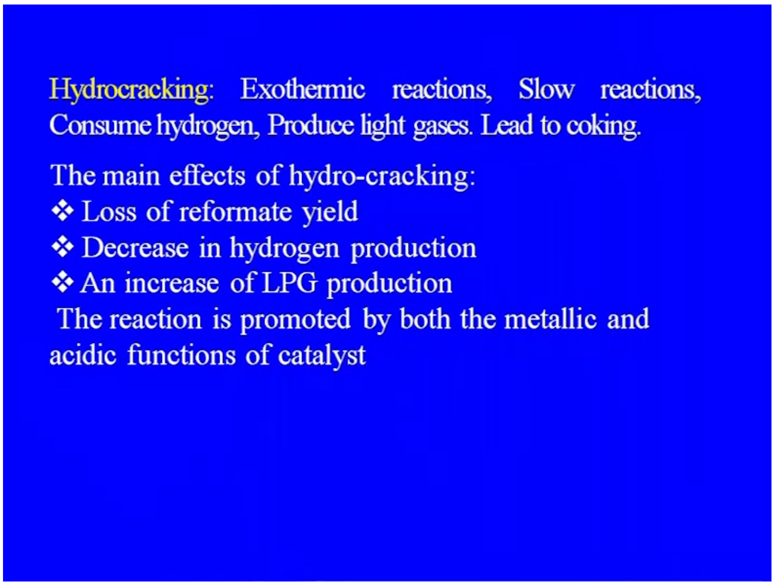

Hydrocracking: Exothermic reactions, Slow reactions, Consume hydrogen, Produce light gases. Lead to coking.

The main effects of hydro-cracking:

❖ Loss of reformate yield
❖ Decrease in hydrogen production
❖ An increase of LPG production

The reaction is promoted by both the metallic and acidic functions of catalyst

The main effects of the hydro-cracking loss of the reformate yield, decrease in the hydrogen production and increase of the LPG production the reaction is promoted by both metallic and acidic function of the catalyst. Now, let us discuss about the, what are the process variables in case of the catalytic reforming? Because this is very important part in case of the catalytic reforming or any reaction the operating condition that has to be maintain properly to have the optimum yield. So, here the some of the major parameters which affecting the reform material or the quality of the reformat octane number, reformate.

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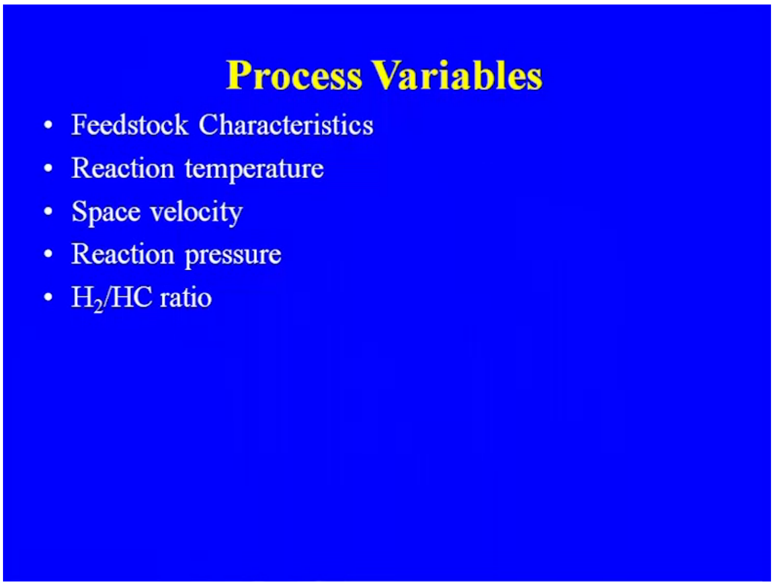

Process Variables

- Feedstock Characteristics
- Reaction temperature
- Space velocity
- Reaction pressure
- H_2/HC ratio

First is the feed characteristic, reaction temperature, space velocity, reaction pressure, hydrogen 2 hydro carbon ratio.

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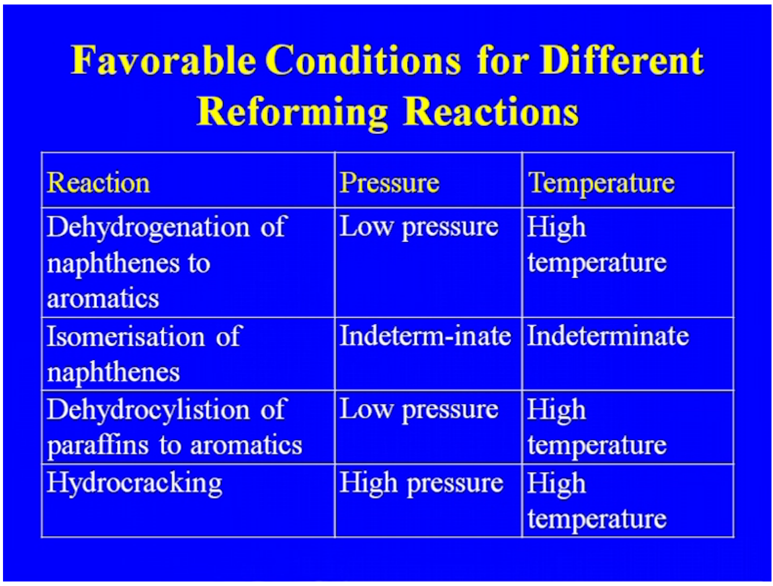

Favorable Conditions for Different Reforming Reactions

Reaction	Pressure	Temperature
Dehydrogenation of naphthenes to aromatics	Low pressure	High temperature
Isomerisation of naphthenes	Indeterm-inate	Indeterminate
Dehydrocylistion of paraffins to aromatics	Low pressure	High temperature
Hydrocracking	High pressure	High temperature

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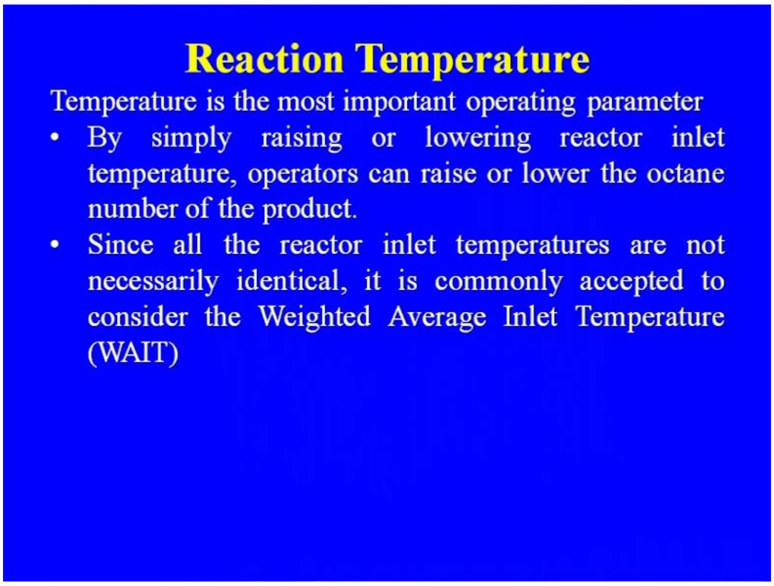

Reaction Temperature

Temperature is the most important operating parameter

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

These are the actually the, I was telling about the favorable condition of the operating parameters which are there, dehydrogenation of the naphthenes to aromatics, low pressure, high temperature that is required. High temperature means not more than if you are going beyond 500 to 510. Then other side reactions that will be more predominate will predominate and the formation of the coke is there, isomerization of the naphthenes determinate, indeterminate, dehydro cylisation of the paraffins, low Pressure, high temperature, hydro-cracking, high pressure and the high temperature.

Reaction temperature; reaction temperature is the most important operating parameter what is happening? By simply raising or lowering the reactor inlet temperature, operators can raise or lower the octane number of the product. But at the same time if we are going for the higher temperature then the loss of the reformate will be there. Since all the reactor inlet temperature are not necessarily identical, it is commonly accepted to consider the weighted average inlet temperature.

Feed quality; feed quality that is very important and depending upon pressure we are operating the reformer and the gasoline more or we are operating on the aromatic. Because if again in case of the aromatic production whether we are interested only in benzene whether we are interested if in parazylene, accordingly you will have to take the feed quality the naphtha which was there if the you are going for the aromatic of the whole range. Then you will have to take the 90 plus to, because you see the boiling point of the benzene is around 90, toluene around 110 and the xylene is that is 136 to 140 degree centigrade. So, depending upon the requirement you will have to adjust the feed quality and the type of the naphtha which you are taking.

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Feed Quality

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

N = Naphthenes %A = Aromatics %

So, naphthenes dehydrogenate very fast and give rise to. Therefore, N plus 2, 2 A is taken as index of reforming. Higher the N plus 2 A, naphthenes and aromatic higher the

N plus 2 A better is the quality to produce high aromatics N is the naphthenes, A is the aromatic that has been co related with the characterization factor also, because the characterization factor is also giving idea of the whether if the feed is the naphthene or the paraffinic or intermediate.

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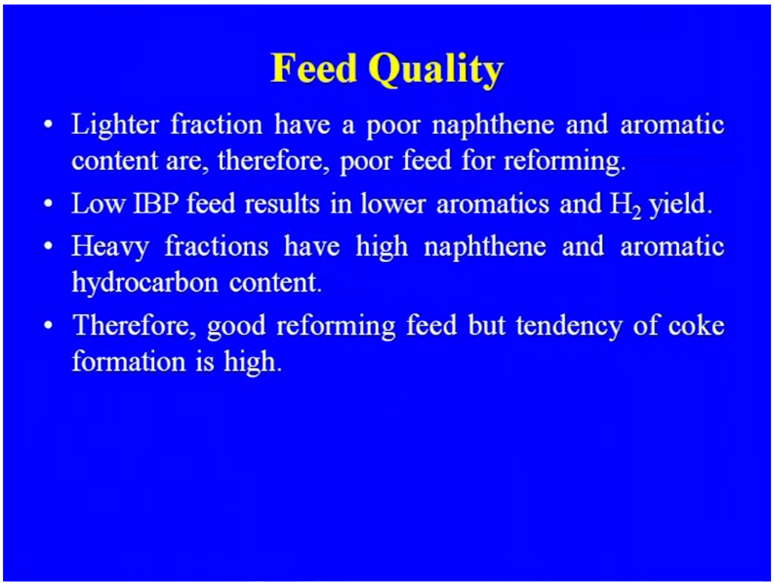

Feed Quality

- Lighter fraction have a poor naphthene and aromatic content are, therefore, poor feed for reforming.
- Low IBP feed results in lower aromatics and H_2 yield.
- Heavy fractions have high naphthene and aromatic hydrocarbon content.
- Therefore, good reforming feed but tendency of coke formation is high.

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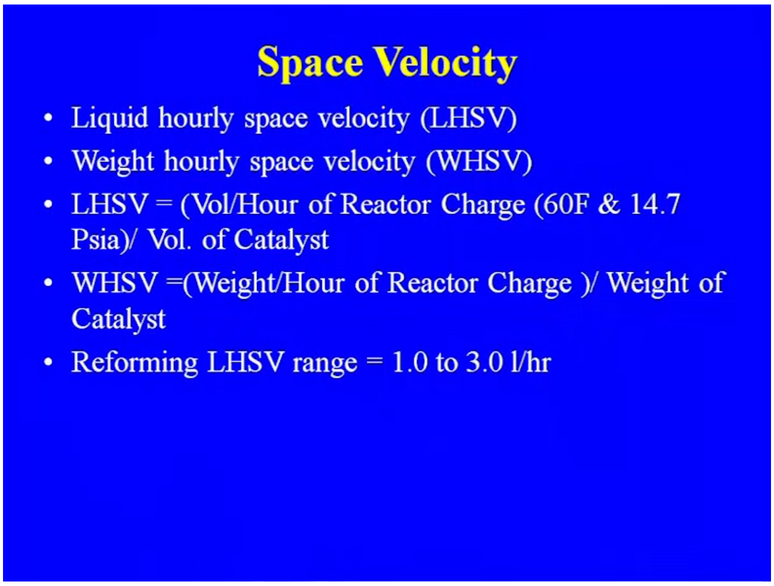

Space Velocity

- Liquid hourly space velocity (LHSV)
- Weight hourly space velocity (WHSV)
- LHSV = (Vol/Hour of Reactor Charge (60F & 14.7 Psia)/ Vol. of Catalyst
- WHSV =(Weight/Hour of Reactor Charge)/ Weight of Catalyst
- Reforming LHSV range = 1.0 to 3.0 l/hr

So, about the feed quality I was telling the lighter fraction have a poor naphthene and aromatic content are higher. Therefore, poor feed for the reforming, low IBP feed results in lower aromatics and hydrogen yield. Heavy fraction have high naphthene and aromatic hydro carbon content. Therefore, good reforming feed, but tendency of the coke formation is high so that is why this heavy fraction is also not accepted. So, temperature I was telling about the temperature, already we have discuss about the temperature part space velocity, because these are the two terms. Normally, we are using in case of the space velocity; one is the liquid hourly velocity and this is the weight hourly velocity.

And this is the actually the, how the LHSV liquid hourly velocity in weight hourly velocity volume up on hour of the reactor charge divide in volume of the catalyst. And weight hour of the reactor charge divided by the volume weight of the catalyst, reforming LHSV should be in the range of 1.2 3.0.

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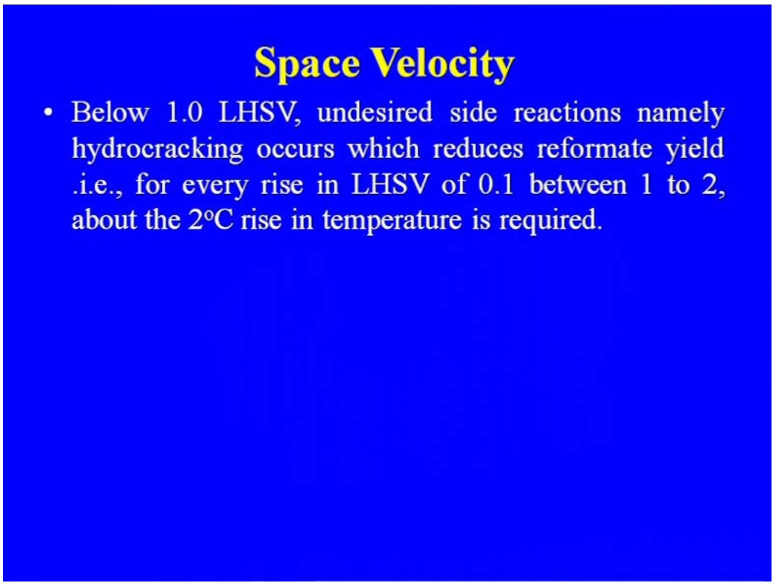

Space Velocity

- Below 1.0 LHSV, undesired side reactions namely hydrocracking occurs which reduces reformate yield .i.e., for every rise in LHSV of 0.1 between 1 to 2, about the 2°C rise in temperature is required.

So, below 1.0 LHSV, undesired side reaction namely hydro cracking occurs which reduces reformate yield, for every rise in the LHSV 0.1 between 1 to 2, about the 2 degree centigrade in the temperature is required. The lower the space velocity, the higher the severity assuming all other condition change, as I told you the, the rise in the temperature that will 2 degree raise in the temperature. So, lowering the space velocity has the same effects as increasing the temperature, increase the octane decrease the product yield, decrease the hydrogen purity increase the coke deposit.

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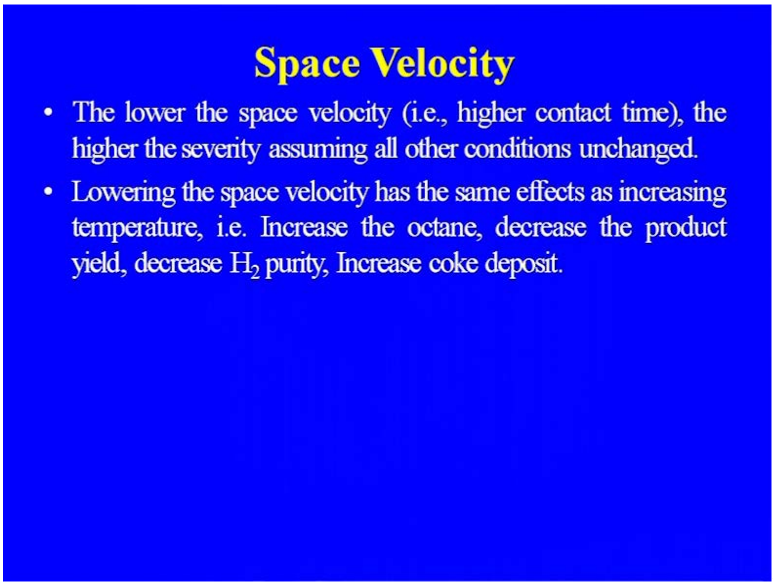

Space Velocity

- The lower the space velocity (i.e., higher contact time), the higher the severity assuming all other conditions unchanged.
- Lowering the space velocity has the same effects as increasing temperature, i.e. Increase the octane, decrease the product yield, decrease H_2 purity, Increase coke deposit.

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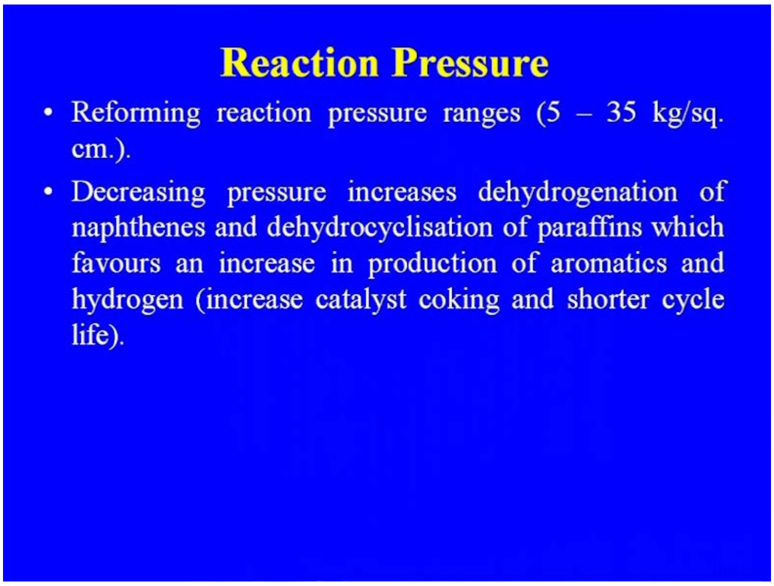

Reaction Pressure

- Reforming reaction pressure ranges (5 – 35 kg/sq. cm.).
- Decreasing pressure increases dehydrogenation of naphthenes and dehydrocyclisation of paraffins which favours an increase in production of aromatics and hydrogen (increase catalyst coking and shorter cycle life).

Reaction pressure; this is the pressure normally we are maintaining. Decreasing the pressure increases the de hydrogenation of the naphthene and de-hydro cyclisation of the paraffins which favors a, an increase in the production of the aromatics and hydrogen increase catalyst coking and shorter cycle life.

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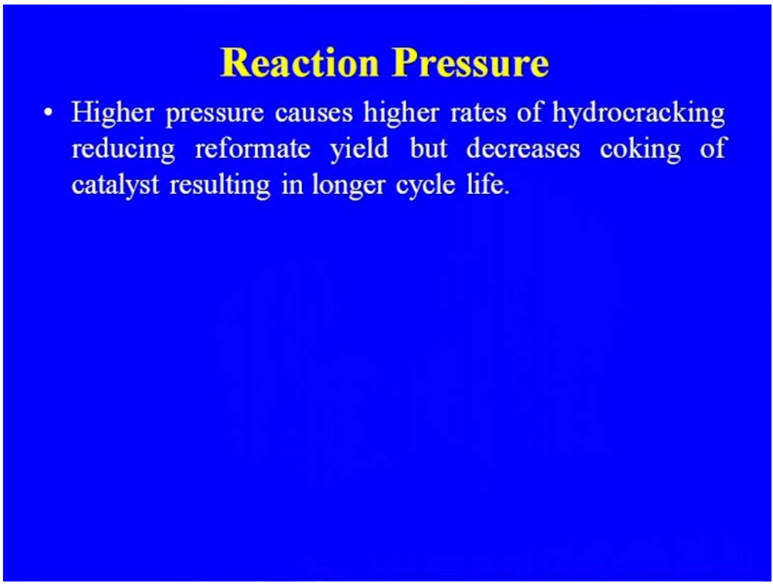

Reaction Pressure

- Higher pressure causes higher rates of hydrocracking reducing reformate yield but decreases coking of catalyst resulting in longer cycle life.

Higher pressure causes higher rates of hydro-cracking reduces the reformate yield, but decreases the coking of the catalyst resulting in the longer life. So again we will have to take a optimal condition in case of the, because some reactions are favored some reaction are not favored by the pressure.

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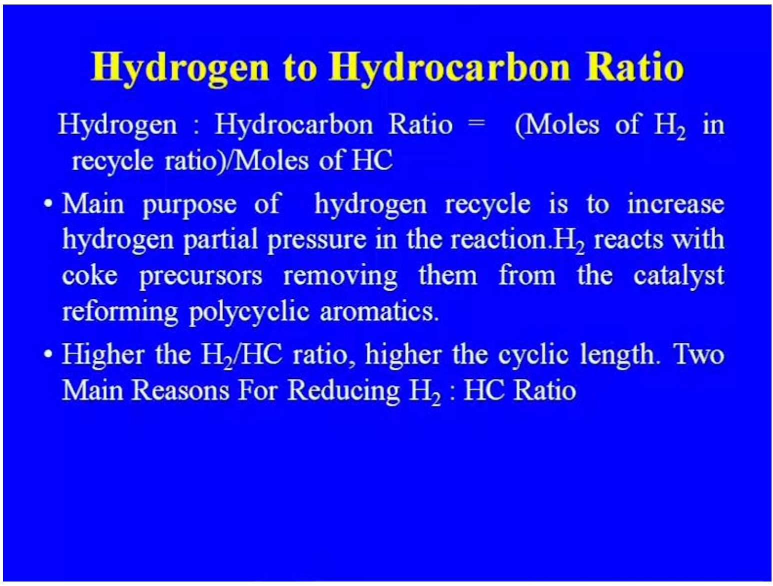

Hydrogen to Hydrocarbon Ratio

Hydrogen : Hydrocarbon Ratio = (Moles of H_2 in recycle ratio)/Moles of HC

- Main purpose of hydrogen recycle is to increase hydrogen partial pressure in the reaction.H_2 reacts with coke precursors removing them from the catalyst reforming polycyclic aromatics.
- Higher the H_2/HC ratio, higher the cyclic length. Two Main Reasons For Reducing H_2 : HC Ratio

Hydrogen to hydrocarbon ratio that is very important actually in case of the catalytic reforming process. And this is defined by the hydrogen hydrocarbon ratio moles of hydrogen in the recycle divided by the moles of the hydrocarbon. Main purpose of the hydrogen recycle is to increase the hydrogen partial pressure in the reaction. Hydrogen reacts with the coke precursor removing them from the catalyst reforming polycyclic aromatics. Higher the hydrogen 2 hydrocarbon ratio, higher the cyclic length, two main reaction for reducing hydrogen and hydrocarbon ratio.

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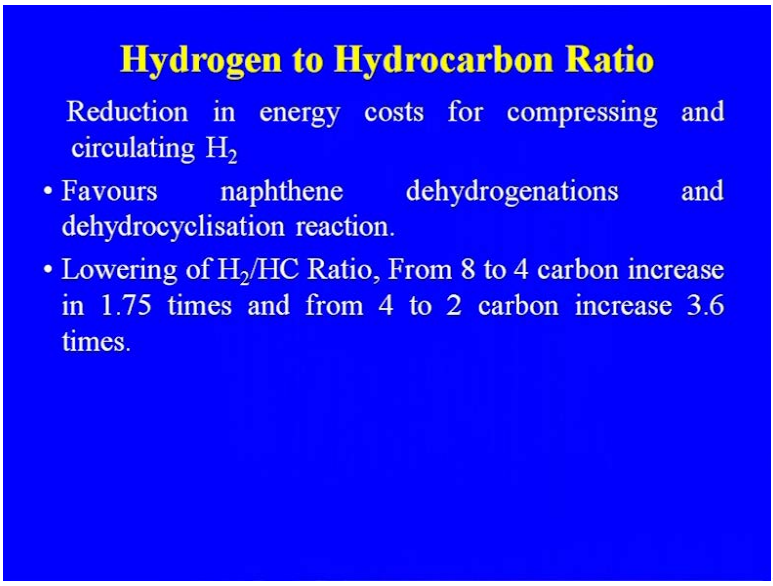

Hydrogen to Hydrocarbon Ratio

Reduction in energy costs for compressing and circulating H_2

- Favours naphthene dehydrogenations and dehydrocyclisation reaction.
- Lowering of H_2/HC Ratio, From 8 to 4 carbon increase in 1.75 times and from 4 to 2 carbon increase 3.6 times.

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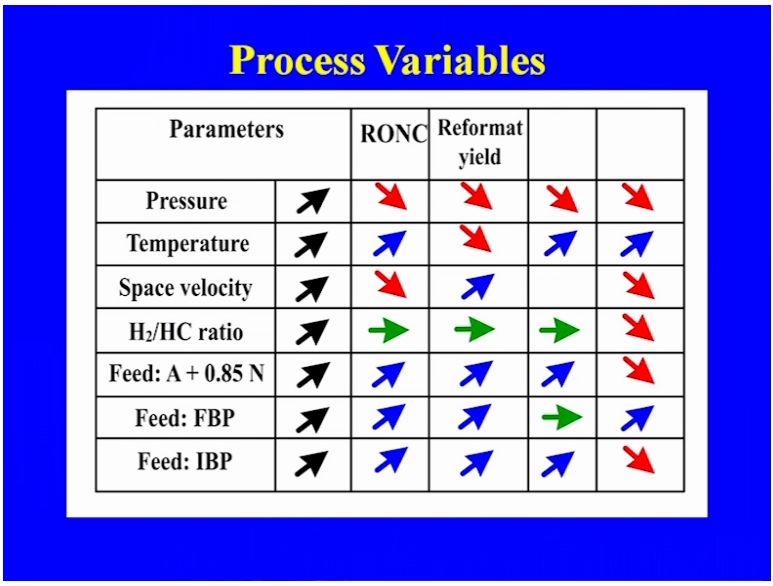

Process Variables

Parameters		RONC	Reformat yield		
Pressure	↗	↘	↘	↘	↘
Temperature	↗	↗	↘	↗	↗
Space velocity	↗	↘	↗		↘
H_2/HC ratio	↗	→	→	→	↘
Feed: A + 0.85 N	↗	↗	↗	↗	↘
Feed: FBP	↗	↗	↗	→	↗
Feed: IBP	↗	↗	↗	↗	↘

This is also another effect of hydrogen to hydrocarbon ratio, reduction in the energy costs for compressing and recirculating hydrogen. Favours naphthene de-hydrogenation and de hydrocyclisation reaction. Lowering hydrogen and hydrocarbon ratio from 8 to 4 carbon increase in the 1.75 time and from 4 to 2 carbon increase at 3.6 time.

This is the process variables which we discussed, just to summarize the effect of pressure increasing or decreasing on the, what is the effect of the pressure, temperature, space velocity, hydrogen 2, hydrocarbon ratio, feed A plus 0.5 N, final boiling point and the initial boiling point of the feed. And depending upon that the research octane number, if the pressure increasing the pressure that will decrease, increasing the temperature that will increase space velocity that it will decrease the octane number if you are increasing. So, this is the how the effect of the various parameter which we discussed earlier. Similarly, in case of the reformate yield also we can see the fewer increasing the temperature means beyond the optimum temperature.

Then the, you will be losing useful material means the deform material, there will be deduction in the deform material. Hydrogen yield that will be also affected by the various operating parameter coke formation that is as I told you that is the, if you are decreasing then the more, coke formation.

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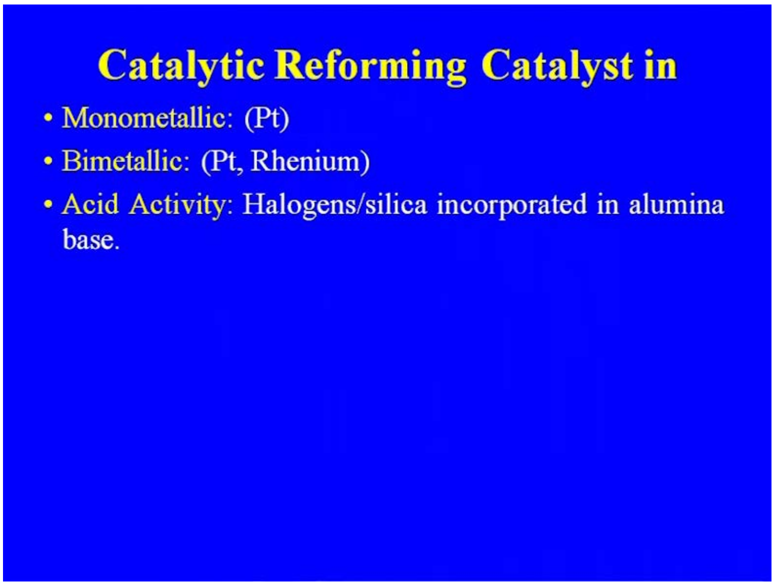

Catalytic Reforming Catalyst in

- Monometallic: (Pt)
- Bimetallic: (Pt, Rhenium)
- Acid Activity: Halogens/silica incorporated in alumina base.

Temperature increase, again the more coke formation and the, these are the some other parameter which affect the coke deposit. Now, let us discuss, because as I told you there has been continuous development in the catalytic reforming, because there has been changes in the quality of the naphtha. And at the same time requirement of the octane number gasoline, requirement of the even the aromatics whether even it is if a parazylene whether it is have been more aromatics like that. And so depending upon that the there has been continuous development in the catalytic reforming catalyst and indigenous catalyst also that has been developed. So, the catalyst are monometallic, bimetallic acid activity that is the halogens silica incorporated in alumina base they give the acid.

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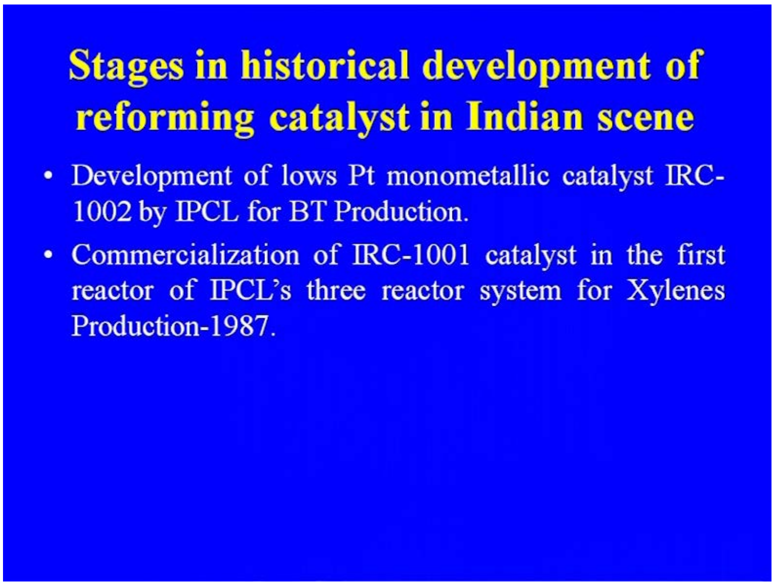

Stages in historical development of reforming catalyst in Indian scene

- Development of lows Pt monometallic catalyst IRC-1002 by IPCL for BT Production.
- Commercialization of IRC-1001 catalyst in the first reactor of IPCL's three reactor system for Xylenes Production-1987.

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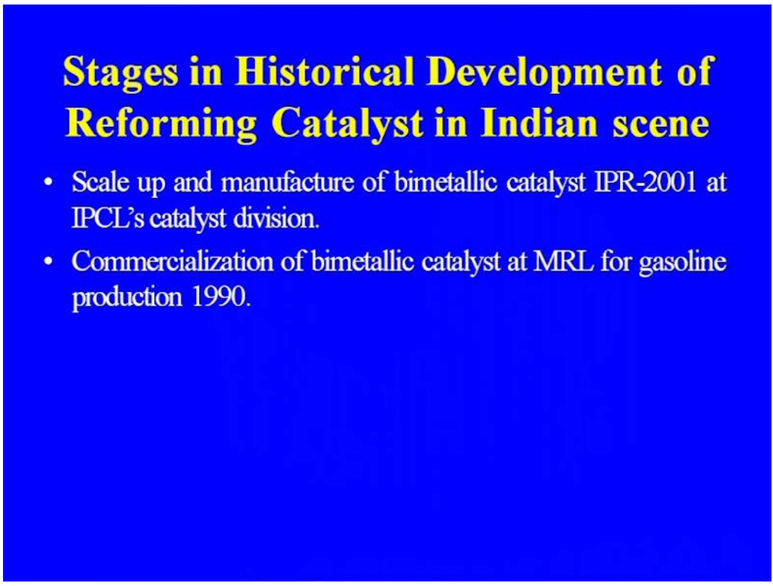

Stages in Historical Development of Reforming Catalyst in Indian scene

- Scale up and manufacture of bimetallic catalyst IPR-2001 at IPCL's catalyst division.
- Commercialization of bimetallic catalyst at MRL for gasoline production 1990.

Because in both the acid and metal function of the catalyst, they are having the different role, stages in the historical development, the reforming catalyst in Indian scene development of the low platinum monometallic catalyst that was first IPCL. Now, it is reliance for the benzene toluene production, commercialization of IRC 101 catalyst in the first reactor of the IPCL three reactor system of the xylene production.

Scale up and manufacture of IPR 2001 at IPCL catalyst division, commercialization of the bimetallic catalyst at MRPL for gasoline production, commercialization of the bimetallic catalyst, and solid. Now, let us discuss the two function which was telling in case of the catalytic reforming, catalyst metallic function and the acid function and each function they have different role in the catalytic reforming action.

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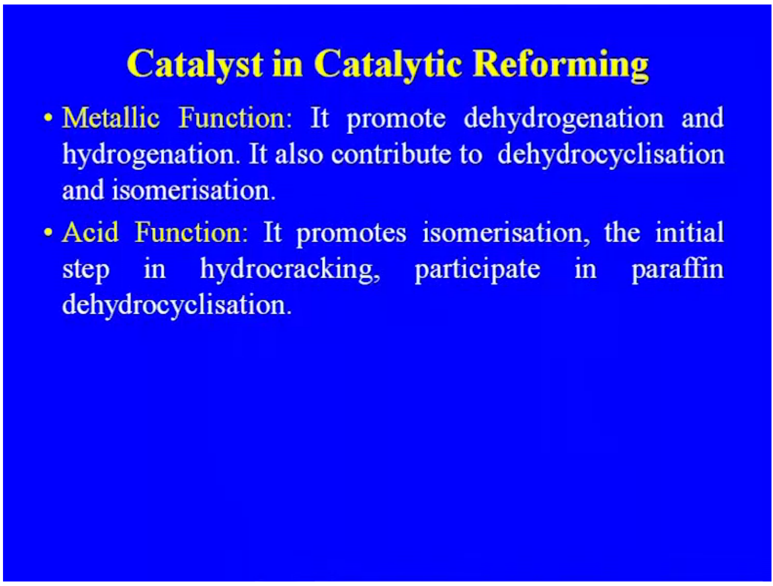

Catalyst in Catalytic Reforming

- Metallic Function: It promote dehydrogenation and hydrogenation. It also contribute to dehydrocyclisation and isomerisation.
- Acid Function: It promotes isomerisation, the initial step in hydrocracking, participate in paraffin dehydrocyclisation.

So, metallic function; it promote the de-hydrogenation and the hydrogenation reaction, it also contributed to the hydrocyclisation and isomerisation. Acid function; It promotes isomerization, the initial steps in the hydro cracking participate in the paraffin dehydrocyclisation. Advantage; what are the advantage, why we have gone for the bimetallic or the multi metallic catalyst? Enhance the resistance to coke as I told you now the catalyst have been developed, they should have more and more resistance towards coke more resistance towards the sulphur compound.

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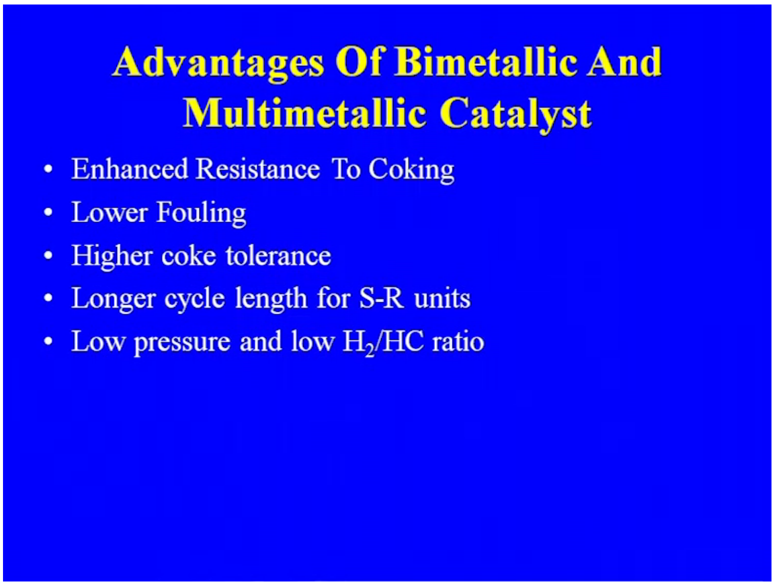

Advantages Of Bimetallic And Multimetallic Catalyst

- Enhanced Resistance To Coking
- Lower Fouling
- Higher coke tolerance
- Longer cycle length for S-R units
- Low pressure and low H_2/HC ratio

Lower fouling, high, higher coke tolerance, longer cycle length for your reforming units slope ratio and low hydro carbon ratio, because that is also if you are increasing hydrogen then the other your operating cost that is increasing.

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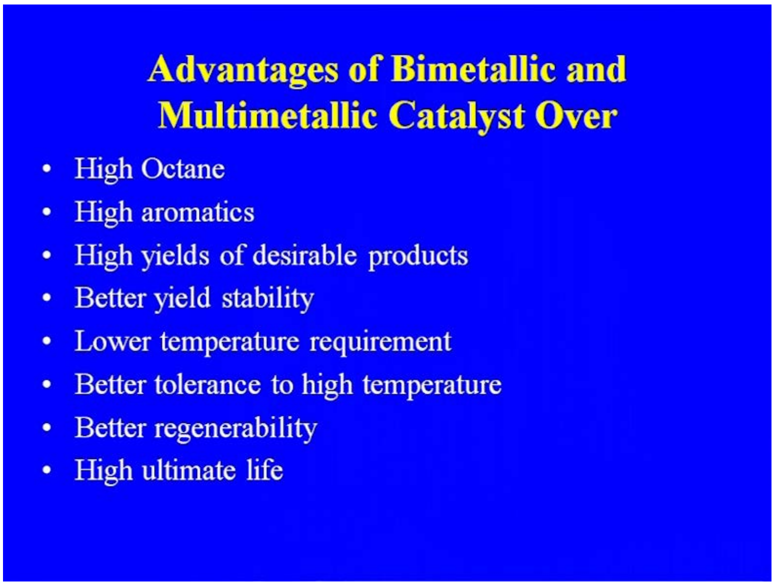

Advantages of Bimetallic and Multimetallic Catalyst Over

- High Octane
- High aromatics
- High yields of desirable products
- Better yield stability
- Lower temperature requirement
- Better tolerance to high temperature
- Better regenerability
- High ultimate life

So, these are the some of the advantages just to summarize high octane, high aromatics, high yields of the desirable products, better yield stability, lower temperature requirement, better tolerance to high temperature, better regenerability and high ultimate life.

Now, let us discuss about the some one more, one two slides on the catalyst poison, because the catalyst poisoning that affect the whole working of the any reaction system. So, we are having in case of the naphtha, we are having the 2 types of the poisons, catalyst poison not only in case of the catalytic reforming by any reaction we are having the two types of the poison.

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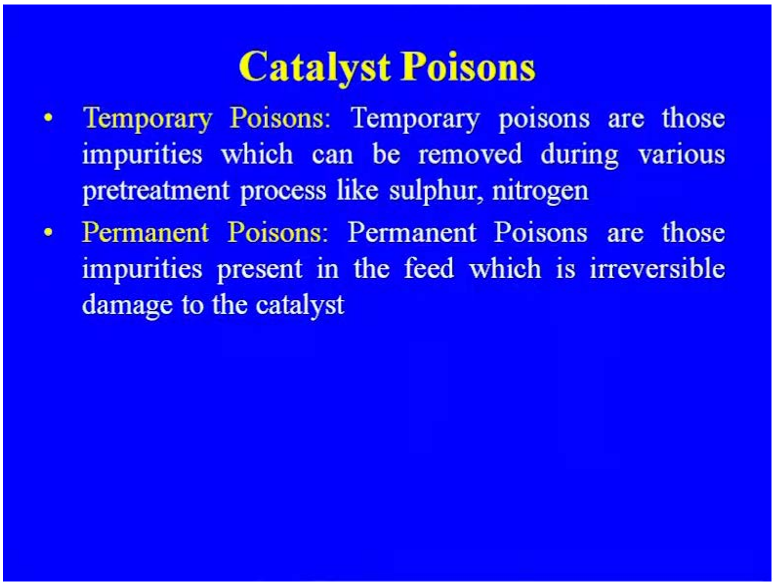

Catalyst Poisons

- **Temporary Poisons:** Temporary poisons are those impurities which can be removed during various pretreatment process like sulphur, nitrogen
- **Permanent Poisons:** Permanent Poisons are those impurities present in the feed which is irreversible damage to the catalyst

One is the temporary poisons are those impurities which can be removed during the various pretreatment process like sulphur, nitrogen and some of the metal. Now, the, we have the catalyst which we are having metal removal is also taking place. Permanent poisons; permanent poisons are those impurities present in the feed which is irreversible damage to the catalyst. So, that is the reason why the maximum removal of the metals that has to be there.

These are the actually the various maximum level of the catalyst poison; arsenic, lead, copper, mercury. And so this is the, from where various sources from where these are coming that. Then we from the cracked naphtha, recycled, corrosion, naphtha condensate, corrosion, then the foaming additives corrosion, corrosion. And so the, this will be the actually, but this is the maximum level that is required in case of the. So, this was about the catalytic reforming process, which is being used in case of the refinery and that is one of the very important process.

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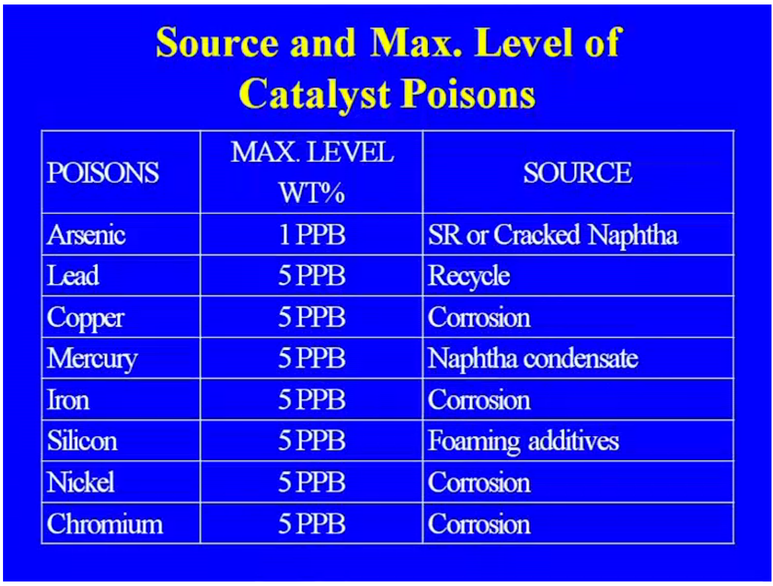

Source and Max. Level of Catalyst Poisons

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

Another development that has taken place in case of the refinery, that is the, just to improve the quality of the naphtha the, to have the higher gasoline that was the actually isomerization alkylation and the process. So, in the next lecture, will be discussing about the more alkylation process, isomerization process and the polymerization which also actually it is the not the actual polymerization. So, there should not be any confusion.