Organic Chemical Technology
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Lecture – 21
Petroleum Refinery Processes-2

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is petroleum refinery processes part 2.

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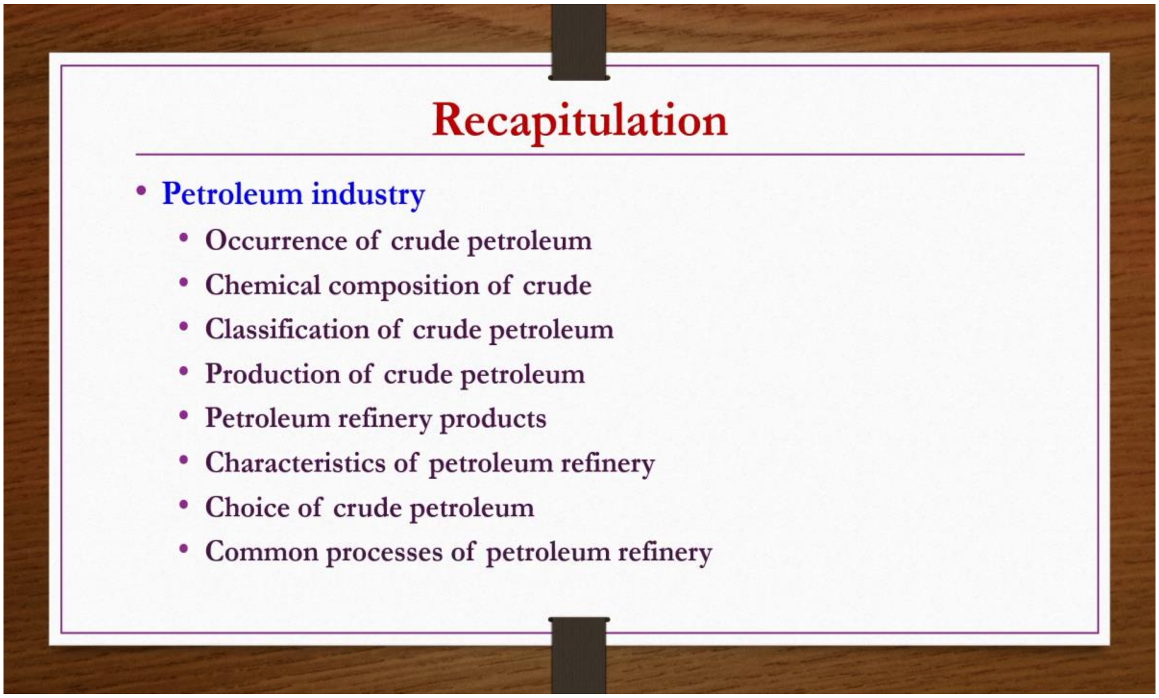

Recapitulation

- Petroleum industry
  - Occurrence of crude petroleum
  - Chemical composition of crude
  - Classification of crude petroleum
  - Production of crude petroleum
  - Petroleum refinery products
  - Characteristics of petroleum refinery
  - Choice of crude petroleum
  - Common processes of petroleum refinery

First we will have recapitulation of what we have discussed in last 3 lectures on petroleum industry. We started with a brief introduction of petroleum industry. We discussed occurrence of crude petroleum, how does it occur, chemical composition of crude petroleum, classification of crude petroleum, what are the different types of products possible by fractionating the crude petroleum, what are the petroleum refinery products etc., those things we have discussed.

Then characteristics of petroleum refinery, we discussed choice of crude petroleum, how to select a particular crude based on the product spectrum or distribution of the products that you are having because from the petroleum crude you are not going to get one single product, you are going to have a number of products as we have already discussed in a complex flow chart of a given petroleum refinery process.

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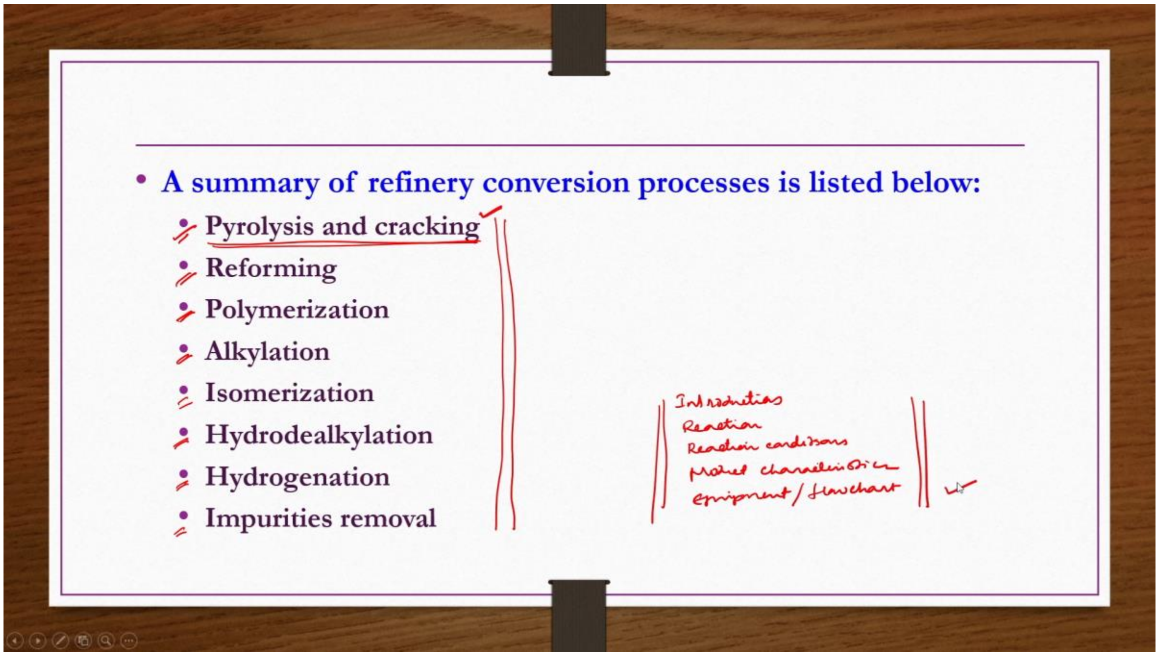

- A summary of refinery conversion processes is listed below:
  - Pyrolysis and cracking
  - Reforming
  - Polymerization
  - Alkylation
  - Isomerization
  - Hydrodealkylation
  - Hydrogenation
  - Impurities removal

Introduction
Reaction
Reaction conditions
Product characteristics
equipment / flowchart

Finally, we discussed common processes of petroleum refinery which are listed below here they include pyrolysis and cracking, reforming, polymerization, alkylation, isomerization, hydrodealkylation, hydrogenation and impurities removal. Actually in the petrochemical production or in the petroleum refinery processes, these conversion processes are very very essential. Pyrolysis and cracking often occur, reforming you do for a given particular purpose, polymerization.

In the case of a petroleum industry, polymerization does not mean that you are forming very big molecules or high molecular weight polymers, it is not like that you take a smaller olefins and then try to form their dimers or trimers so that you know octane number of the final product will increase because of such dimer and trimers of olefins. Alkylation is also important because when you do the alkylation, branched paraffins in general form and then branched paraffins have a better octane number compared to the normal paraffins, same is true with the isomerization. Hydrodealkylation is also required, hydrogenation and then impurities removal or all of them are essential from the end product point of view. So, in a given refinery all of them may not be involved, it depends on the type of crude that you have taken and then what are the types of products you are expecting to have. So, depending on that one, some of them or many of them or even all of them also possible if your refinery is very complex refinery as we have discussed in one of the previous lecture, okay? Now, in these aspects, it is essential to know some introductory information about these processes, what are the reactions or reaction mechanisms available or existing, then reaction conditions or variables, process variables, you know, product characteristics.

So, if you have a process and then you have certain kind of products and then what are their characteristics, advantages, benefits, etc. Then equipment required or the flowchart for a given process are very essential to understand for all of them in fact, right? So, in the previous lecture, this particular process pyrolysis and cracking we have already completed where we discussed all of these points. Now, we are going to discuss about remaining of the important refinery conversion processes. For each of them, we are going to discuss the subheadings as well.

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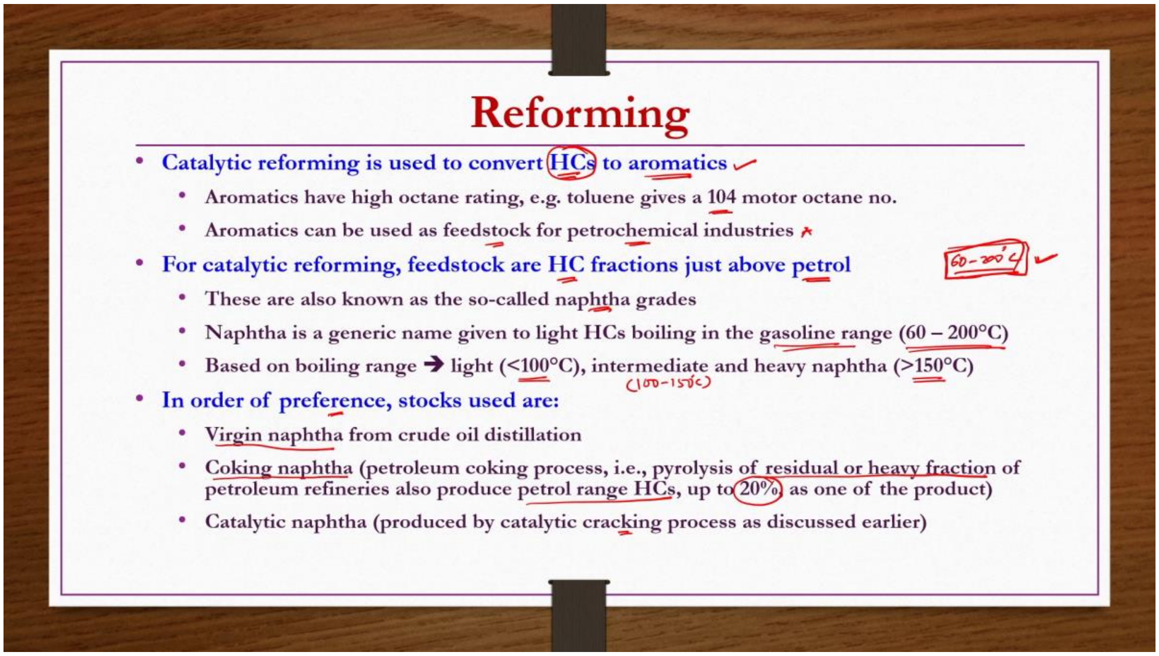

Reforming

- Catalytic reforming is used to convert HCs to aromatics
  - Aromatics have high octane rating, e.g. toluene gives a 104 motor octane no.
  - Aromatics can be used as feedstock for petrochemical industries
- For catalytic reforming, feedstock are HC fractions just above petrol
  - These are also known as the so-called naphtha grades
  - Naphtha is a generic name given to light HCs boiling in the gasoline range (60 – 200°C)
  - Based on boiling range ➔ light (<100°C), intermediate and heavy naphtha (>150°C)
- In order of preference, stocks used are:
  - Virgin naphtha from crude oil distillation
  - Coking naphtha (petroleum coking process, i.e., pyrolysis of residual or heavy fraction of petroleum refineries also produce petrol range HCs, up to 20% as one of the product)
  - Catalytic naphtha (produced by catalytic cracking process as discussed earlier)

60-200°C

(100-150°C)

So, let us start with reforming. Catalytic reforming is used to convert hydrocarbons to aromatics. We see why aromatics formation, what kind of hydrocarbons are required. Aromatics are in general, you know better and then they improve the octane number if they are present in the final petrol product, right? Aromatics have high octane rating. For example, toluene gives 104 motor octane number, right? In addition to that one, aromatics are also used as a feedstock for different types of petrochemical industries, which we are going to discuss subsequently, right? Then what kind of hydrocarbons are used for reforming so that to get aromatics, that is the next question. So, in general, naphtha grade hydrocarbons are used.

For catalytic reforming, feedstock or hydrocarbon fractions just above the petrol or lightens whatever are there. In the lightens primarily you have the petrol, right? There are other components as well as we have already discussed, but primarily it is having petrol. So, that petrol having the mixture of the fraction of hydrocarbons where petrol is dominating, the boiling range may be between 60 to 200 degrees centigrade. So, such fractions are in general considered and these fractions are also known as the naphtha, right? So, naphtha is generic name given to hydrocarbons boiling in the gasoline range like petrol range having 60 to 200 degrees centigrade, right? Again 60 to 200 degrees centigrade is also very wide range. So, because of that one, naphtha can be again intermediate naphtha, light naphtha and heavy naphtha.

It is called as light naphtha if the mixture is boiling at less than 100 degrees centigrade. It is called as heavy naphtha if the hydrocarbons fraction naphtha mixture whatever is there if that boils at more than 150 degrees centigrade. If it boils between 100 to 150 degrees centigrade, then we call it intermediate naphtha, okay? So, what kind of naphtha are used in general? So, in the previous lecture also we have seen like you know pyrolysis of residual refinery waste or heavy ends if you do then also some amount of petrols approximately 20 percent you are getting, right? If you do the fractionation of crude petroleum, then also you get naphtha. So, which one are preferred? So, in the preference order, primarily it is better if you have virgin naphtha from crude oil distillation that we have already discussed in the complex flow chart of the refinery processes. Then coking naphtha is also possible like in the previous lecture we discussed like you know if you do the pyrolysis of residual or heavy fractions of petroleum refineries, they also produce petrol range hydrocarbons and then that may be up to 20 percent by volume percent, right? So, that can also be used as a naphtha for the reforming purpose and then catalytic naphtha can also be used.

Catalytic cracking process when you do there is a possibility that you know naphtha would be you know produced, but this catalytic naphtha in general also contains sufficient quantity of olefins. So, wherever olefins are there we try to avoid them in the petroleum refinery. We do not prefer to have olefins because they try to get polymerized and then form high molecular weight polymers if the process conditions etc. are not properly you know managed or controlled, okay?

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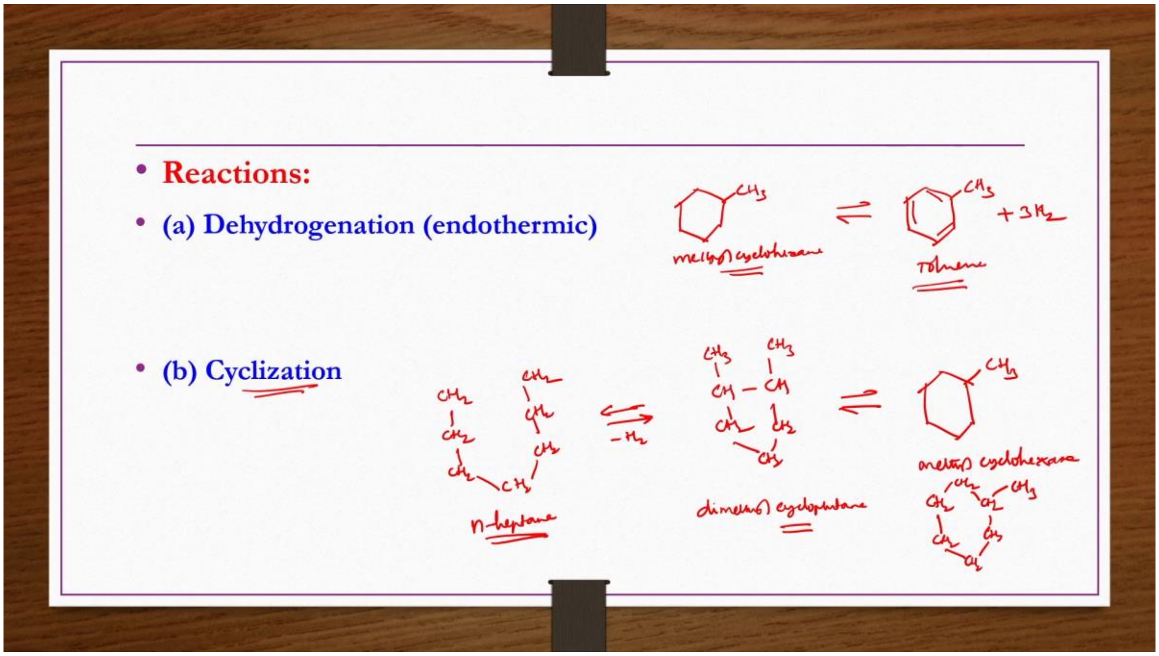

- **Reactions:**
- **(a) Dehydrogenation (endothermic)**
- **(b) Cyclization**

Now, we discuss about the reactions which are common in reforming, right? So, in the reforming of crude petroleum, some of the following reactions are very common. So, one of them is dehydrogenation which is endothermic reaction.

Let us say you have methyl cyclohexane, this is nothing but methyl cyclohexane, 6 carbons are there and there are no double bonds. So, it is a cyclic component, it is not aromatic component, right? It is cyclic but it is not benzene kind of component. So, this methyl cyclohexane if you do the dehydrogenation that is if you try to remove the hydrogen from it, then what you can get? You can get toluene like this plus hydrogen, hydrogen you are removing so obviously that would be there, right? So, now here in the circle I am showing that means alternatively what you are having? You are having double bonds, either way we can represent. Here there are no double bonds, so you get toluene here. This is one type of reaction which is commonly occurring in the catalytic reforming of a crude petroleum or naphtha whatever you have taken.

So, this reaction is known as the dehydrogenation and it is endothermic reaction, it requires lot of energy for the reaction to undergo. Next one is the cyclic reaction. Let us say you have n-heptane. So, let us say CH2 CH2 CH2 you are having and then CH2 CH2

CH2 CH2 actually it is n-heptane linearly we can represent different representations are there. Since we are doing cyclization, so a kind of you know such kind of cyclic kind of form I am you know representing you know here.

So, then if you remove the hydrogen from here then what you get? This is also a reversible reaction you get dimethyl cyclopentane that is CH CH CH2 CH2 and CH2. Now, here to this pentane you have 2 methyl functional groups that is CH3 here CH3 here. So, that is nothing but dimethyl cyclopentane. From the linear component you got the cyclic component. Now, further this reaction may undergo more cyclization to get methyl cyclohexane that is this one.

Methyl cyclohexane. So, this representation this way you can represent or you can represent like this also CH2 CH2 CH2 CH2 CH2 CH2 and then this CH3 here it is there so methyl cyclohexane. So, this is one of the reaction. So, this methyl cyclohexane again undergo dehydrogenation to get the toluene. So, these are the reaction that you know you are not controlling any one of the reaction all these reactions in general they happen in sequence and then the conditions are made such a way that more of dehydrogenation taking place so that you get more of the aromatics.

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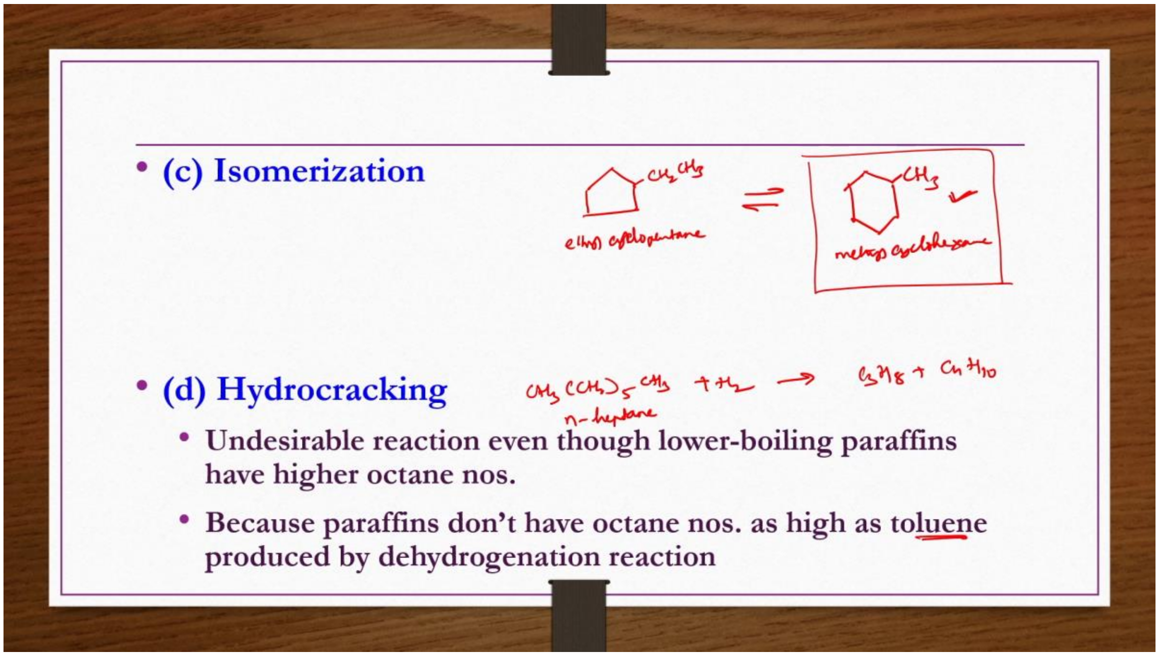

- **(c) Isomerization**
- **(d) Hydrocracking** $CH_3(CH_2)_5CH_3 + H_2 \rightarrow C_3H_8 + C_4H_{10}$

  n-heptane
  - Undesirable reaction even though lower-boiling paraffins have higher octane nos.
  - Because paraffins don’t have octane nos. as high as toluene produced by dehydrogenation reaction

More reactions also possible let us say isomerization. Why isomerization? Because when you do the isomerization whatever the compounds they are formed they will be having more octane number compared to the non-isomeric components. Let us say you have ethyl cyclopentane that is you have this pentane to this one you have CH_2 CH_3 or C_2H_5 directly you can write. So, this is nothing but ethyl cyclopentane. So, now this also reversibly undergoes isomerization reaction to give methyl cyclohexane that is nothing but this one which is there in the previous slide also.

This cyclohexane again can be undergoing dehydrogenation to give the toluene. Then another type of reaction is hydrocracking which is not desirable though what happens when this hydrocracking taking place you get propane and butane. So, propane and butane are also good from the product point of view but their octane number is less than the corresponding aromatics. That is the reason it is less preferred if you are planning for reforming of a naphtha. So, here what kind of reactions you have let us say CH_3 CH_2 5 CH_3 that is n heptane we are having and then when you do the hydrogenation hydrocracking means that you are reacting with hydrogen and then forming smaller molecules from the larger molecules.

So, you get C_3H_8 that is propane and then C_4H_{10} which is nothing but butane and then it is exothermic reaction. So, this is undesirable reaction even though lower boiling paraffins have higher octane numbers because paraffins do not have octane numbers as high as toluene produced by dehydrogenation reaction. So, whatever the addition isomerization reactions also happening such a way that you get a metal cyclohexane kind of components which can further undergo dehydrogenation to get the toluene components.

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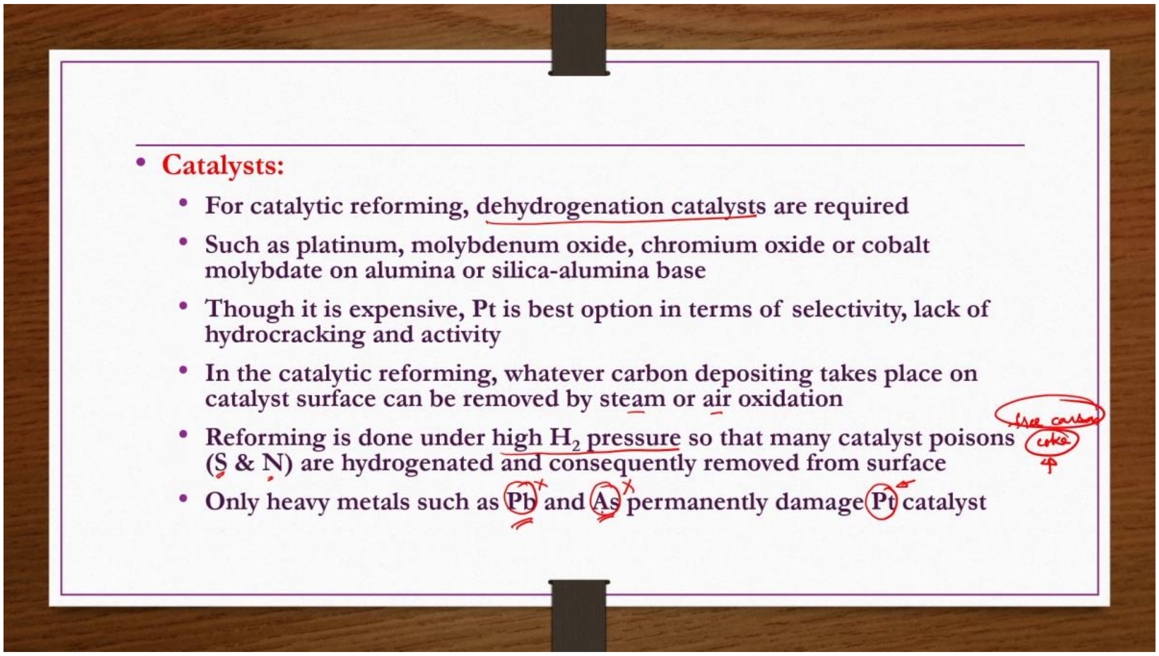

- **Catalysts:**
  - For catalytic reforming, dehydrogenation catalysts are required
  - Such as platinum, molybdenum oxide, chromium oxide or cobalt molybdate on alumina or silica-alumina base
  - Though it is expensive, Pt is best option in terms of selectivity, lack of hydrocracking and activity
  - In the catalytic reforming, whatever carbon depositing takes place on catalyst surface can be removed by steam or air oxidation
  - Reforming is done under high H_2 pressure so that many catalyst poisons (S & N) are hydrogenated and consequently removed from surface
  - Only heavy metals such as Pb and As permanently damage Pt catalyst

free carbon

coke

Catalyst for catalytic reforming of naphtha in general dehydrogenation catalyst are used platinum is the best one for dehydrogenation reaction though it is expensive and there is a coking problem there is a poisoning problem etc. But you have to make sure that you know coking and then other problems are reduced or negligible or regeneration can be done quickly.

If you can manage that one without any high depreciation then platinum is the best catalyst for the most of the petroleum refinery processes. So, here some examples are given platinum molybdenum oxide, chromium oxide or cobalt molybdate supported on alumina or silica alumina support are in general you know preferred. Though it is expensive platinum is best option in terms of selectivity, lack of hydrocracking and activity because you do not want hydrocracking because if you do if the hydrocracking reaction is dominating in the reforming process, then what happens n paraffins should be forming. So n paraffins active number is much less than the aromatics like you know toluene etc. So you do not prefer hydrocracking.

In the catalytic reforming whatever carbon depositing takes place on catalytic surface can be removed by steam or air oxidation. So, in the previous lecture we have discussed you know any of the refinery process you take definitely there would be some free carbon or coke formation. This coke obviously deposit on the catalyst surface if the catalytic reaction is there. So this coke has to be removed from the catalytic surface so that to regenerate the catalytic activity of the whatever the catalyst you have selected and then for that steam or air oxidation process in general used that is very common and there may be some amount of you know poisons like you know sulfur and nitrogen are also possible in the naphtha or in the feedstock. So what you have to do you have to do the reforming under high hydrogen pressure so that these will be converted into the hydrogen sulfide kind of components or amines kind of thing and may be easily separated.

However, if the feedstock is having lead or arsenic kind of metals then they will permanently damage platinum catalyst. So you try to avoid as much as possible in fact rather as much as possible completely you have to make sure that such kind of metals are not present in the feedstock because the catalyst that you are using platinum is the best one and that can be permanently deactivated because of such kind of impurities like lead and arsenic.

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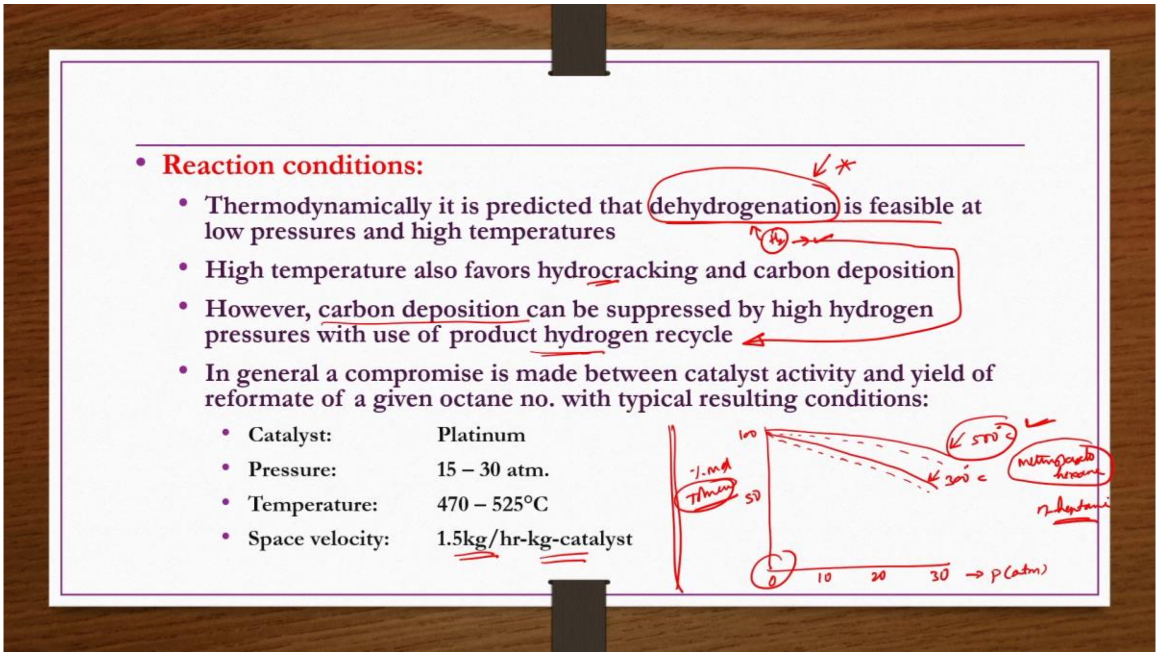

- **Reaction conditions:**
  - Thermodynamically it is predicted that dehydrogenation is feasible at low pressures and high temperatures
  - High temperature also favors hydrocracking and carbon deposition
  - However, carbon deposition can be suppressed by high hydrogen pressures with use of product hydrogen recycle
  - In general a compromise is made between catalyst activity and yield of reformate of a given octane no. with typical resulting conditions:
    - Catalyst: Platinum
    - Pressure: 15 – 30 atm.
    - Temperature: 470 – 525°C
    - Space velocity: 1.5kg/hr-kg-catalyst

Now we discuss about reaction conditions. Thermodynamically it has been found that dehydrogenation is feasible at low pressures and high temperature. Why dehydrogenation only? Because in the reforming process you know when you do the dehydrogenation of the cyclic components it is possible that you can get the aromatics like you know methyl cyclohexane you take and then you can get the toluene.

And toluene is the best option from the octane number point of view so that is the reason thermodynamics have been studied with respect to the dehydrogenation. How to improve the dehydrogenation and then thermodynamically it has been found that low pressures and high temperatures are better one. High temperatures obviously favor the cracking also in this case hydro cracking so carbon deposition will take place. But nevertheless in the dehydrogenation process you are getting you know hydrogen. So this hydrogen can be used to suppress the coke formation because of the hydro cracking.

So carbon deposition can be suppressed by high hydrogen pressure with the use of product hydrogen recycle because in the dehydrogenation or when the reforming process is going on because of the dehydrogenation reaction hydrogen you are getting and then that hydrogen you can utilize to generate a high pressure situation within the reactor so that to suppress the carbon deposition on the catalyst surface. In general a compromise is made between catalyst activity and yield of reformate of a given octane number with a typical resulting condition. Let us say if you have a platinum catalyst then pressure between 15 to 30 atmospheres temperature 470 to 525 degrees centigrade space velocity 1.5 kg per hour of naphtha fed per kg of the catalyst are suitable. Now let us say in the previous slide we have seen different reactions where we try to obtain the toluene.

So mole percent of toluene if you calculate with respect to the pressures 0, 10, 20, 30 like this, this is x axis is pressure in atmospheres. Then yield what happens it is maximum at low pressures and then gradually decreases like this. This is if you maintain the temperature 500 degrees centigrade. It further decreases with pressure if the temperature decreases to 300 degrees centigrade. So that is the reason low pressure high temperatures are better thermodynamically that is has been proved and then these results are experimental results.

The same thing is proved here again. So this is these things are you know if you are using methyl cyclohexane as a reactant to get the toluene. Let us say if you use n-heptane then also possible we have seen n-heptane that you can use from n-heptane you can get the methyl cyclohexane and then that can again be used to get the toluene. So that if you do the trends are same with respect to the temperature pressure trends are same that is low pressure and then high temperatures. But you know in addition to that one yield of toluene would be lesser compared to the feed material you know methyl cyclohexane. If you are using methyl cyclohexane as the base material then more yield of toluene you can get compared to the feed material of n-heptane.

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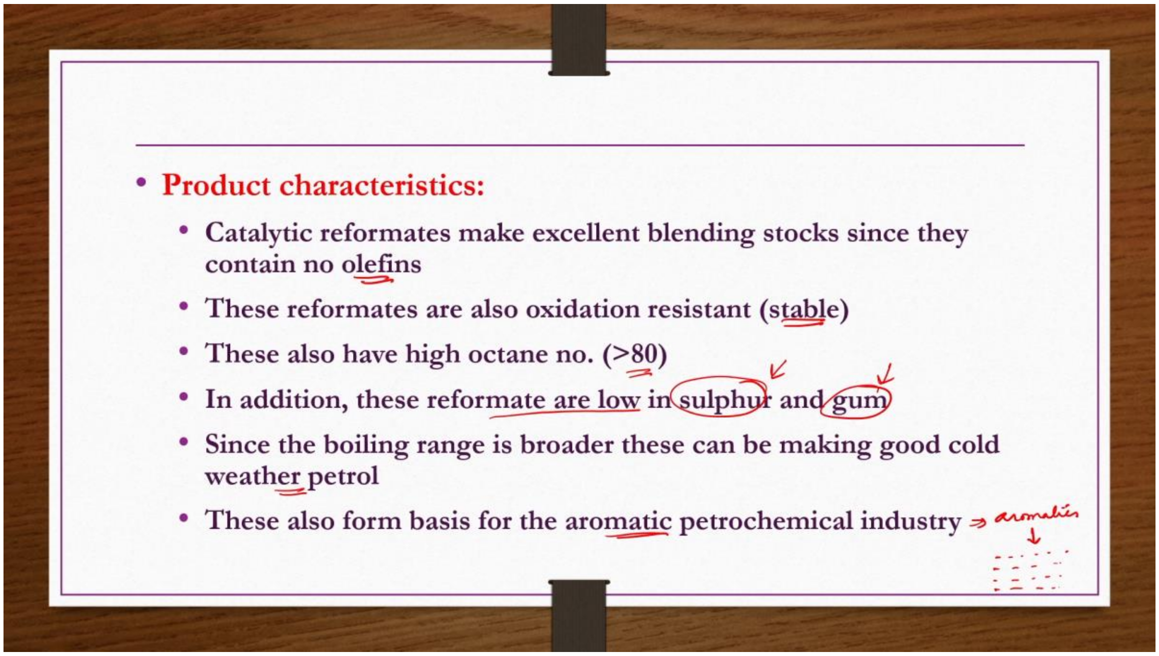

- **Product characteristics:**
  - Catalytic reformates make excellent blending stocks since they contain no olefins
  - These reformates are also oxidation resistant (stable)
  - These also have high octane no. (>80)
  - In addition, these reformate are low in sulphur and gum
  - Since the boiling range is broader these can be making good cold weather petrol
  - These also form basis for the aromatic petrochemical industry ⇒ aromatics ↓

Now coming to the product characteristics, catalytic reformate make excellent blending stocks since they contain no olefins. Olefins we do not want because olefins if they are present and then if you do not maintain or control the process conditions like temperature pressure and contact time properly then they will be forming high molecular weight polymers which is highly undesirable. Forming dimer and trimers are good up to that part polymerization is good but beyond that one it is not good. These reformates are also good oxidation resistance since they are oxidation resistance they are very much stable. These also have high octane numbers at least 80 octane number is possible if you have reformates in the product.

In addition these reformates are low in sulfur and gum. In the purification of end products we are going to see removal of sulfur and then gum these kind of things you know is very essential. So already if these are low so then your purification load will decrease. Since the boiling range is broader these can be making good cold weather petrol as well because the reformate whatever that you produce their boiling range is low it is not very high. These also form basis for the aromatic petrochemical industries whatever the aromatics that you get from those aromatics n number of products you can produce.

Those things we are going to discuss in one of the subsequent chapter anyway with flowchart. So we are not going to discuss those products now.

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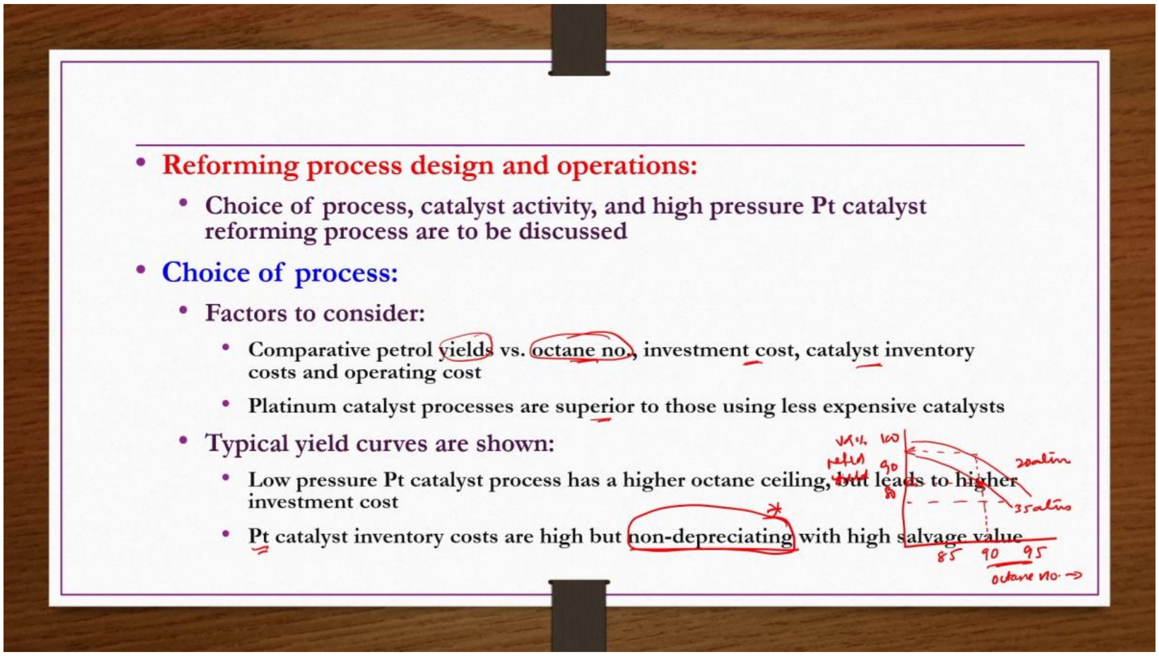

- **Reforming process design and operations:**
  - Choice of process, catalyst activity, and high pressure Pt catalyst reforming process are to be discussed
- **Choice of process:**
  - Factors to consider:
    - Comparative petrol yields vs. octane no., investment cost, catalyst inventory costs and operating cost
    - Platinum catalyst processes are superior to those using less expensive catalysts
  - Typical yield curves are shown:
    - Low pressure Pt catalyst process has a higher octane ceiling, but leads to higher investment cost
    - Pt catalyst inventory costs are high but non-depreciating with high salvage value

Now coming to the reforming process design and operations what are the things that you have to select first as a kind of checklist or criteria for the selection of the process design and operation. The first one is the choice of processes and then you have to select out of the existing processes then catalyst activity and then high pressure platinum catalyst reforming process are essential to be discussed here. So under choice of processes factors to be considered are comparative petrol yields versus octane number is very essential because it is not only the yield but also octane number because some of the petrol fractions they are not much stable and the octane number is also less.

We are going to see in alkylation and in isomerization processes anyway. Such less stabilized petrol with high yields are not good because their octane numbers would be less. Investment cost, catalyst inventory cost, operating cost all these things one has to consider and appropriately one has to choose the process. Platinum catalyst processes are superior wherever this dehydrogenation kind of reactions are taking place. So it should be better to use platinum catalyst even though they are expensive.

Typical yield curves we see now. So let us say you have volume percent of petrol yield which is 80, 90, 100 like this and then against the octane number if you try to plot let us say 85, 90, 95 octane number on x axis. So low pressures usually you know you get the better high octane number high yield you can get but if you increase the pressure so then corresponding in order to maintain the corresponding high octane numbers your yield would be compromised. Let us say you are targeting is 90 octane number product. If you go for the higher pressure then you may get only approximately 85 percent of yield but if you do the same process at 20 atmosphere so then you may get approximately 95 percent yield.

So higher yield you may get. So low pressure platinum catalyst process has a higher octane ceiling but leads to higher investment cost obviously because it is expensive. However, platinum catalyst inventory costs are high but non-depreciating with high salvage value because of this one still you can go for this platinum catalyst even though it is expensive.

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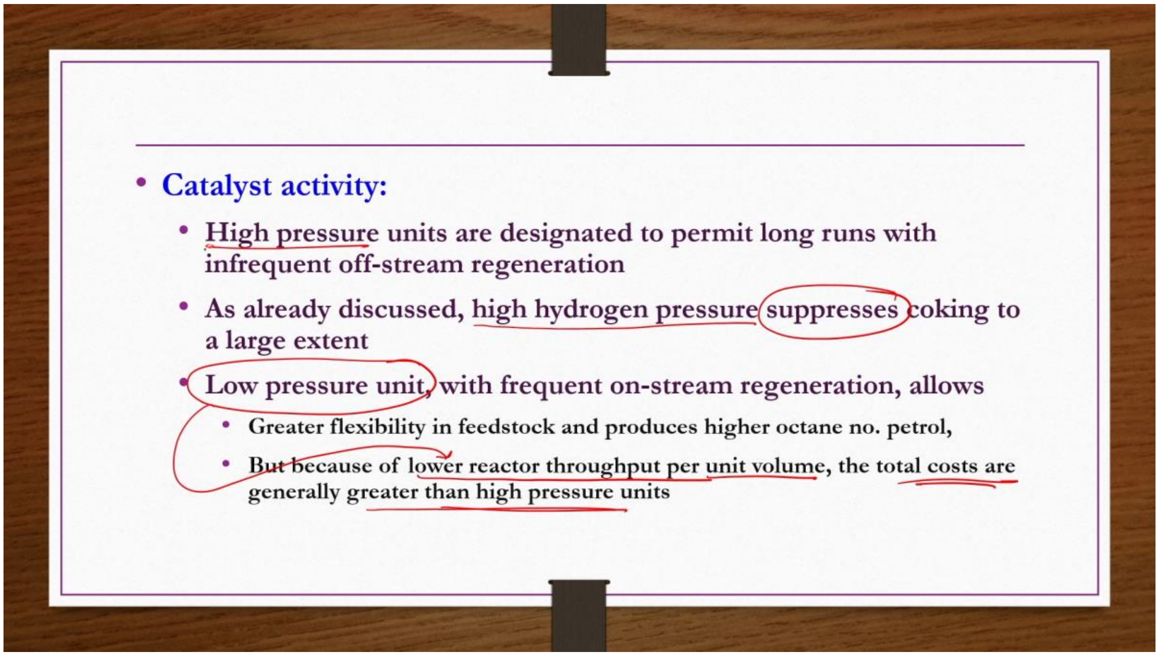

- **Catalyst activity:**
  - High pressure units are designated to permit long runs with infrequent off-stream regeneration
  - As already discussed, high hydrogen pressure suppresses coking to a large extent
  - Low pressure unit, with frequent on-stream regeneration, allows
    - Greater flexibility in feedstock and produces higher octane no. petrol,
    - But because of lower reactor throughput per unit volume, the total costs are generally greater than high pressure units

Catalyst activity high pressure units are designated to permit long runs with infrequent off-stream operations for the regeneration purpose. As we have already discussed under the reaction conditions and then reactions etc. if you have the high hydrogen pressure it will suppress the coking.

So if the coking is suppressed to large extent so then danger of platinum being deactivated is less. Low pressure unit with frequent on stream regeneration allows greater flexibility in stock feedstock and produces higher octane number petrol but because of lower reactor throughput if you use low pressure units then what is the problem your reactor throughput per unit volume would be low. So because of that one total cost in the case of low pressure units are generally greater than high pressure units. So despite of you know having the problems other problems it is better to go for the high pressure units with the upstream regeneration. What do you mean by upstream regeneration? You have to stop the reforming process and then regenerate the catalyst and then restart the reforming process that is cyclic option kind of thing.

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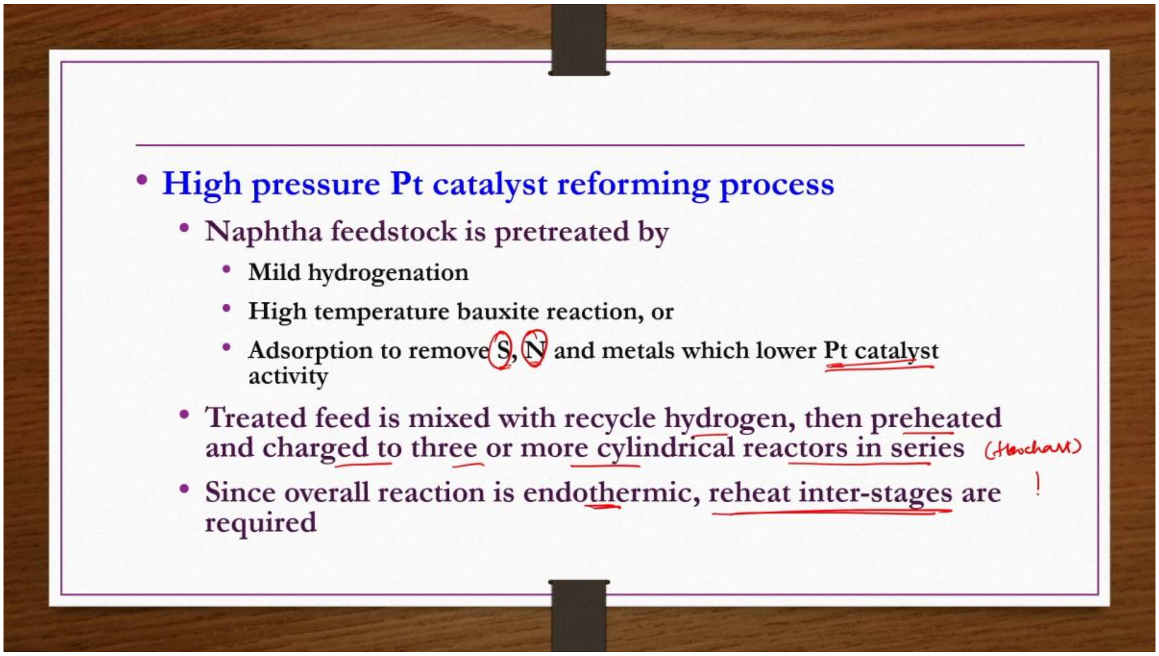

- **High pressure Pt catalyst reforming process**
  - Naphtha feedstock is pretreated by
    - Mild hydrogenation
    - High temperature bauxite reaction, or
    - Adsorption to remove S, N and metals which lower Pt catalyst activity
  - Treated feed is mixed with recycle hydrogen, then preheated and charged to three or more cylindrical reactors in series (flowchart)
  - Since overall reaction is endothermic, reheat inter-stages are required !

Now we discuss high pressure platinum catalyst reforming process. Naphtha feedstock is in general pre-treated before the reforming process. How it can be done? It can be done by the mild hydrogenation or may be treated with high temperature bauxite reaction or by adsorption to remove sulfur, nitrogen and metals which in general lower platinum catalyst activity. So these things should be removed otherwise catalyst reactivity decreases. Treated feed is mixed with recycled hydrogen then preheated and charged to 3 or more cylindrical reactors in series.

We are seeing flow chart in the next slide anyway. So since overall reaction is endothermic reheat inter stages are required.

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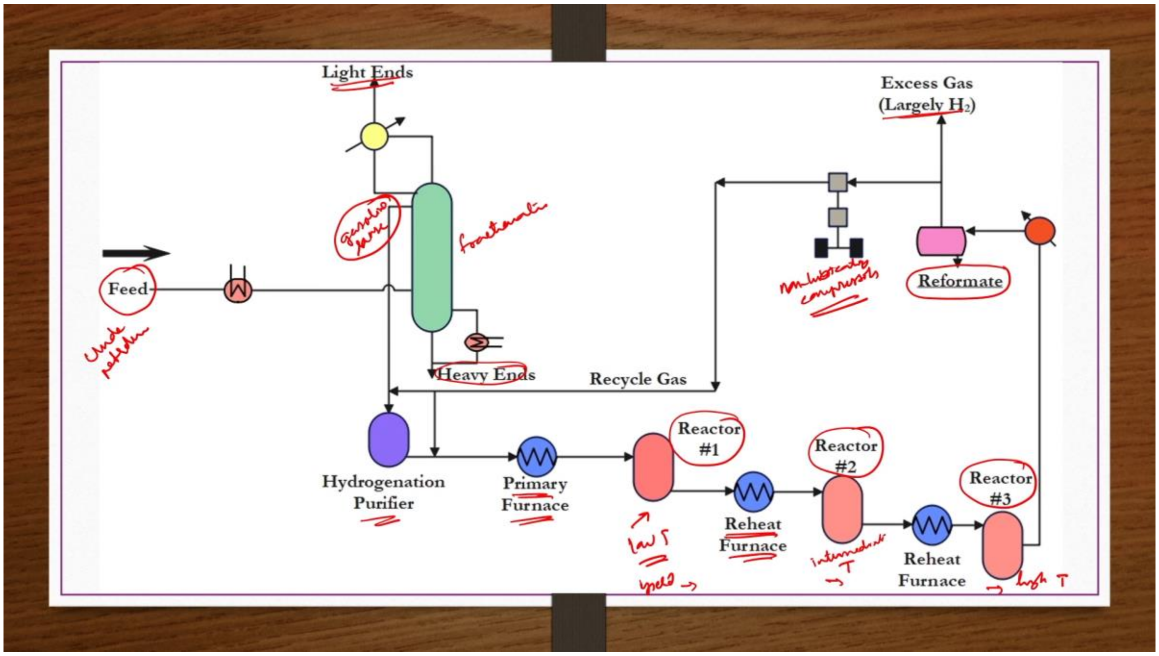

What does it mean that we see in the flow chart in the next slide here. So what you do? You take the feed. What is this feed? This feed is not the naphtha actually whatever the crude petroleum that you have that you take you do the fractionation.

So you separate out the light ends and then heavy ends. Whatever the gasoline range components are there that is naphtha that you take and then pass through hydrogenation purifier. Then pass through a primary furnace then reactor 1, reactor 2, reactor 3 subsequently with reheat furnace because this reactions are endothermic you need to provide the sufficient energy. So rather giving high energy in one reactor itself certain low temperature is maintained in the first reactor then whatever the products are there they would be reheated and then intermediate temperatures are provided in the second reactor and then whatever the products form they would be further reheated to increase the temperature and then high temperatures you know used in the reactor 3. So this is one of the advantage of having cascade kind of or series kind of reactors. Another option is that you know yield increasing yield whatever is there if you have the multiple reactor like this it increases.

If you use only one single reactor the yield may not be sufficiently high enough. So then whatever the final products are there after the reactor 3 they will be collected as a reformate after separation of gases which are largely containing H2. These gases would be compressed purifier and then passed as a recycle gas to the hydrogenation purifier again. So here for this compressing purpose non-lubricating compressors are used. Why because if you use non-lubricating compressors the coke formation would be less and then catalyst deactivation would be less. So typically reforming process you know these are the units operations and unit processes are involved in general.

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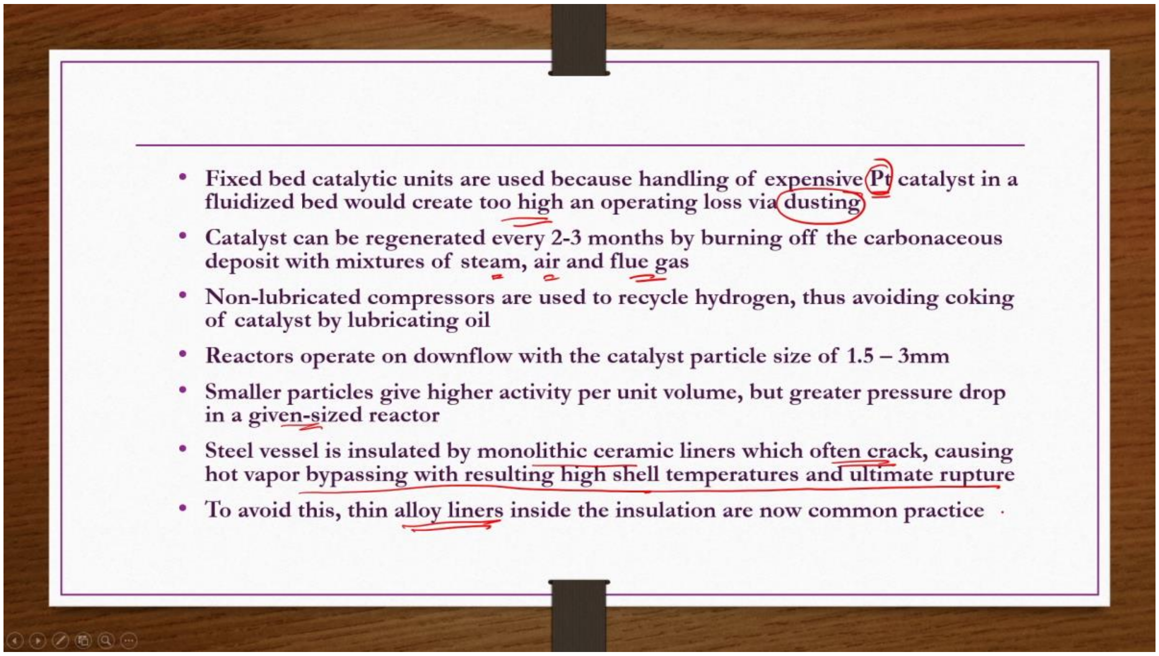

- Fixed bed catalytic units are used because handling of expensive Pt catalyst in a fluidized bed would create too high an operating loss via dusting
- Catalyst can be regenerated every 2-3 months by burning off the carbonaceous deposit with mixtures of steam, air and flue gas
- Non-lubricated compressors are used to recycle hydrogen, thus avoiding coking of catalyst by lubricating oil
- Reactors operate on downflow with the catalyst particle size of 1.5 – 3mm
- Smaller particles give higher activity per unit volume, but greater pressure drop in a given-sized reactor
- Steel vessel is insulated by monolithic ceramic liners which often crack, causing hot vapor bypassing with resulting high shell temperatures and ultimate rupture
- To avoid this, thin alloy liners inside the insulation are now common practice

The details are presented here. Fixed bed catalytic units are used because handling of expensive platinum catalyst in fluidized bed would create too high an operating loss via dusting. Because in the fluidization you have to use some fluid medium to do the required fluidization of the feed material. So for that when you do this one you know whatever the catalyst particles are there they are taken in a granulated form or powder form in general.

So there might be loss of such catalyst because of the dusting while fluidization process is taking place and then you cannot afford dusting losses of a platinum catalyst because it is very very expensive. Catalyst can be regenerated every 2 to 3 months by burning of the carbonaceous deposit with mixtures of steam, air and flue gases which is a standard process. That is when you do the combustion of this deactivated catalyst then whatever the carbonaceous material deposited on the catalyst surface they will be burnt off and then you get CO, CO2 and flue gases etc. leaving behind the catalyst particle without any carbonaceous material.

So after this one regeneration you can reuse the catalyst. Non-lubricated compressors are used to recycle hydrogen thus avoiding coking of catalyst by lubricating oil. Reactors operate on downflow with the catalyst particle size of 1.5 to 3 mm. Smaller particles give higher activity per unit volume but greater pressure drop in a given size reactor that is one problem. Steel vessel is insulated by monolithic ceramic liners which often crack causing hot vapor bypassing with resulting high shell temperatures and ultimate rupture.

So in order to avoid this one thin alloy liners inside the insulations are now a very common practice. This is about the reforming of a naphtha to get a reformates.

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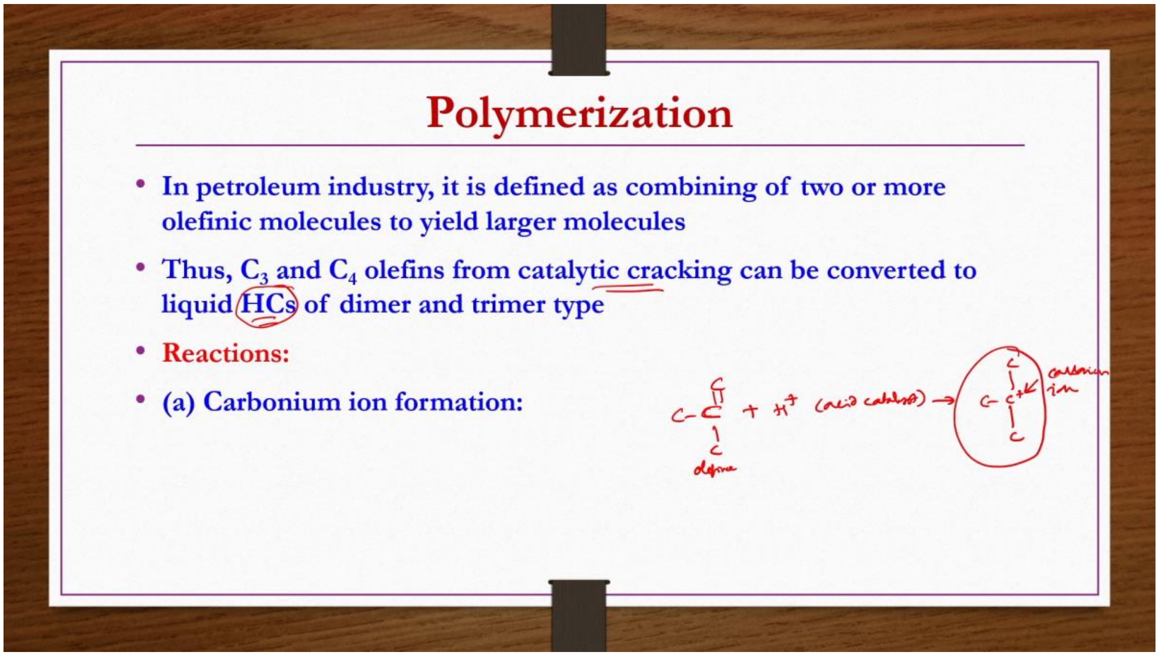

Polymerization

- In petroleum industry, it is defined as combining of two or more olefinic molecules to yield larger molecules
- Thus, C_3 and C_4 olefins from catalytic cracking can be converted to liquid HCs of dimer and trimer type
- **Reactions:**
- (a) Carbonium ion formation:

Now we talk about the polymerization. In petroleum refinery processes polymerization does not mean like you know falling very large or high molecular weight polymers. It is simply you know making you know dimers or trimers of olefins because olefins are not good from the petroleum products point of view.

So if you do the partial or you know slight polymerization to have dimers and trimers so that you know petroleum gasoline would be formed or polymer gasoline would be formed that can improve the octane number of the product. In petroleum industry it is defined as combining of 2 or more olefinic molecules to yield larger molecules. Thus whatever the C3, C4 olefin slag that is propene, butene, etc. are there which you obtain by catalytic cracking of crude petroleum they can be converted to liquid hydrocarbons of dimer and trimer type. These liquid hydrocarbons are nothing but polymer gas oil or polymer gasoline.

Now we discuss about some of the reactions which are very common in the petroleum refinery which occur you know for the formation of dimers or trimers from the olefins. Let us say if you have olefin, so this is one olefin it reacts with the hydrogen free radical in the presence of acid catalyst it will form carbonium ion like C, C plus, C, C. So now this plus is carbonium ion formation is taking place.

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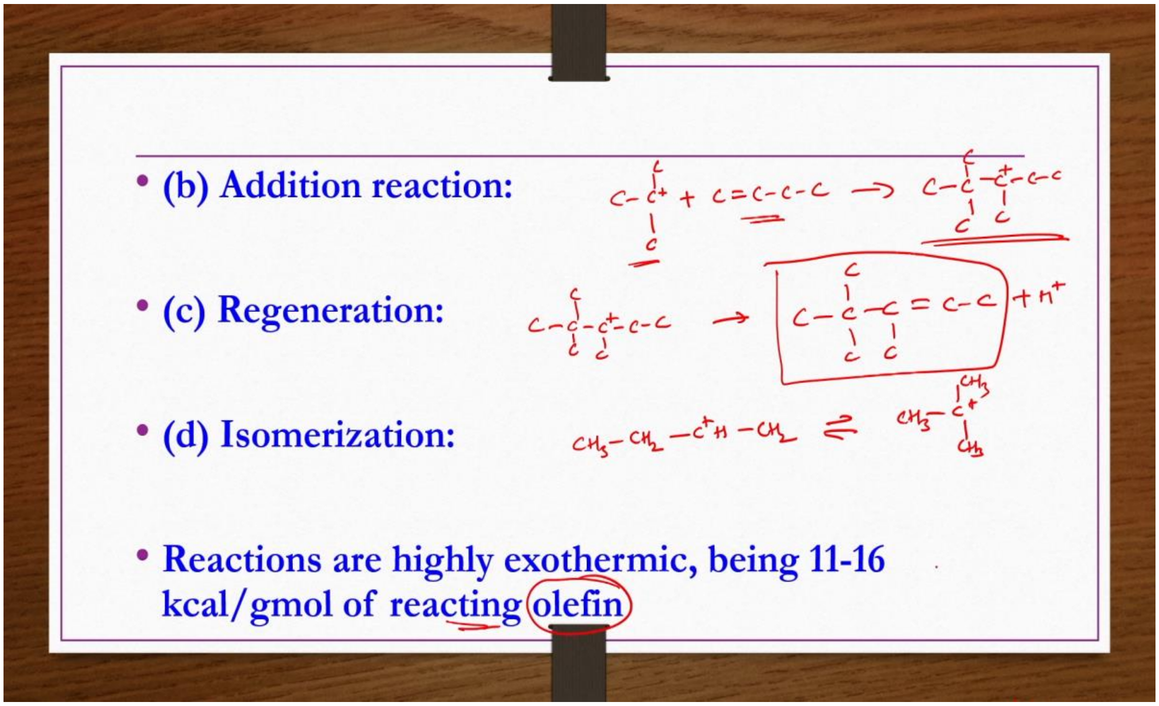

- **(b) Addition reaction:**
- **(c) Regeneration:**
- **(d) Isomerization:**
- **Reactions are highly exothermic, being 11-16 kcal/gmol of reacting olefin**

This ion will undergo addition reaction with the olefin like C, C, C, C this carbonium ion is reacting with olefin let us say you have butene. This carbonium ion reacts with the butene by addition reaction to give carbonium intermediate ion that is C, C, C, C, C, C, one more C and then one more C but this is also an ion.

After that what happens regeneration reaction takes place where two of these kind of intermediate carbonium ions they will form dimers let us say here. These ions couple of them are forming like a dimer like this. Actually we are writing only C corresponding H you can fill as per the number of bonds that are available and then it also releases the hydrogen free radical. So these are the reactions so now see here you have got a dimer from the olefin. So in the polymerization process of a petroleum refinery industry some amount of isomerization also takes place where let us say you have CH3 CH2 C plus H and then CH2 this will form reversibly isomer like CH3 C CH3 CH3.

Such kind of reactions are also possible. Reactions are highly exothermic being 11 to 16 kilocalorie per gram mole of reacting olefin only. This is about reacting olefin only products it is going to be very high that is because of that one reaction is very highly exothermic. Since reactions are highly exothermic in the process in order to temperature control in order to do the temperature control cooling is provided or quenching is provided.

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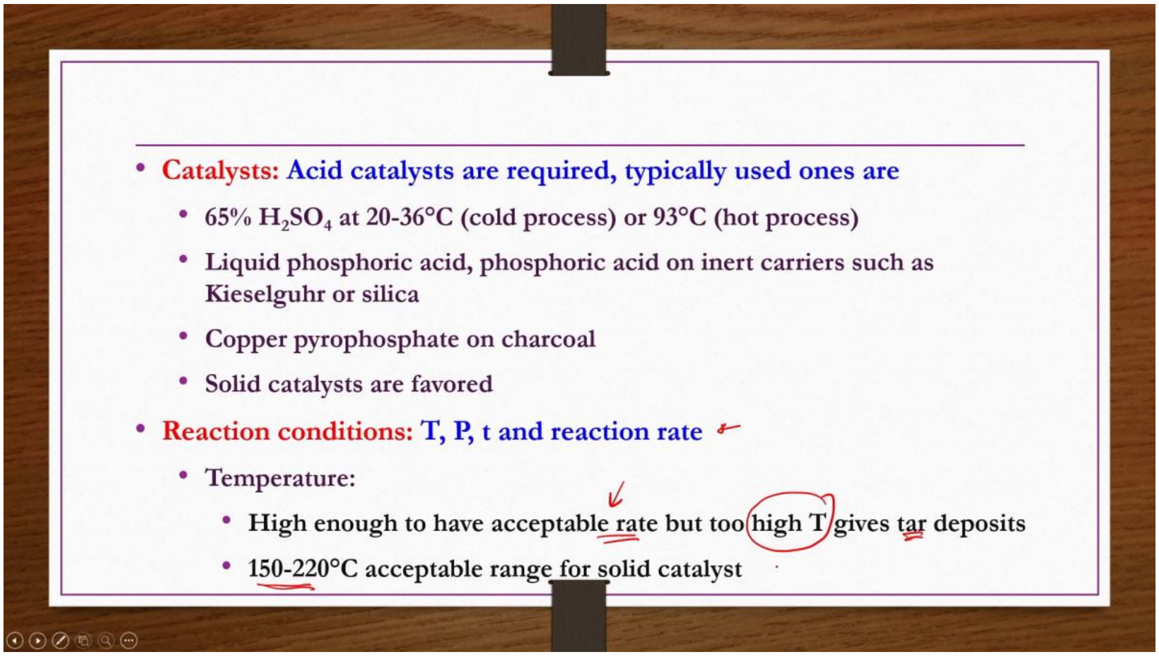

- **Catalysts:** Acid catalysts are required, typically used ones are
  - 65% H_2SO_4 at 20-36°C (cold process) or 93°C (hot process)
  - Liquid phosphoric acid, phosphoric acid on inert carriers such as Kieselguhr or silica
  - Copper pyrophosphate on charcoal
  - Solid catalysts are favored
- **Reaction conditions:** T, P, t and reaction rate
  - Temperature:
    - High enough to have acceptable rate but too high T gives tar deposits
    - 150-220°C acceptable range for solid catalyst

What are the catalyst used for such kind of polymerization? Liquid catalyst or solid catalyst are in general used these are but acid in nature. So acid catalyst are required typically used ones are 65 percent H2SO4 at 20 to 36 degrees centigrade if it is a cold process or 93 degrees centigrade if it is hot process.

Liquid phosphoric acid also used phosphoric acid on inert carriers such as Kieselguhr or silica are also used as catalyst. Copper pyrophosphates on charcoal supported on charcoal are also used as a catalyst. However, solid catalyst are favored in general. Reaction conditions for any of the reactions temperature pressure contact time and then they are very essential.

So in addition to this one here reaction rate is also important. Temperature polymerization high temperature is better one if you have high enough temperature so that to have the acceptable rate it is better. But if you use too high like 400, 500 degrees centigrade then tar deposition will take place. So that is the reason though high temperatures are preferred you go for 150 to 220 degrees centigrade which is mostly acceptable range for solid catalyst.

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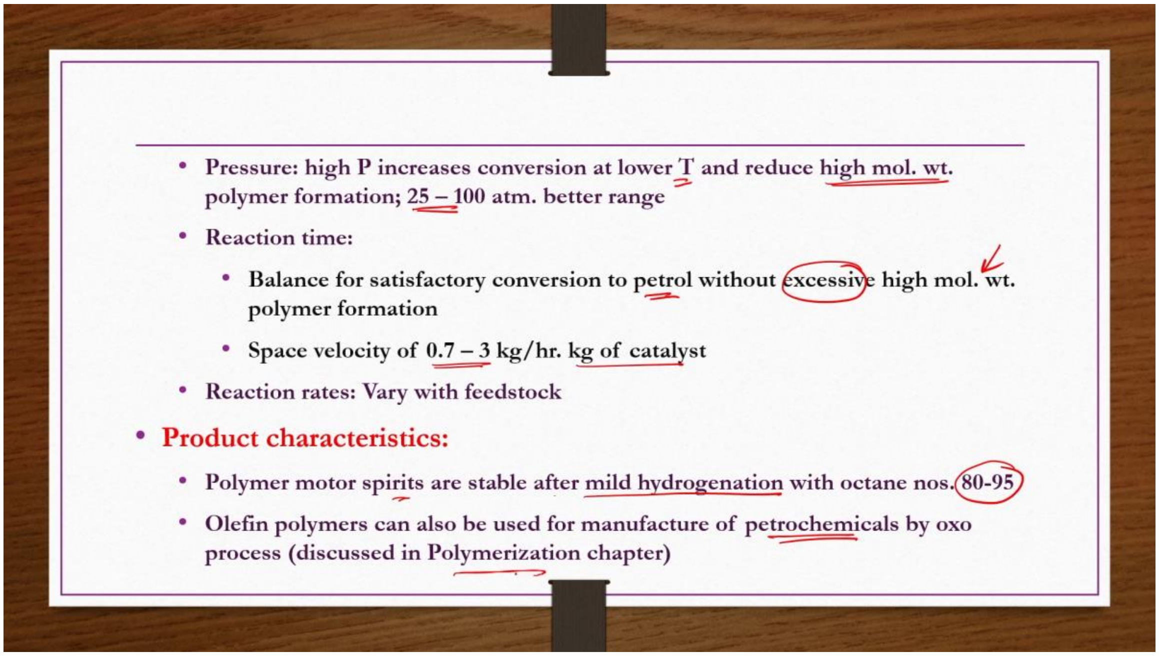

- Pressure: high P increases conversion at lower T and reduce high mol. wt. polymer formation; 25 – 100 atm. better range
- Reaction time:
  - Balance for satisfactory conversion to petrol without excessive high mol. wt. polymer formation
  - Space velocity of 0.7 – 3 kg/hr. kg of catalyst
- Reaction rates: Vary with feedstock

- **Product characteristics:**
  - Polymer motor spirits are stable after mild hydrogenation with octane nos. 80-95
  - Olefin polymers can also be used for manufacture of petrochemicals by oxo process (discussed in Polymerization chapter)

High pressure increases conversion at lower temperature and reduces high molecular weight polymer formation. You want like you know polymer gasoline formation but with very less or negligible high molecular weight polymers because this process itself is a polymerization process if you do not control the process conditions properly then high molecular weight polymers may also be forming.

So you have to do the polymerization so that only dimers or trimers falling but not high molecular weight polymers are forming. If you use the high pressure so then it is better to control the formation of high molecular weight polymers. For that 25 to 100 atmosphere range is found to be better one. Reaction time it should be decided based on the balance for satisfactory conversion to petrol without excessive high molecular weight polymer formation. So based on that particular balance you have to decide how much reaction time should be.

Space velocity should be between 0.7 to 3 kg per hour of feed material per kg of the catalyst. Reaction rates obviously vary with the feedstocks. Now product characteristics polymer motor spirits are stable after mild hydrogenation with octane numbers 80 to 95.

Olefin polymers can also be used for manufacture of petrochemicals by other processes like oxo process that we will be discussing in the polymerization chapter.

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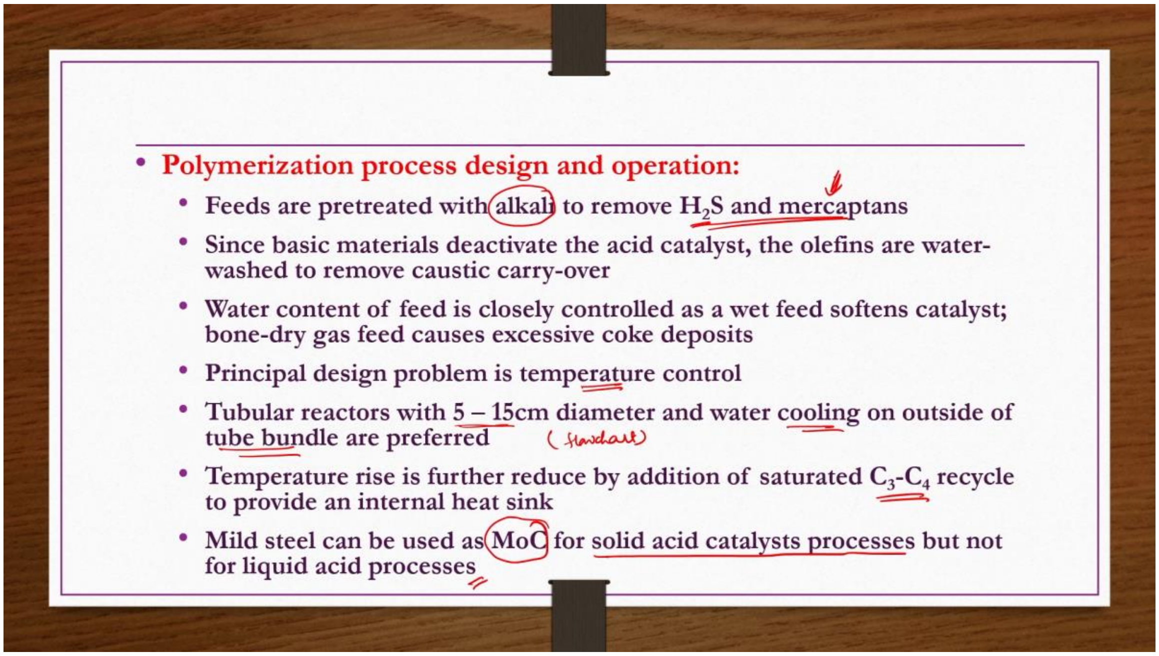

- **Polymerization process design and operation:**
  - Feeds are pretreated with alkali to remove H_2S and mercaptans
  - Since basic materials deactivate the acid catalyst, the olefins are water-washed to remove caustic carry-over
  - Water content of feed is closely controlled as a wet feed softens catalyst; bone-dry gas feed causes excessive coke deposits
  - Principal design problem is temperature control
  - Tubular reactors with 5 – 15cm diameter and water cooling on outside of tube bundle are preferred (standard)
  - Temperature rise is further reduce by addition of saturated C_3-C_4 recycle to provide an internal heat sink
  - Mild steel can be used as MoC for solid acid catalysts processes but not for liquid acid processes

Now coming to the polymerization process design and operation feeds are pretreated with alkali to remove H2S and mercaptans. So since you are using alkali to remove H2S and then mercaptans or indirectly you are removing the sulfur components. So mercaptans also having sulfur so that we know already. So for that purpose you are pretreating the feeds with alkali. Now but when you use the alkali for the pretreating and then subsequently after pretreating that mixture pretreated feed whatever is there if you are doing polymerization using the acid catalyst then acid may be deactivated because of traces of alkalis present that is present along with the feed.

Because of the pretreatment so such alkali should be water washed. After that water content of feed is closely controlled as a wet feed softens the catalyst. Bone dry gas feed causes excessive coke deposit so then accordingly water content has to be closely monitored when you do the washing with water to remove the caustics. Principle design problem is to test temperature control because these reactions are highly exothermic if you do not control the temperature properly so then you know high molecular weight polymers may form. Tubular reactors with 5 to 15 centimeter diameter and then water cooling on outside of the tube bundle are preferred.

So flow chart we are discussing in the next slide anyway. Temperature rise is further reduced by addition of saturated C3 C4 recycle to provide an internal heat sink. Mild steel can be used as material of construction for solid acid catalyst processes only but not for liquid acid processes. For liquid acid processes different MOCs should be used for the reactor construction.

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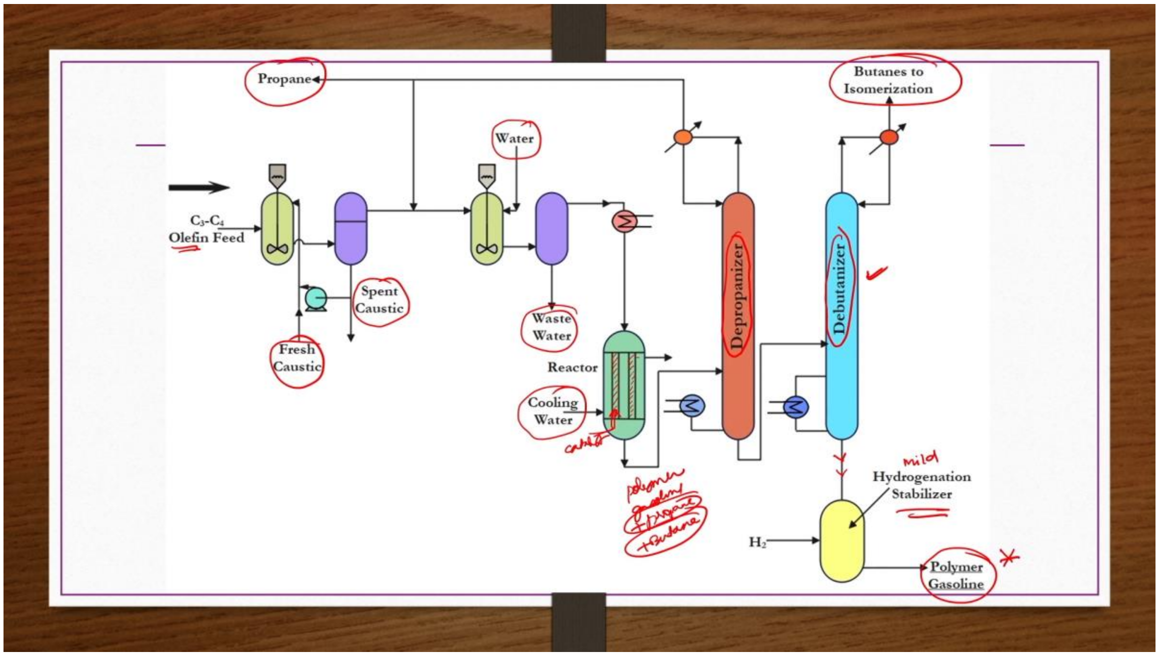

So this is the flow chart. So here olefin feed primarily we are taking propene and butane and now this feed may not be having pure propene and butane because it is one of the product coming because of the fractionation of the crude petroleum.

So there may be sulfur components those things has to be removed by treating with the caustic. So after removal whatever the spent caustic whatever is there that you have to take regenerate it and then reuse it. So that to make the process effective. For the pretreating whatever caustic you are using they will not be completely removed.

So some olefins may be carrying caustic also. If that is present so that is going to reduce the activity of the acid catalyst subsequently in the reactor. So for that purpose the feed is also washed with the water and then waste water is collected. After pretreating with caustic and then washing with water purified olefins are taken to the reactor. Here in the reactor multiple tubes would be there like a bundle. So two are only shown here or alternatively if you see so in these tubes what you are having you are having catalyst.

And then through these bundles you allow the purified olefins to pass through. Then reaction takes place so this reaction is exothermic reaction highly exothermic reaction. So cooling water has to be supplied to the shell of the reactor assembly. Reactor assembly is now within a shell tube bundles are there. Within the tubes that are forming tube bundles the catalyst are there.

Through those catalytic tube bundles only the feed is coming and then reaction is taking place. But the reaction is exothermic so that is the reason we are not taking completely packed bed of the catalyst. Between the tube bundles there is a space so that you know that heat whatever is generated because of the reactor that would not be causing damage. Further in addition to that one cooling water is also supplied to the shell side of the reactor to control the temperature. So then whatever the products are formed are polymer gasoline but some amount of propane and then butane may also be there.

So you have to separate them by process where depropanizer and then debutanizers are there. After doing the depropanizer whatever the propanes are you are getting you can collect them. Similarly, after removing the propane so along with the polymer gasoline whatever the butane is there that is removed in this section. So those butanes you can take for the isomerization process because isomerization you get branched chemicals which are good from the octane number point of view. So from here you get the polymer gasoline but that is not stable one. For that purpose mild hydrogenation is done so that to make this product stable and then collect it as polymer gasoline. So that is all about the polymerization occurring in petroleum refinery processes.

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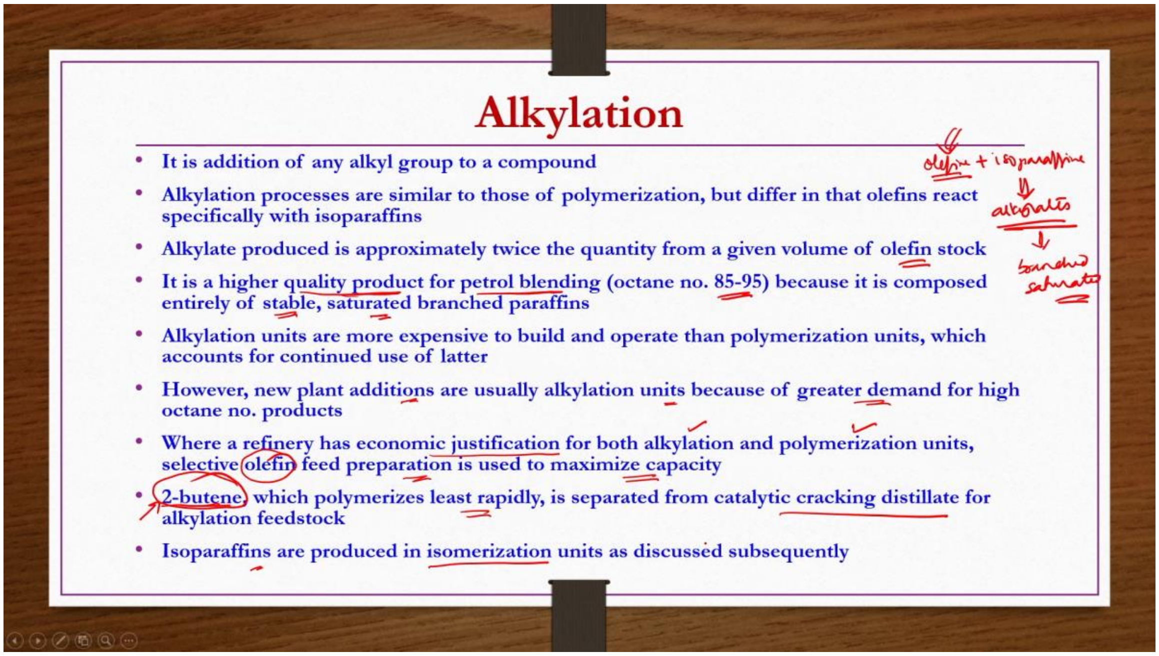

Alkylation

- It is addition of any alkyl group to a compound
- Alkylation processes are similar to those of polymerization, but differ in that olefins react specifically with isoparaffins
- Alkylate produced is approximately twice the quantity from a given volume of olefin stock
- It is a higher quality product for petrol blending (octane no. 85-95) because it is composed entirely of stable, saturated branched paraffins
- Alkylation units are more expensive to build and operate than polymerization units, which accounts for continued use of latter
- However, new plant additions are usually alkylation units because of greater demand for high octane no. products
- Where a refinery has economic justification for both alkylation and polymerization units, selective olefin feed preparation is used to maximize capacity
- 2-butene, which polymerizes least rapidly, is separated from catalytic cracking distillate for alkylation feedstock
- Isoparaffins are produced in isomerization units as discussed subsequently

olefins + isoparaffins
⇓
alkylates
↓
branched
saturated

Now we talk about alkylation. Alkylation by name as it suggests you know adding some kind of alkyl functional group to a compound so that is known as the alkylation. Alkylation processes are similar to those of polymerization but how it is different olefins whatever present they are reacting specifically with iso-paraffins to give alkylates. Alkylates are the product generic name like reformer products or reformates they are generic name.

Here also alkylation process products are having generic name of alkylates. So olefins reacting with the iso-paraffins to give the alkylates as a product whereas in the polymerization olefins whatever are there they are undergoing polymerization to form dimers and trimers. Alkylate produced is approximately twice the quantity from a given volume of olefin stock. Let us say if you have 100 tons of olefin and then you are doing alkylation process then approximately 200 tons of alkylates you may be getting or even more. It is a higher quality product for petrol blending because the octane number is having 85 to 95 because it is composed entirely of stable saturated branched paraffins. We are going to see the reactions by this reaction between olefin and iso-paraffins whatever the alkylates that you are getting they are firstly branched ones and then they are saturated ones.

They are not unsaturated ones. So whatever the unsaturation is there in the olefins because of the double bond that would be removed by alkylation process. Alkylation units are more expensive to build and operate than polymerization units which accounts for continued use of polymerization units in general. However, new plant additions are usually alkylation units because of greater demand for high octane number products where a refinery has economic justification for both alkylation and polymerization units. Selective olefin feeds preparation is used to maximize the capacity.

What does it mean by in the olefins? One or two of olefins may be least reactive to forms polymers. So they may be selectively separated and then reacted with iso-paraffins to get the alkylates. That is what it means. For example, 2-butene whatever is there which polymerizes least rapidly is separated from catalytic cracking distillates for alkylation feedstock. So this butene since its polymerization ability is very least so this can be used as a feedstock for the alkylation process. Iso-paraffins are produced in isomerization units which we are going to discuss anyway after the completion of alkylation topics.

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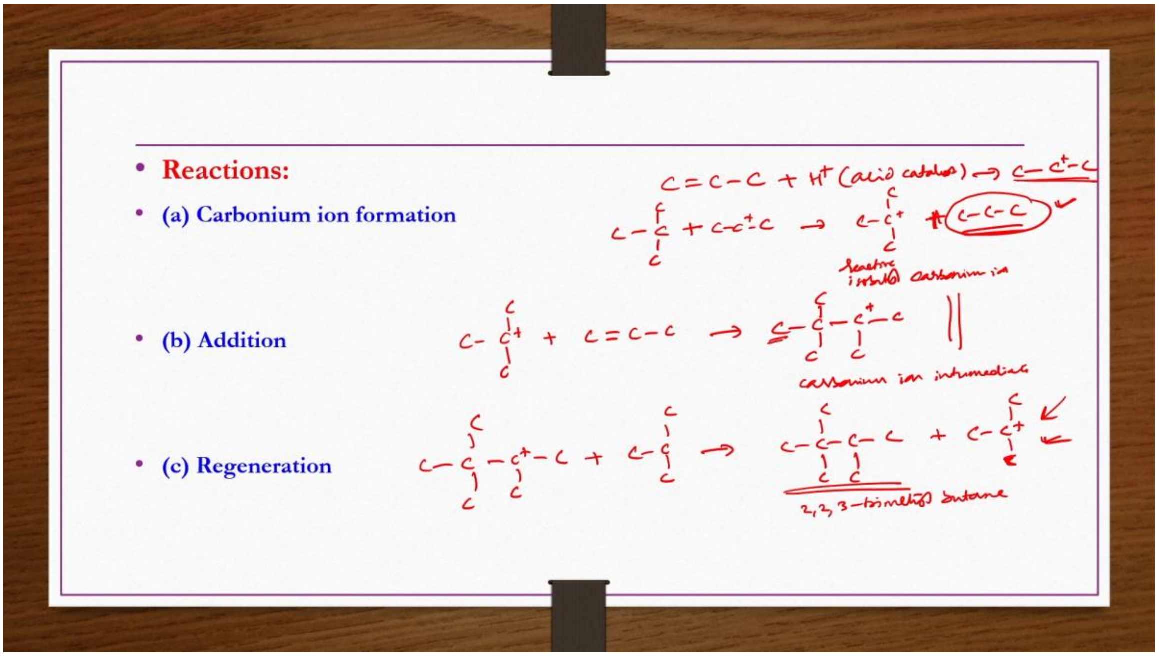

- **Reactions:**
- **(a) Carbonium ion formation**
- **(b) Addition**
- **(c) Regeneration**

Now we discuss the reactions that are involved in the alkylation process of petroleum refinery industry reactions. Carbonium ion formation since in the alkylation process 2 reactants are there. One is the olefin another one is the iso-paraffin. So 2 different types of carbonium ions may be forming. The first one is let us say if you have a olefin C double bond C C, then if it reacts with H plus in the presence of acid catalyst, then it will give C double bond C plus C, carbonium ion.

Let us say you have a paraffin C C C like this or you know you can call it isobutane. This isobutane reacts with the carbonium ion that formed in the above reaction to give reactive isobutyl carbonium ion plus propane also you get. So here also propane is forming like in polymerization process so separation is required. Then another reaction is the addition reaction where this carbonium ion reacts with the olefin to give carbonium ion intermediates that is C C C C plus carbonium ion plus olefin C double bond C C that is propane giving rise to C C C C C C C. So I hope you understand this organic chemistry H wherever is there we do not need to write every time. So if it is C here that means remaining 3 bonds of carbon are saturated by the hydrogen that is what clearly are explicitly known.

Otherwise specifically it is mentioned. So this is nothing but carbonium ion intermediate. So next reaction is the regeneration reaction where these ions react together with whatever the paraffins that are present in the process to get bigger branched alkyllides like this. Here this is nothing but 2, 2, 3-trimethylbutane, isobutane this is what you can say. This is a isomer plus also it gives another carbonium ion and then reaction series continues until these ions react themselves or with reactor surface until then the sequence of reaction continuously goes on chain reaction goes on.

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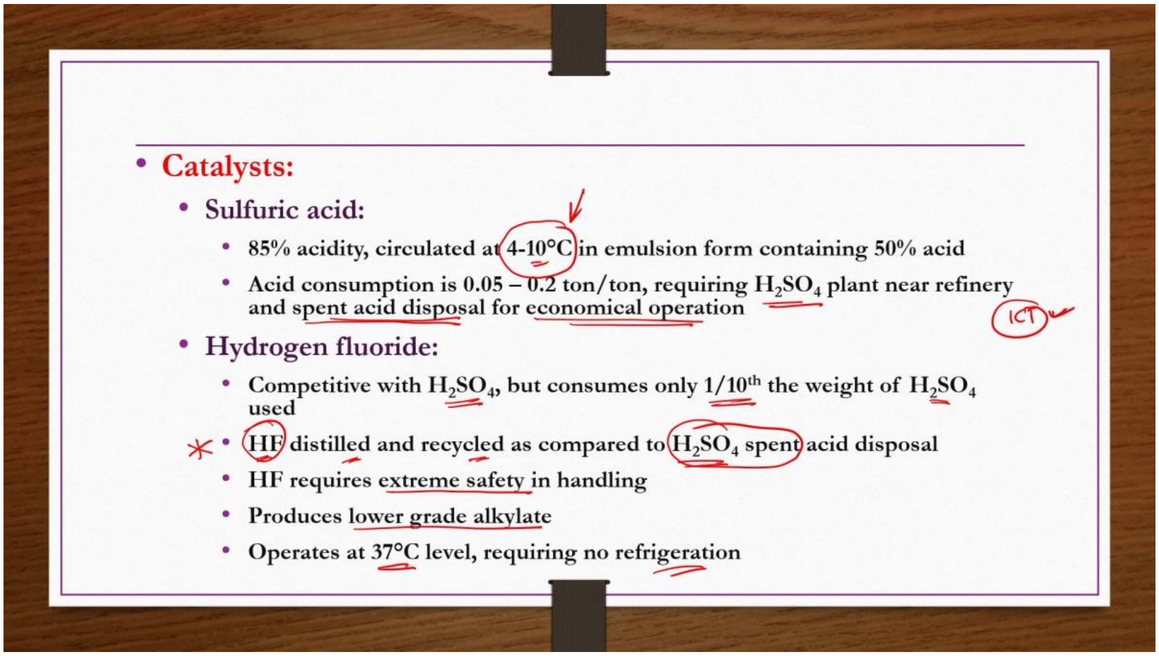

- **Catalysts:**
  - **Sulfuric acid:**
    - 85% acidity, circulated at 4-10°C in emulsion form containing 50% acid
    - Acid consumption is 0.05 – 0.2 ton/ton, requiring H_2SO_4 plant near refinery and spent acid disposal for economical operation
  - **Hydrogen fluoride:**
    - Competitive with H_2SO_4, but consumes only 1/10th the weight of H_2SO_4 used
    - HF distilled and recycled as compared to H_2SO_4 spent acid disposal
    - HF requires extreme safety in handling
    - Produces lower grade alkylate
    - Operates at 37°C level, requiring no refrigeration

Now catalyst sulfuric acid catalyst are used and then hydrogen fluoride catalyst are also used. Sulfuric acid 85 percent acidity circulated at 4 to 10 degrees centigrade in emulsion form containing 50 percent acid. Acid consumption is 0.05 to 0.2 tons per ton of the feed requiring H2SO4 plant near refinery and spent acid disposal also near the refinery for the economical operations because this acid whatever is there once it is diluted when the spent acid would also be in large quantities. So such large quantities of spent acid you cannot discard easily. Either you have to sell to some other vendors who required such kind of spent catalyst so that they can regenerate and use for the different purposes. Such kind of things we have discussed in the ICT course in organic chemical technology which is available on NPTEL MOOCs platform anyway. Other catalyst is hydrogen fluoride it is competitive with H2SO4 but it consumes only one tenth of the weight of H2SO4 used.

So that is a better one less consumed and then also it is distilled and recycled as compared to H2SO4 spent acid disposal. H2SO4 you have to dispose whatever the spent catalyst that you are getting whereas HF you can distill and recycle it. So that is the advantage but the disadvantage or the problem is that you know it requires extreme safety in handling. So another disadvantage that it produces lower grade alkylate. Operate as 37 degrees centigrade so does not require any refrigeration whereas this one requires it 4 to 10 degrees centigrade operating condition.

So refrigeration would be very much essential. Why it is because whatever the H2SO4 you are using that is having lower limit of 0 degrees centigrade because of the viscosity issues and then upper limit of 21 degrees centigrade because of a sulfation takes place. You do not want sulfation takes place so you cannot go more than 20 degrees centigrade. So you try to maintain fixed temperature not above the 10 degrees centigrade.

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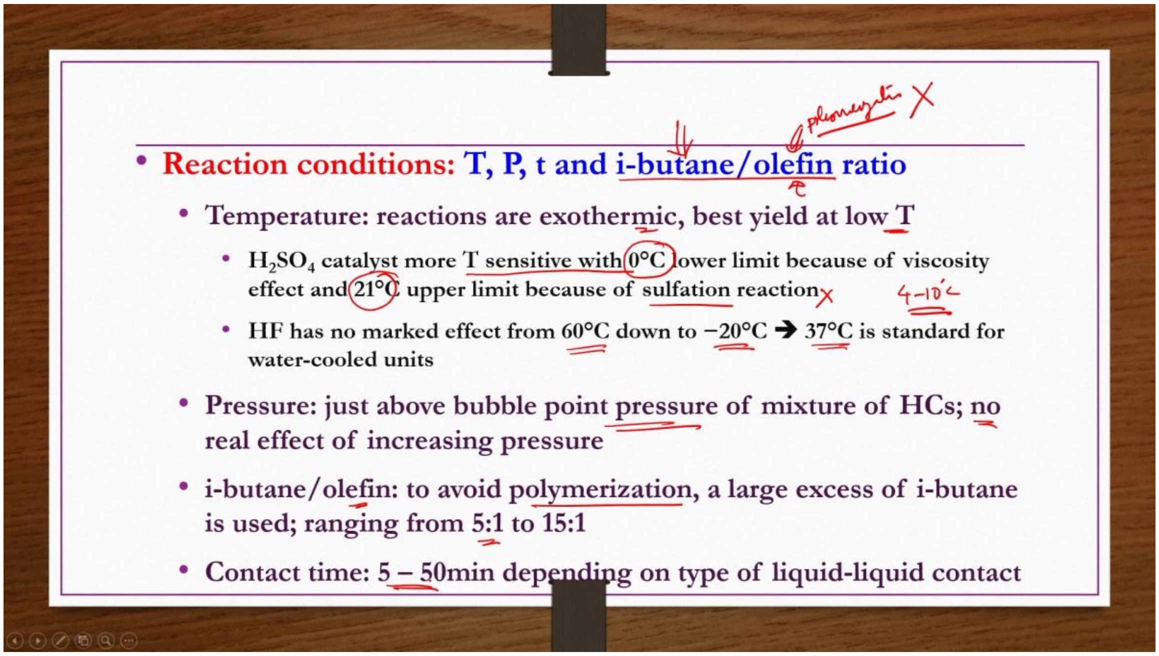

- **Reaction conditions: T, P, t and i-butane/olefin ratio**
  - Temperature: reactions are exothermic, best yield at low T
    - H_2SO_4 catalyst more T sensitive with 0°C lower limit because of viscosity effect and 21°C upper limit because of sulfation reaction X 4-10°C
    - HF has no marked effect from 60°C down to −20°C ➔ 37°C is standard for water-cooled units
  - Pressure: just above bubble point pressure of mixture of HCs; no real effect of increasing pressure
  - i-butane/olefin: to avoid polymerization, a large excess of i-butane is used; ranging from 5:1 to 15:1
  - Contact time: 5 – 50min depending on type of liquid-liquid contact

Reaction conditions as usual temperature, pressure and then contact time in addition to that one ratio between isobutene and olefin also important because since olefins are there so obviously polymerization may take place as just we have seen in previous topic.

So in order to make it absent or reduce it you have to add more isobutene. Let us say if you take one part of olefin you have to take 5 to 15 parts of paraffins to reduce or suppress the polymerization reaction. Only alkylation will take place then. Temperature reactions are exothermic so obviously it is best to have a low temperature or best yield would be obtained at low temperature. H2SO4 catalyst is more sensitive to temperature with 0 degrees centigrade lower limit because of the viscosity effect and then 21 degrees centigrade upper limit because of sulfation reaction.

So you do not want the sulfation reaction take place so you try to control the temperature within 10 degrees centigrade. Though you have the temperature controller if you fix it 20 plus or minus 4, 5 degrees also if it is going then it is not possible to stop the sulfation reaction. So that is the reason if you are using the H2SO4 catalyst you have to maintain temperature between 4 to 10 degrees centigrade. HF has no marked effect from minus 20 degrees centigrade to plus 60 degrees centigrade. So any temperature can be used 37 degrees centigrade is standard for water cold units. Pressure just above bubble point pressure of mixture of hydrocarbons can be used though there is no real effect of increasing pressure.

So because of the energy economic some pressure you have to maintain for that purpose up to this pressure you can go. To avoid polymerization large excess of isobutene is used ranging between 5 to 15 times higher than the olefins. Contact time 5 to 15 minutes depending on the type of liquid-liquid contact that you are having.

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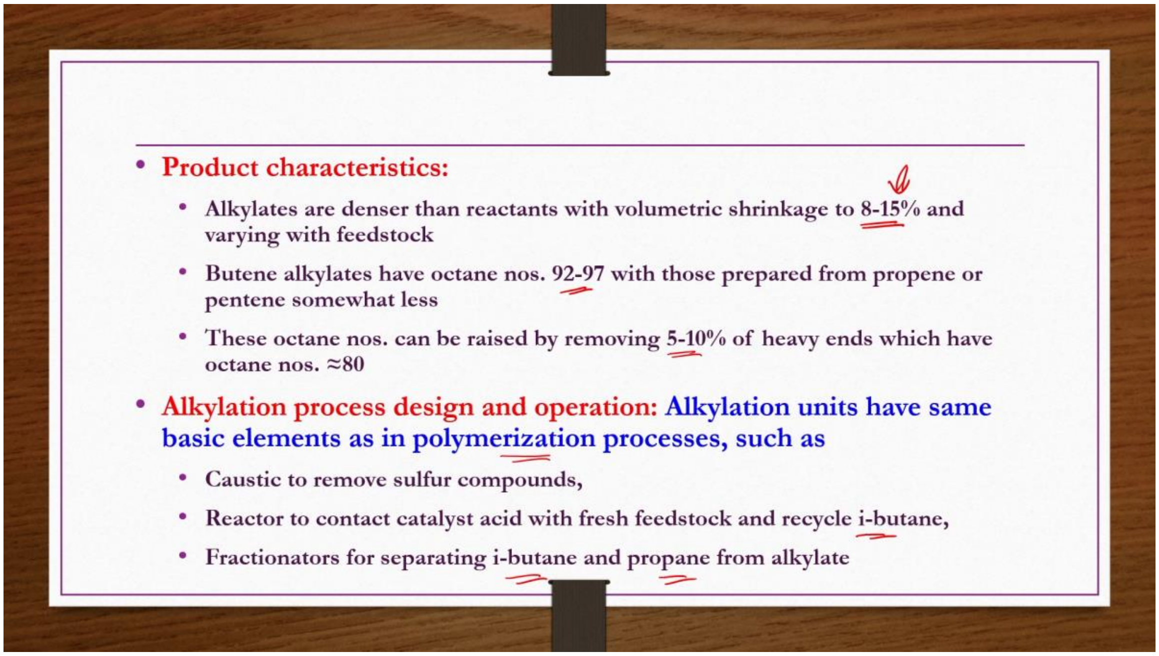

- **Product characteristics:**
  - Alkylates are denser than reactants with volumetric shrinkage to 8-15% and varying with feedstock
  - Butene alkylates have octane nos. 92-97 with those prepared from propene or pentene somewhat less
  - These octane nos. can be raised by removing 5-10% of heavy ends which have octane nos. ≈80
- **Alkylation process design and operation:** Alkylation units have same basic elements as in polymerization processes, such as
  - Caustic to remove sulfur compounds,
  - Reactor to contact catalyst acid with fresh feedstock and recycle i-butane,
  - Fractionators for separating i-butane and propane from alkylate

Product characteristics alkylates are denser than the reactants with volumetric shrinkage 8 to 15 percent that is very high. So whatever the reactants volume is there after the reaction whatever the alkylates if you see the change in volume would be 8 to 15 percent less. So that is very much higher and it also varies with feedstock. Butene alkylates have octane number 92 to 97 with those prepared from propene or pentene somewhat less. These octane numbers can be raised by removing 5 to 10 percent of heavy ends which have octane numbers approximately 80. Now we talk about alkylation process design and operation which is having similar units as in polymerization process such as sulfur removal by caustic then reactor to contact catalyst with fresh feedstock and recycle isobutene. Then fractionators for separating the isobutene and propane from the alkylates similar like polymers or polymerization. In the polymerization also you have the purification of the feedstock followed by the reaction followed by the removal of the propane and butane. So here also such kind of sequence is followed.

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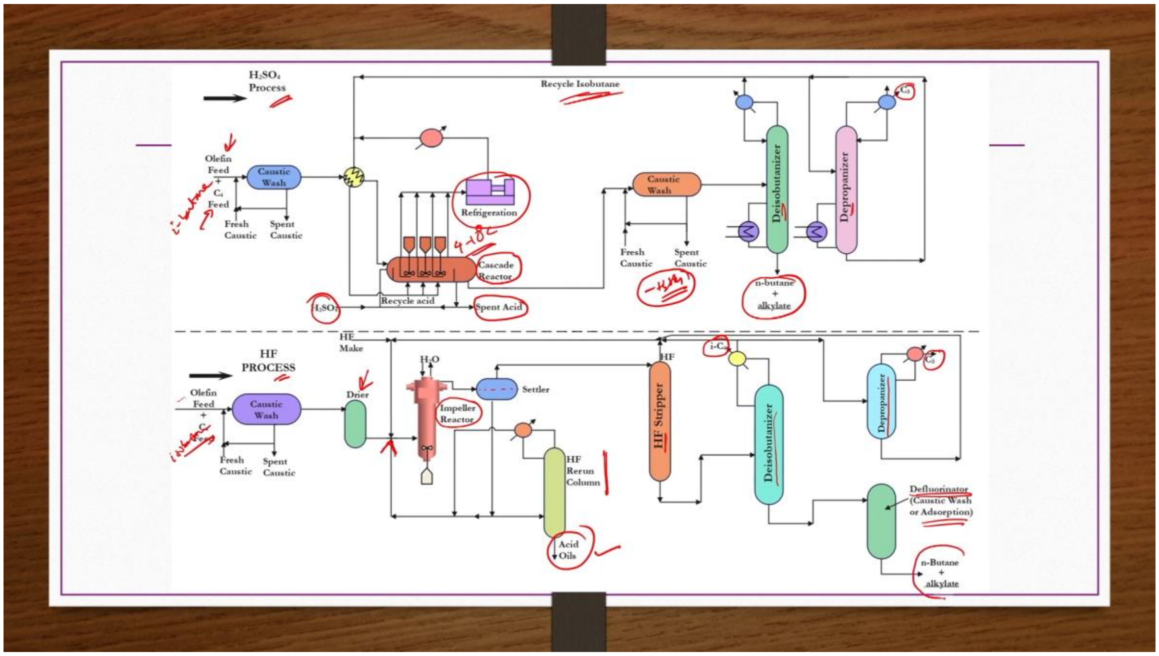

That we see for both of the processes in the sense in terms of the catalyst you are using you know you can have H2SO4 process or HF process. So olefin feed plus C4 feed whatever is there or olefins plus C4 here is nothing but isobutene. So these are you know washed with caustic then sent to a reactor cascade reactor to which H2SO4 is supplied.

Recycled acid also supplied sometimes. After the reactions spent catalyst is taken and discarded disposed. In this reactor the temperature is maintained between 4 to 10 degrees centigrade for that purpose refrigeration is there. After the reaction whatever the products are there they are washed with caustic to remove whatever the traces of sulfuric acid catalyst etc. may be present along with the product. Then mixture is passed through series of deisobutanizer, depropanizer.

From the deisobutanizer you remove the isobutane and then feed back to the reactor. After removing the isobutane whatever the n-butane and alkylate is there that you can take it as a product. So let us say that product you are taking from the n-butane and alkylates you are taking from the bottom from the top you may be getting isobutane. If that isobutane is not pure enough if it is also containing the propane so that mixture is also sent to the depropanizer where propane is being separated out and then whatever the isobutane is there that is sent back as a recycle. Because isobutane more isobutane if it is present in the feed that is going to the reactor polymerization would be suppressed.

So that is the reason as much isobutane as possible you have to recover and then recycle. Whereas in the HF process, the process is similar but after the caustic washing of olefin feed and then isobutane feed you know you need to dry the feed. So after drying the mixture goes to the impeller reactor where HF is also supplied for the reaction to take place. Now here excess of water formation may be taking place. So that because of that reason that reaction mixture is taken to the settler where HF is removed and then taken to HF rear end column to recover the acid oils and after recovering the acid oils whatever the HF is there that is recycled back to the reactor as catalyst. Whereas the product from the settler whatever are there they would be further sent to the HF stripping column to remove if at all any HF is still remaining along with the products.

Then standard deisobutanizer and depropanizer steps are there to remove the isobutanes and then propanes you can collect them as well as after collecting you can feed them back to the reactor for the subsequent recycling purpose. So here whatever the material that you are getting after deisobutanizer that may be having some amount of HF also for that purpose defluorinators are used or some fluoride impurities may be there along with the product. So for that purpose caustic wash or adsorption would be done to remove the impurities of fluorides and then you can get n-butane and alkylate as the products.

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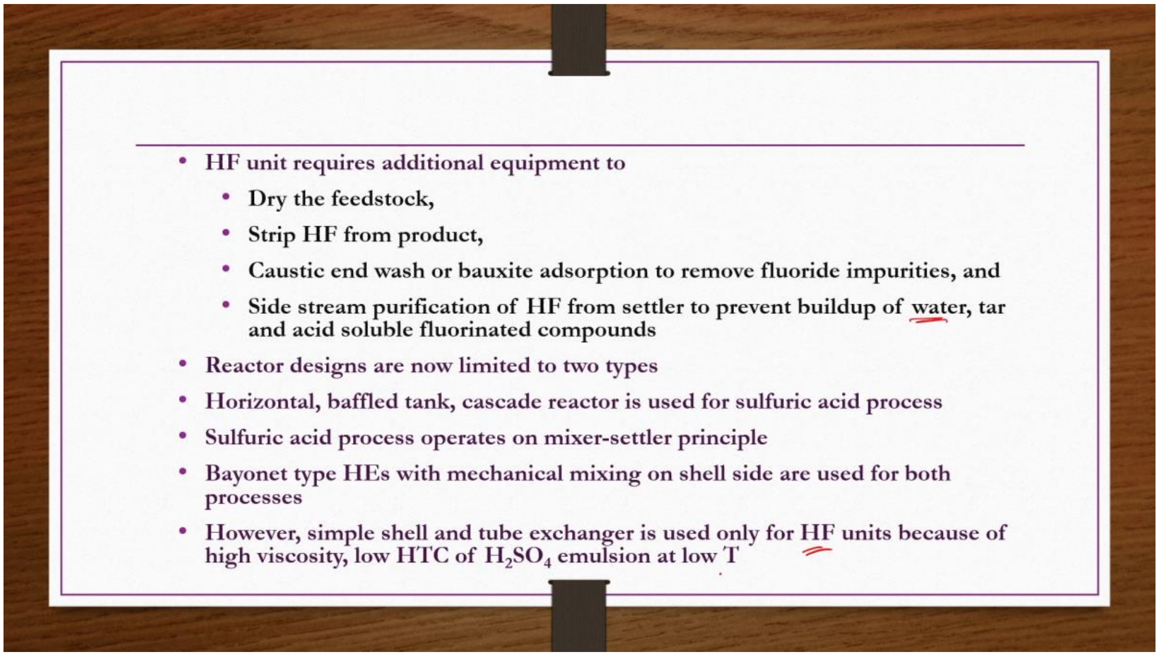

- HF unit requires additional equipment to
  - Dry the feedstock,
  - Strip HF from product,
  - Caustic end wash or bauxite adsorption to remove fluoride impurities, and
  - Side stream purification of HF from settler to prevent buildup of water, tar and acid soluble fluorinated compounds
- Reactor designs are now limited to two types
- Horizontal, baffled tank, cascade reactor is used for sulfuric acid process
- Sulfuric acid process operates on mixer-settler principle
- Bayonet type HEs with mechanical mixing on shell side are used for both processes
- However, simple shell and tube exchanger is used only for HF units because of high viscosity, low HTC of H_2SO_4 emulsion at low T

So briefly discuss the same process here HF unit requires additional equipment to dry the feedstock, strip HF from the product, caustic end wash or bauxite adsorption to remove fluoride impurities and side stream purification of HF from settler to prevent buildup of water, tar and acid soluble fluorinated compounds.

Reactor designs are now limited to 2 types where horizontal, baffle tank, cascade reactors are used for sulfuric acid processes. Sulfuric acid process operates on mixer settler principle. Bayonet type heat exchangers with mechanical mixing on shell side are used for both processes. However, simple shell and tube exchangers are used only for HF units because of high viscosity and low heat transfer coefficient of H2SO4 emulsion at low temperatures especially.

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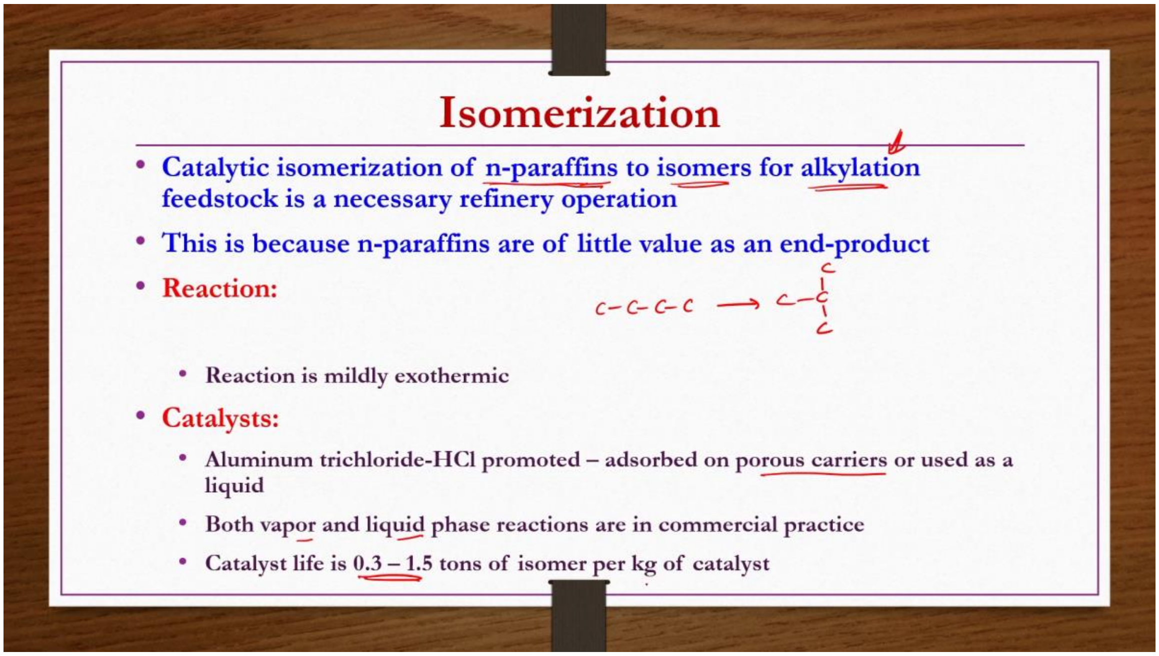

Isomerization

- Catalytic isomerization of n-paraffins to isomers for alkylation feedstock is a necessary refinery operation
- This is because n-paraffins are of little value as an end-product
- **Reaction:**
  - Reaction is mildly exothermic
- **Catalysts:**
  - Aluminum trichloride-HCl promoted – adsorbed on porous carriers or used as a liquid
  - Both vapor and liquid phase reactions are in commercial practice
  - Catalyst life is 0.3 – 1.5 tons of isomer per kg of catalyst

So that is all about alkylation processes occurring in the petroleum refinery. Now quickly we look at isomerization processes. Isomerization of n-paraffins to isomers for alkylation feedstock is necessary refinery operation. Actually n-paraffins whatever are there they are not bad because they are saturated one, but their octane number is very less compared to the isomers or iso-paraffins or cyclic components or aromatics. Because of that one these n-paraffins are isomerized to form some kind of isomers and those isomers would be taken to the alkylation unit to do the required alkylation. So that in the alkylation branched bigger molecules are formed which are very good from the octane number point of view, okay? So whatever the product that you form in the isomerization unit that you take as a feed for the alkylation unit.

Just now we have completed. This is because n-paraffins are of little value as an end product. Now we talk about the reactions involved in the isomerization. Now we take a typical isomerization reaction. Let us say you have n-butane. If it undergoes the isomerization you get isobutane, okay? Reaction is mildly exothermic.

Catalyst used on aluminum trichloride HCl promoted, adsorbed on porous carriers are used as liquid itself without adsorption. Both vapor and liquid phase reactions are in commercial practice for isomerization. Catalyst life is only 0.3 to 1.5 tons of isomer per kg of catalyst.

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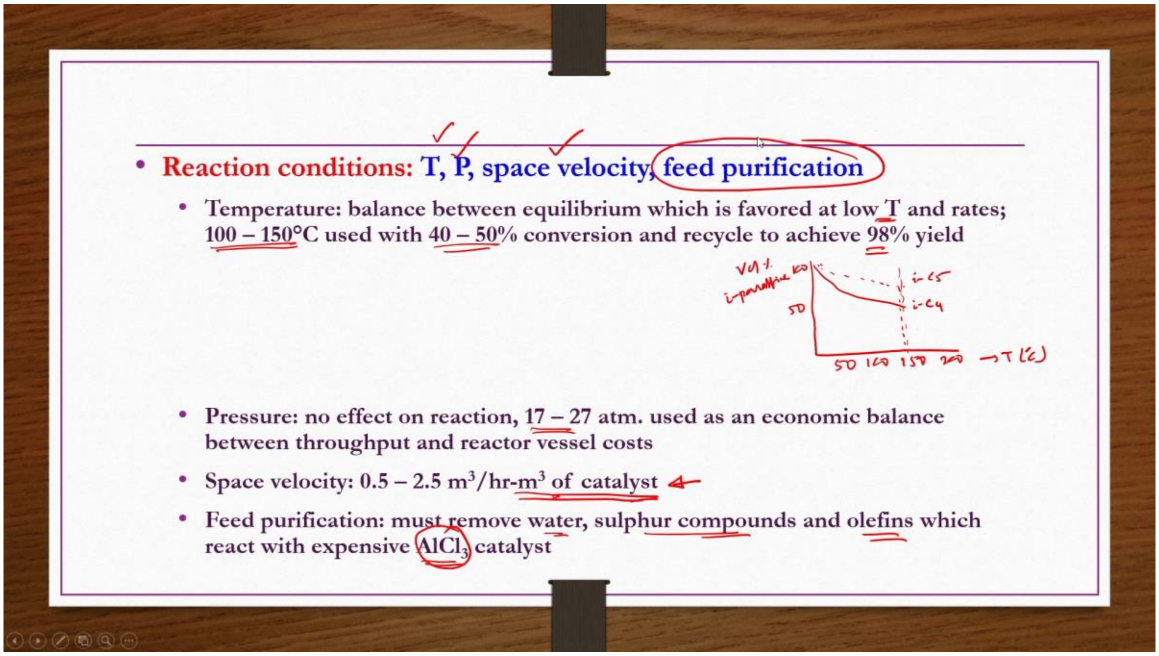

- **Reaction conditions: T, P, space velocity, feed purification**
  - Temperature: balance between equilibrium which is favored at low T and rates; 100 – 150°C used with 40 – 50% conversion and recycle to achieve 98% yield
  - Pressure: no effect on reaction, 17 – 27 atm. used as an economic balance between throughput and reactor vessel costs
  - Space velocity: 0.5 – 2.5 $m^3/hr\text{-}m^3$ of catalyst
  - Feed purification: must remove water, sulphur compounds and olefins which react with expensive $AlCl_3$ catalyst

Reaction conditions in addition to the temperature, pressure and space velocity, feed purification is also very much essential in the isomerization. Temperature should be decided based on the balance between equilibrium which is favored at low temperature and rates. So 100 to 150 degrees centigrade is used in general with 40 to 50 percent conversion. If you do the recycling you can get the 98 percent yield as well. So for example, you have temperature variations from 50 to 200 degrees centigrade.

So what is the corresponding volume percentage of isoparaffins? I hope you understand that i stands for the iso. So let us say 50, 100 percent. Now if you are planning for isopentane, so the yield would be like this. If you are planning for isobutane, yield curve would be like this, right? So it is better to go only up to 150 degrees centigrade because after that further increasing the temperature, the yield of these paraffins subsequently decreases, okay? Whereas the pressure does not have any effect but however, 17 to 27 atmosphere is used as economic balance between throughput and reactor vessel cost.

Space velocity is between 0.5 to 2.5 meter cube per hour per meter cube of the catalyst because here liquid catalyst are used. That is the reason, you know, this is space velocity is represented in the volume units as well as the volumetric flow rate units. Feed purification must remove the water, sulphur compounds and olefins which react with expensive aluminum chloride catalyst, right? So that is the reason. In addition to the temperature, pressure and space velocity, feed purification is also very much essential in isomerization processes of petroleum refinery industries, okay? Otherwise, they will be reacting with the expensive aluminum chloride catalyst which is not good.

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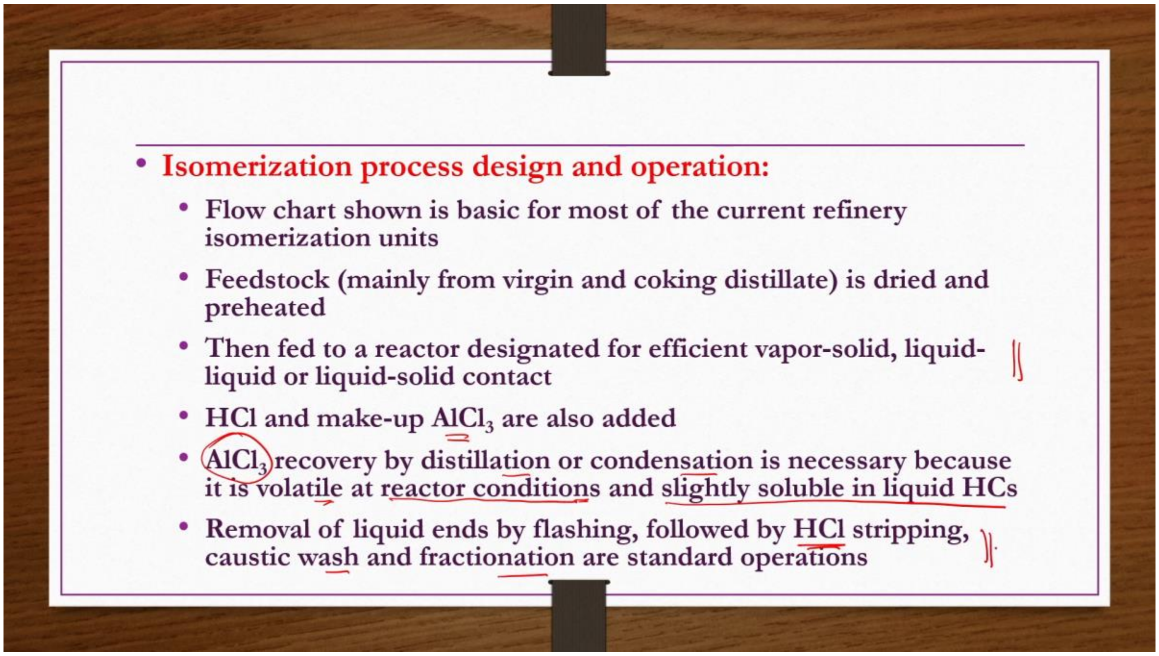

- **Isomerization process design and operation:**
  - Flow chart shown is basic for most of the current refinery isomerization units
  - Feedstock (mainly from virgin and coking distillate) is dried and preheated
  - Then fed to a reactor designated for efficient vapor-solid, liquid-liquid or liquid-solid contact
  - HCl and make-up $AlCl_3$ are also added
  - $AlCl_3$ recovery by distillation or condensation is necessary because it is volatile at reactor conditions and slightly soluble in liquid HCs
  - Removal of liquid ends by flashing, followed by HCl stripping, caustic wash and fractionation are standard operations

Isomerization process design and operation, if you see flow chart shown in the next slide is a basic one for most of the current refinery isomerization units. Feed stock mainly from a virgin and coking distillate is dried and preheated. Then fed to a reactor designated for efficient vapor solid, liquid-liquid or liquid-solid contact because this reaction can be taken place in any of the form, vapor form or liquid form also. So HCl and make up aluminum chloride are also added to the reactor. Aluminum chloride recovery by distillation or condensation is necessary because it is volatile at reactor conditions of 100 to 150 degrees centigrade and then pressures of 17 to 27 atmospheres.

It is also slightly soluble in liquid hydrocarbon. So because of such reasons, recovery is very much essential by distillation or condensation. Removal of liquid ends by flashing followed by HCl stripping, caustic wash and fractionation are the standard operations to get the isomers as we are going to discuss in the flow chart here.

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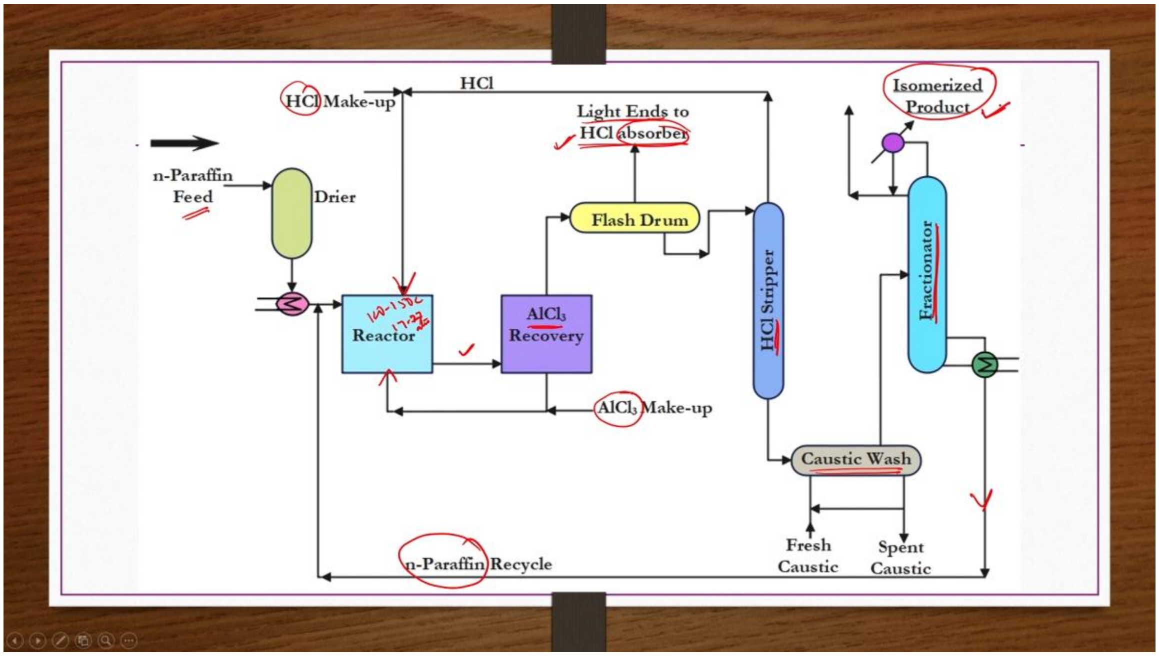

So the flow chart for the isomerization process is shown here. Whatever the n-paraffin feed is there that is dried and then sent to the reactor. To the reactor aluminum chloride catalyst along with the HCl are fed to the reactor. So the reaction takes place at 100 to 150 degrees centigrade and then 17 to 27 atmospheric pressures. Then after the reaction whatever the products are there from the products you try to recover aluminum chloride otherwise it will be soluble in the hydrocarbons. After that the mixture is sent to the flash drum where the light ends are separated to HCl absorber. So because in the light ends if at all HCl vapors are also there, fractions are also there.

So they should be removed in an absorption column. That is the separate process. After removing or after this flash whatever the product is there that is sent to the HCl stripping to recover the HCl or separate the HCl from the product and then that is taken as a recycle to the reactor. After removing the HCl if at all still any HCl traces are there, they would be removed by the caustic wash. Then after that fractionator would be used to separate the isomerized products whereas the non-reacted or unreacted n-parafins whatever are there, they will be collected as bottom and then sent back to the reactor. Whereas the isomerized products you get as a top product of the fractionator.

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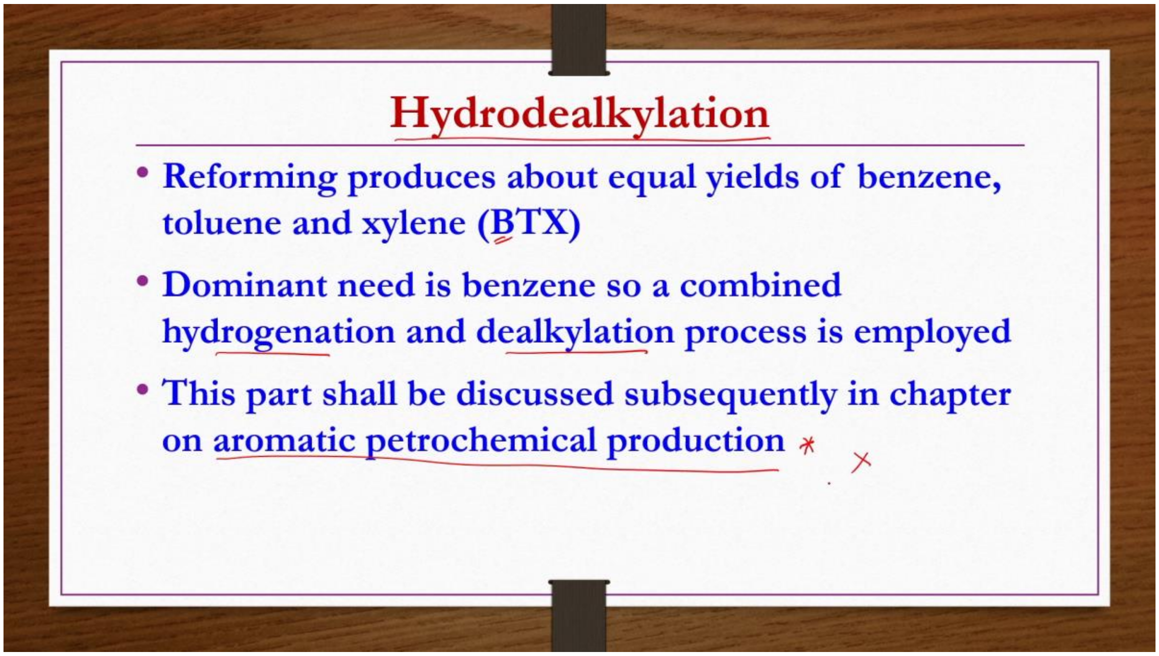

Hydrodealkylation

- Reforming produces about equal yields of benzene, toluene and xylene (BTX)
- Dominant need is benzene so a combined hydrogenation and dealkylation process is employed
- This part shall be discussed subsequently in chapter on aromatic petrochemical production *

Now the hydrodealkylation in general in refineries equal yields of benzene, toluene and xylene are expected or produced at equal amounts but the market for the benzene is very high. So if you wanted to get benzene, combined hydrogenation and then dealkylation process are used. So that is the reason this is known as the hydrodealkylation. However, this process we are going to discuss when we discuss petrochemicals production from the aromatics. In that chapter we are going to discuss this one. So we are not going to discuss this one.

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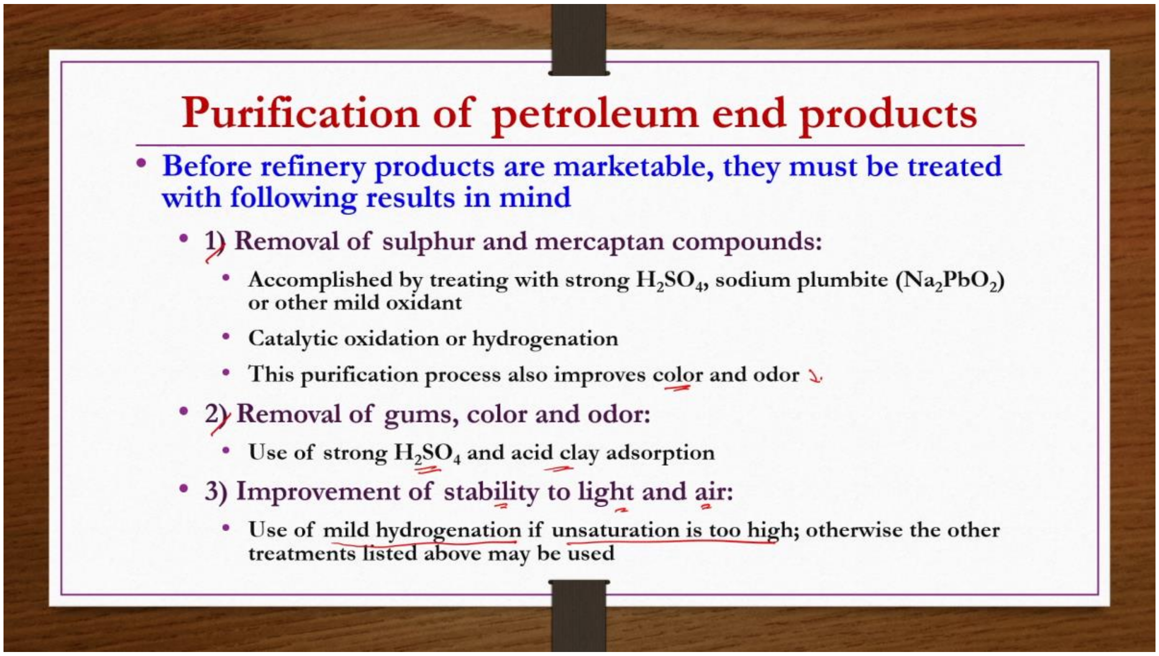

Purification of petroleum end products

- **Before refinery products are marketable, they must be treated with following results in mind**
  - 1) Removal of sulphur and mercaptan compounds:
    - Accomplished by treating with strong H_2SO_4, sodium plumbite (Na_2PbO_2) or other mild oxidant
    - Catalytic oxidation or hydrogenation
    - This purification process also improves color and odor
  - 2) Removal of gums, color and odor:
    - Use of strong H_2SO_4 and acid clay adsorption
  - 3) Improvement of stability to light and air:
    - Use of mild hydrogenation if unsaturation is too high; otherwise the other treatments listed above may be used

Finally the most important part of refinery conversion processes is the purification of petroleum end products. You do so many of the process like pyrolysis, cracking, then reforming, polymerization, alkylation, isomerization, hydrodealkylation, etc. but the product if is having some impurities, so market would not be good. So purification of the end products whatever you get because of these refinery processes they should be purified. Before refinery products are marketable, they must be treated with following results in mind. Removal of sulfur and mercaptan compounds like you know mercaptans also containing the sulfur in general.

So this can be accomplished by treating with strong sulfuric acid or treating with sodium plumbite or other mild oxidants can be used. Catalytic oxidation or hydrogenation may also be used for this purpose. This purification process also improves the color and then reduces the odor. Removal of gums, color and odor is also one important purification step.

This can be done by use of strong H2SO4 and acid clay adsorption process. Then improvement of stability to light and air, some of the products may not be stable. So for that purpose one can do the mild hydrogenation if the unsaturation is too high in the products. If the unsaturation is negligible, very small, then you can use any of the above processes that we have listed out here. So this is all about refinery conversion processes.

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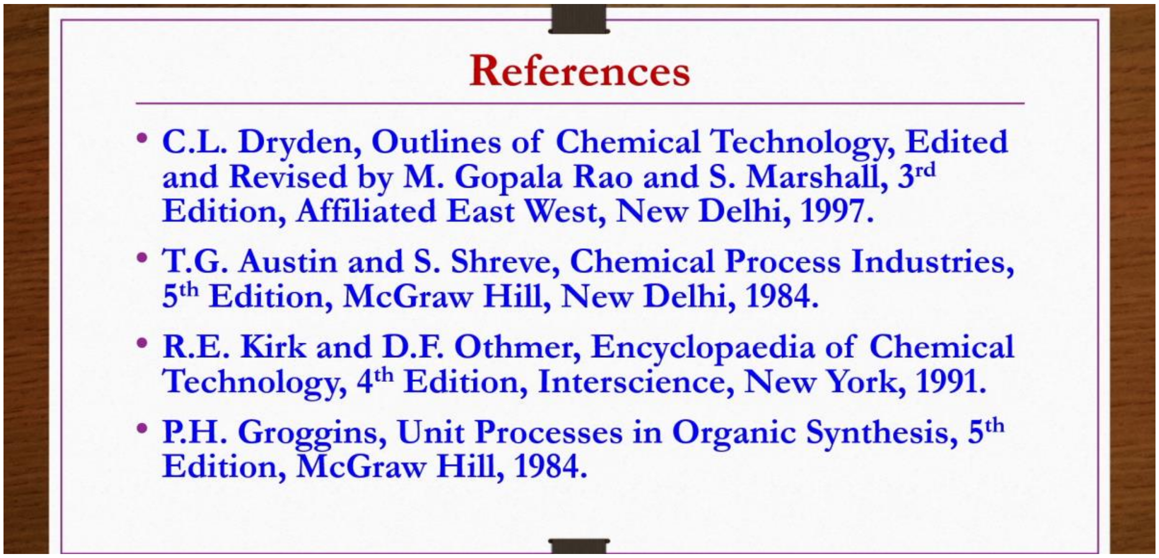

References

- C.L. Dryden, Outlines of Chemical Technology, Edited and Revised by M. Gopala Rao and S. Marshall, 3rd Edition, Affiliated East West, New Delhi, 1997.
- T.G. Austin and S. Shreve, Chemical Process Industries, 5th Edition, McGraw Hill, New Delhi, 1984.
- R.E. Kirk and D.F. Othmer, Encyclopaedia of Chemical Technology, 4th Edition, Interscience, New York, 1991.
- P.H. Groggins, Unit Processes in Organic Synthesis, 5th Edition, McGraw Hill, 1984.

The references for today's lecture are provided here. However, the entire lecture notes is prepared from this reference book. Thank you.