# Lec 28: Chemicals from $C_4$ Compounds.

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is chemicals from $C_4$ compounds.

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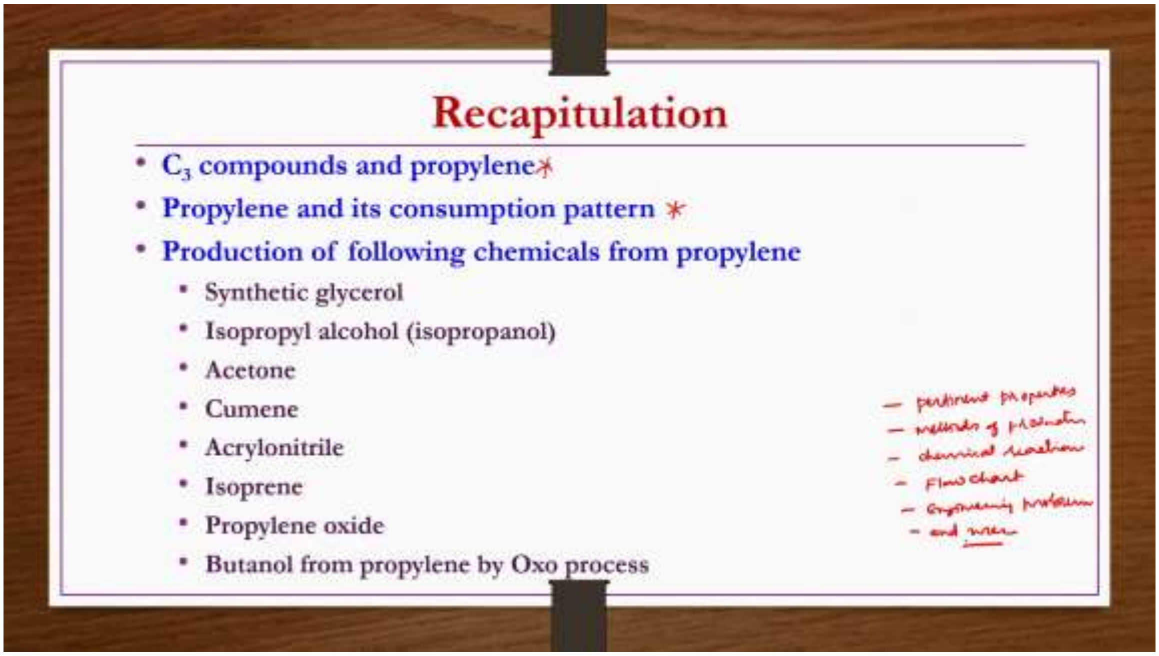

## Recapitulation

- $C_3$ compounds and propylene *
- Propylene and its consumption pattern *
- Production of following chemicals from propylene
  - Synthetic glycerol
  - Isopropyl alcohol (isopropanol)
  - Acetone
  - Cumene
  - Acrylonitrile
  - Isoprene
  - Propylene oxide
  - Butanol from propylene by Oxo process

– pertinent properties
– methods of production
– chemical reactions
– Flow chart
– Engineering problems
– end uses

We have a recapitulation of what we have discussed in previous couple of lecture in this particular chapter. In this chapter, we started discussing on production of different types of synthetic chemicals from $C_3$ and $C_4$ compounds. $C_3$ compounds in the sense the raw material whichever we have taken that should be having 3 carbon atoms.

$C_4$ in the sense the raw material whatever we have taken that must be having 4 carbon atoms, right? So, under the category of $C_3$ compounds we have considered the propylene because this is the one which is produced at almost like 50% rate of whatever the rate ethylene is produced in steam cracking of hydrocarbons as well as the other processes, right? Actually, propylene is also produced along with the ethylene and acetylene in the same process of steam cracking of hydrocarbons that is what we have seen not only ethylene, acetylene, propylene, but also propane, butane, butylene, butadiene, etc. These kinds of products are also produced when we do the steam cracking of hydrocarbons that is what we have seen. The same thing we have seen twice actually we have seen in the complex flowcharts part when we started discussing the petroleum industry as well as in the previous chapter where we were discussing the chemicals production from $C_1$ and $C_2$ compounds. So, there for the production of ethylene and acetylene because under the $C_2$ compounds category we have considered the ethylene and acetylene and then how to produce this ethylene and acetylene from the resources like hydrocarbons like naphtha, etc.

that is what we have seen. So, there we have discussed the steam cracking of hydrocarbons to produce ethylene, acetylene and in the same process we also got the propylene and then from the applications point of view what we have ethylene is the one which is having the huge number of applications out of the all olefins ethylene is the most important one because of such applications, huge number of applications. Applications in the sense you can produce large number of intermediates and then end chemicals from ethylene. After the ethylene, propylene is the such important component because from the propylene also you can produce large number of intermediate as well as the end chemicals. So, under the category of olefins first we taken the ethylene now then we started discussing about the propylene and then compounds derived from the propylene.

So that we realized the importance of propylene through the consumption pattern where we have seen from the propylene we can produce huge number of synthetic chemicals out of which we have selectively considered 8 different types of synthetic chemicals and then we have discussed their production process. They include synthetic glycerol or glycerin, isopropyl alcohol or isopropanol, acetone, cumene, acrylonitrile, isoprene, propylene oxide and butanol from propylene by oxo process. For all of these chemicals we discussed their pertinent properties. We discussed the methods of production of such chemicals and then selectively we have taken a 1 or 2 methods and then we discussed corresponding chemical reactions of such methods. Then we discussed the process through flowchart and then engineering problems and end uses.

This is what we have discussed in the previous couple of lecture in this particular chapter. Now we will be discussing the production of different types of synthetic chemicals from $C_4$ compounds. $C_4$ compounds in the sense butanes or butylenes are both.

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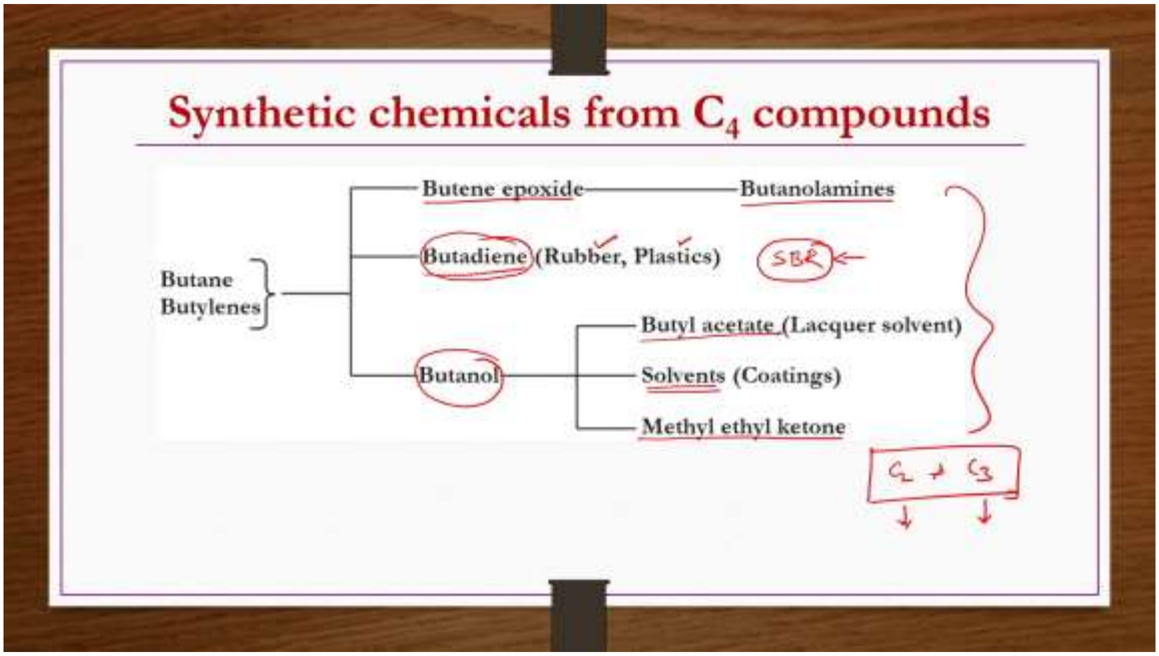

Synthetic chemicals from $C_4$ compounds

Butane
Butylenes

Butene epoxide — Butanolamines

Butadiene (Rubber, Plastics) SBR

Butanol
- Butyl acetate (Lacquer solvent)
- Solvents (Coatings)
- Methyl ethyl ketone

$C_2 + C_3$

So, here first we have a pictorial representation of what kind of synthetic chemicals you can produce from the butane or butylenes. So, then we have option of butylene epoxide which can be further converted to the butanolamines.

You can produce butadiene which is largely used for the plastics and rubbers especially in SBR that is styrene butadiene rubber in that one it is primarily used. It is also used for other kind of rubbers manufacturing as well which we will be discussing in polymerization industry chapter as well as the rubber industry chapter which we will be discussing subsequently. Then we can also produce butanol from the $C_4$ compounds. These butanols primarily used as solvents or to produce butyl acetate, methyl ethyl ketone. Now what you can understand from this chart that you know compared to the chemicals that you can produce from $C_2$ and then $C_3$ compounds less number of chemicals are being produced from $C_4$ compounds.

That is the reason most of the importance were also given for the production of different types of chemicals from $C_2$ and $C_3$ compounds of olefin category that is ethylene and then propylene respectively. Now in this lecture primarily we will be discussing production of butadiene by different processes and then conclude this particular chapter.

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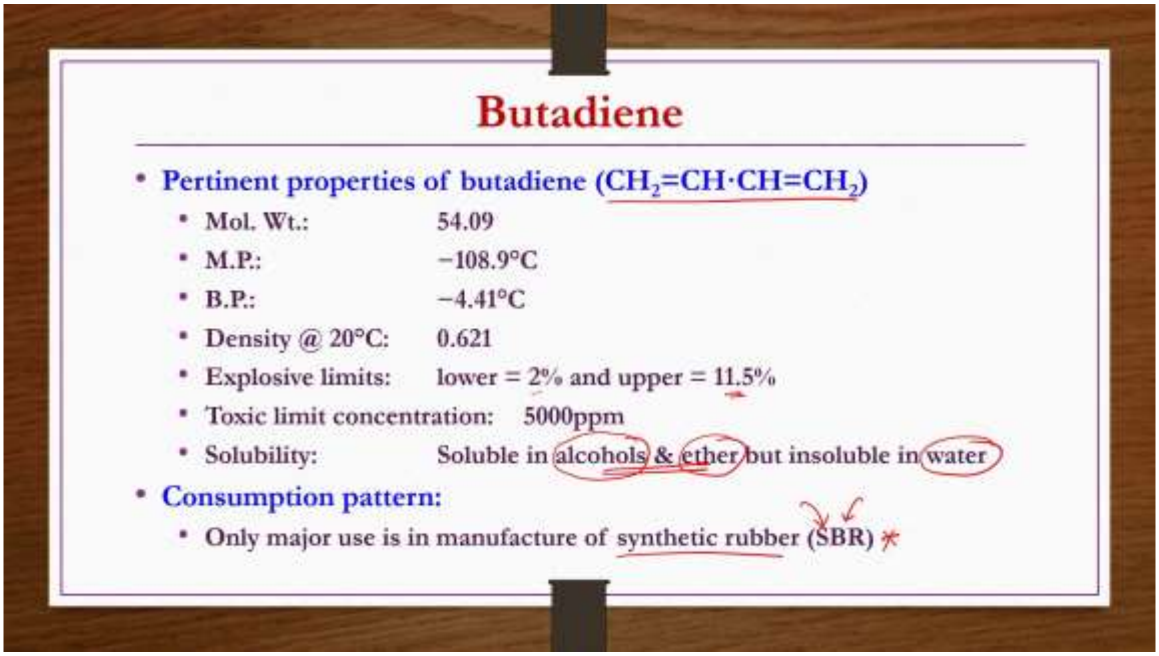

## Butadiene

- Pertinent properties of butadiene ($CH_2=CH \cdot CH=CH_2$)
  - Mol. Wt.: 54.09
  - M.P.: −108.9°C
  - B.P.: −4.41°C
  - Density @ 20°C: 0.621
  - Explosive limits: lower = 2% and upper = 11.5%
  - Toxic limit concentration: 5000ppm
  - Solubility: Soluble in alcohols & ether but insoluble in water
- Consumption pattern:
  - Only major use is in manufacture of synthetic rubber (SBR) *

Butadiene it is nothing but $CH_2$ double bond CH CH double bond $CH_2$. First, we will have a pertinent properties of butadiene. Molecular weight is 54.09, melting point is minus 108.9 degrees centigrade, boiling point is minus 4.41 degrees centigrade, density at 20 degrees centigrade is 0.621 gram per cc, explosive limits lower and upper limits are 2 and 11.5% respectively whereas toxic limit is 5000 ppm.

It is soluble in alcohols and then ether but not soluble in water that is the reason it is mostly used to make a rubber. Consumption pattern, only marketable use of this particular butadiene is in the manufacturing of synthetic rubber especially SPR, styrene butadiene rubber. Production of this SPR also we are going to discuss in the last chapter of the course which is on rubber industry, okay? Whereas the production of other monomer styrene we will be discussing in the polymerization chapter of the particular course, okay?

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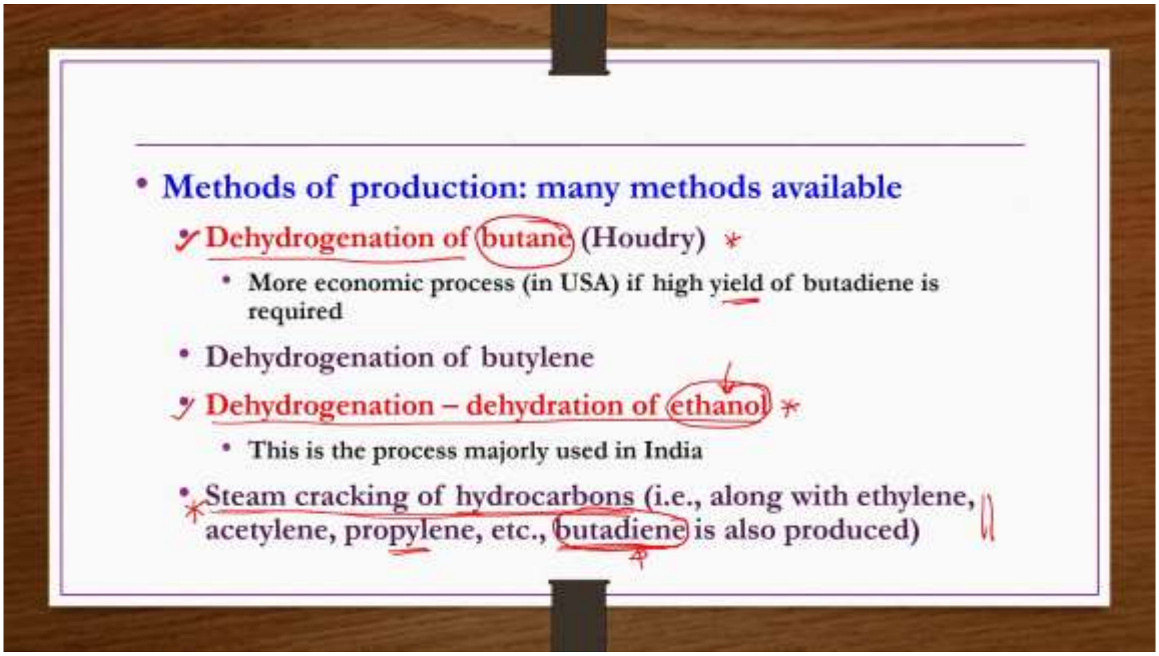

- Methods of production: many methods available
  - Dehydrogenation of butane (Houdry)
    - More economic process (in USA) if high yield of butadiene is required
  - Dehydrogenation of butylene
  - Dehydrogenation – dehydration of ethanol
    - This is the process majorly used in India
  - Steam cracking of hydrocarbons (i.e., along with ethylene, acetylene, propylene, etc., butadiene is also produced)

Methods of production, many methods are available but however 4 important commercial methods are shown here. First one is the dehydrogenation of butane, Houdry process. Second one is the dehydrogenation of butylene.

Third one is the dehydrogenation and dehydration of ethanol. Fourth one is the steam cracking of hydrocarbons. Remember when we were discussing the production of ethylene and acetylene from hydrocarbons, we have done the steam cracking of hydrocarbons and then we got that ethylene and acetylene. Along with the ethylene, acetylene so many other products were also produced like propylene, propane, butylene, butane, some aromatics, etc. In there we also got butadiene also.

So, the same process may be optimized or tuned such a way that more of the butadiene can be produced, okay? So, that is one of the process which we have already discussed. So, then we are not going to discuss this one. Whereas this dehydrogenation of butane process is very much famous in USA because it is more economic and then if you want high yield, then also it is better to go for this process, but that depends on how much resources are you having for this butane that also makes difference. If you do not have butane resource, then you cannot do the dehydrogenation to produce the lot of butadiene because butane is also having other applications, right? Next one is that in India mostly we use this dehydrogenation, dehydration of ethanol. This process we particularly use in India because of a lack of resources of butane, but ethanol we have lot of natural ethanol by fermentation industry, by corn fermentation you get lot of ethanol.

So, that ethanol you can take and do the dehydrogenation to get the acetaldehyde, than react that acetaldehyde with excess of ethanol to get the butadiene, okay? So, this process also we are going to discuss. So, these 2 processes we are going to discuss. In addition to this one, there is another process oxydehydrogenation of butane to get the butadiene. So, that third process also we are going to discuss in this particular lecture, okay?

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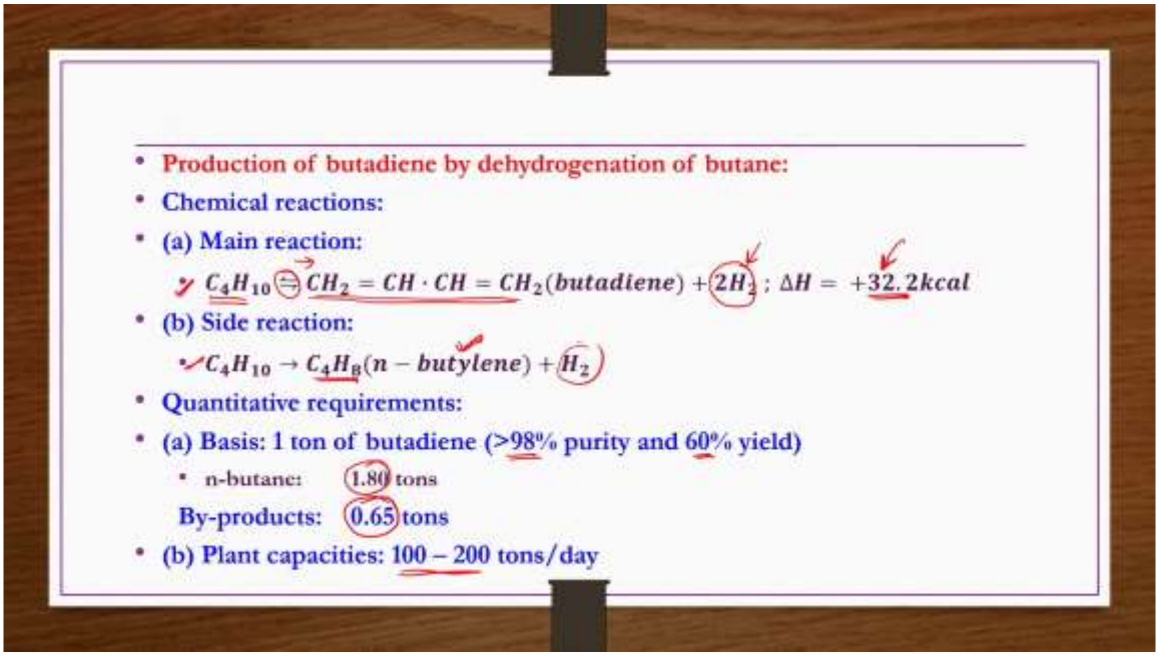

- Production of butadiene by dehydrogenation of butane:
- Chemical reactions:
- (a) Main reaction:

  $C_4H_{10} \rightleftharpoons CH_2 = CH \cdot CH = CH_2(butadiene) + 2H_2\ ;\ \Delta H = +32.2kcal$
- (b) Side reaction:

  $C_4H_{10} \rightarrow C_4H_8(n - butylene) + H_2$
- Quantitative requirements:
- (a) Basis: 1 ton of butadiene (>98% purity and 60% yield)
  - n-butane: 1.80 tons

  By-products: 0.65 tons
- (b) Plant capacities: 100 – 200 tons/day

So, let us start discussion on production of butadiene by dehydrogenation of butane. If you see the chemical reactions, main reaction is that this butane whatever is there that reversibly undergoes to produce butadiene by dehydrogenation reaction releasing hydrogen and then it is endothermic reaction, okay? This is the main reaction and then it is reversible reaction.

So, the conditions you have to make such a way that this reaction moves forward in the positive direction or right side direction so that you can produce butadiene. Otherwise, reversible reaction takes place and then you may get the butane also, okay? So, that is one important thing and then lot of energy is required because it is endothermic reaction and then how to get that energy also is very important to see that we discuss in flow chart. Side reaction, this butane would also be producing n-butylene $C_4H_8$ by the same dehydrogenation reaction. So, when you do the dehydrogenation of butanes, so not only the butadiene, you will also get the n-butylene as well because when you do the dehydrogenation, both of them are being produced and then the main reaction if you do not control towards the positive or right side direction, you may also have the butane production from the butadiene because of the reversible reaction. Quantitative requirements, if you wanted to produce 1 ton of butadiene having more than 98 percent purity and 60 percent yield, only raw material that you required is 1.8 tons because you are doing the dehydrogenation of butane and then for that you need 1.8 tons of butane to produce 1 ton of butadiene of having more than 98 percent purity. There would also be byproducts like butylene and then other kind of products as we are going to see in the flow chart, they would be approximately 0.65 tons. Capacity of the plant is usually 100 to 200 tons per day.

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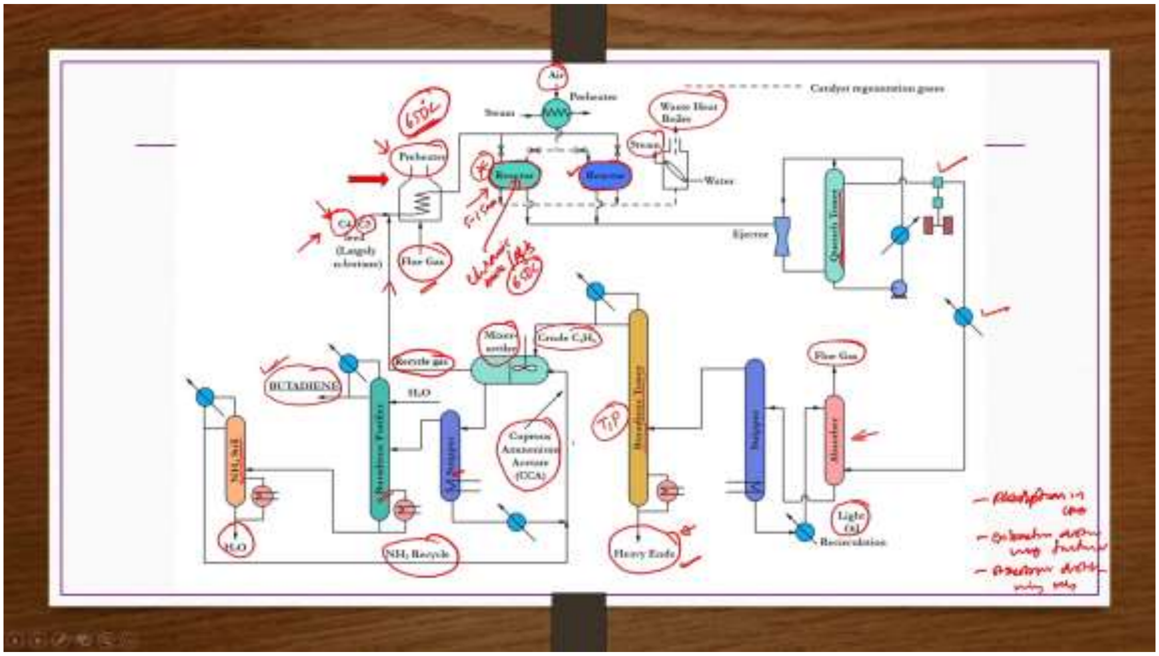

So, this is the flow chart, we will first discuss how to get the butadiene by doing the dehydrogenation of butane. So, for this process what you take? You take $C_4$ and $C_5$ cut of refinery stream primarily having butane and then slightly small amount of isopentane would also be there that you cannot avoid otherwise you know lot of energy and money you may be supplying to purify this raw material itself so which is not required. So, if you have a refinery cut fraction which is largely having butane is good enough, that mixture should be preheated using the flue gas. So, not only that particular mixture, there are also some kind of recycle gases, they will also be mixed with the feed fraction and then they will be preheated to the required temperature of something like 650 degrees centigrade. So, that is the temperature required for the dehydrogenation of n-butane to take place but such high temperature you may not get by the preheating itself.

So, you may get around 250 to 300 degrees centigrade temperature by preheating that preheated feed you take to the reactor system. This reactor system is having a adiabatic cycle of a make period which is taking place in one reactor and another reactor is the regeneration period. So, that is taking place in the second reactor. In the make period, the time is approximately 5 to 15 minutes, within this 5 to 15 minutes whatever the preheated reactant and recycle gases are there, they will be undergoing the dehydrogenation and then you get the butadiene produced. So here in this reactor, the catalyst required is the chromic oxide supported on porous alumina, so that catalyst you use and then in the reaction the temperature required is 650 degrees centigrade and in the reactor required temperature of 650 degrees centigrade should be maintained.

For that purpose, what you do, you supply the preheated air or the steam again that is also possible. So, after 15 minutes of make-up period what happens, regeneration period takes place. What do you mean by regeneration? During the make period, some of the carbonaceous material would be deposited on the catalyst surface. So, that catalyst has to be regenerated. So, that catalyst would be heated up with a preheated air which is at approximately 400 degrees centigrade.

So, that what happens whatever the carbonaceous material deposited on the catalyst surface is there that would be combusted off. So, when this combustion of the carbonaceous material deposited on the catalyst surface takes place, lot of energy would be evolved and that energy would be utilized to maintain the required temperature of 650 degrees centigrade in the reactor to have the make period taking place periodically. So, 5 to 15 minutes you do the make period where the reaction undergoes and then after 15 minutes, another 10 minutes what you do? You do the regeneration of the catalyst and then this cycle continues until the required yield of the butadiene you get it. So, here after utilizing the energy released by the combustion of carbonaceous material that was deposited on the catalyst surface that is most of that energy is utilized by the make period for the dehydrogenation of n-butane to take place on chromic oxide supported on alumina catalyst, but still some energy may also be there. So, that would be taken to the waste heat boiler to produce steam and then utilize for the other heating purposes of the system.

So, after this cycle of makeup and regeneration cycle whatever the products are there through the ejector you take to the quench tower, then you compress the products, cool them and then you take to the absorption tower where absorption is done using the light oil. Usually naphtha fractions are used as light oil for the absorption purpose here. So, where you release the flue gas and then you can reuse them for a preheating purpose of the reactants. After the absorption you do the required stripping and then after the stripping you take the mixture to the butadiene tower where whatever the heavy ends are there you collect from the bottom of the tower temperature and pressure of the tower are maintained such a way that most of the or almost all heavy ends are collected from the bottom. From the top you get butadiene but which is still crude it is not purified.

So, in order to make the purity of this crude butadiene or in order to increase the purity of this butadiene to 98 to 99 percent different options are there that is in the one of the option is the absorption in cuprous ammonium acetate solution, then extractive distillation using furfural and then azeotropic distillation using ammonia. Any of these 3 methods may be used. So, let us say if you use the absorption process which is the best one. So, here this crude butadiene is mixed with the absorption solution of cuprous ammonium acetate in a mixer to which ammonia is also being supplied. While the absorption is taking place in this tower in the settler what will happen you know some of the gases would also be released and then they would be recycled back to the preheater along with the reactants.

The liquids from the mixer would be taken to stripper followed by butadiene purifier so that to get the 99 more than 98 percent butadiene as a top product from the butadiene purifier. Whereas from the bottom of the stripper as well as the bottom of the butadiene purifier you may get the ammonia that you can recycle back to the mixer settler along with this CA so that the required absorption of impurities take place in this CA solution. Then this ammonia whatever is there that you can directly recycle back to the mixer settler or you can take it to the ammonia still and then make it anhydrous ammonia by removing the water from the bottom of the ammonia still and then from the top anhydrous pure ammonia you can get that also you can recycle both the option can be done.

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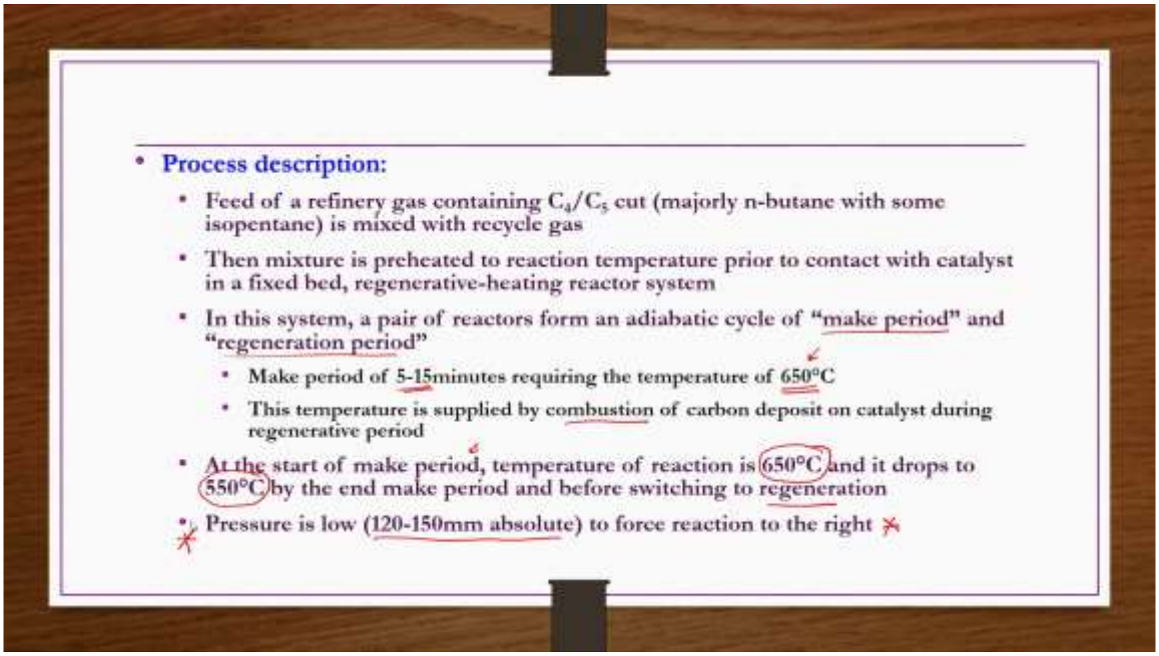

- **Process description:**
  - Feed of a refinery gas containing $C_4/C_5$ cut (majorly n-butane with some isopentane) is mixed with recycle gas
  - Then mixture is preheated to reaction temperature prior to contact with catalyst in a fixed bed, regenerative-heating reactor system
  - In this system, a pair of reactors form an adiabatic cycle of "make period" and "regeneration period"
    - Make period of 5-15minutes requiring the temperature of 650°C
    - This temperature is supplied by combustion of carbon deposit on catalyst during regenerative period
  - At the start of make period, temperature of reaction is 650°C and it drops to 550°C by the end make period and before switching to regeneration
  - Pressure is low (120-150mm absolute) to force reaction to the right

Process description feed off a refinery gas containing $C_4$ to $C_5$ cut majorly n-butane with some isopentane is mixed with recycled gas. Then mixture is preheated to reaction temperature prior to contact with catalyst in a fixed bed regenerative heating reactor system.

In this system a pair of reactors form an adiabatic cycle of make period and regeneration period. Make period of 5 to 15 minutes requiring the temperature of 650 degrees centigrade. So, at the beginning of the make period the required temperature of 650 degrees centigrade should be there but as the make period progressively most increases like towards the 15 minutes then temperature decreases to 550 degrees centigrades. This temperature is supplied by combustion of a carbon deposit on catalyst during regenerative period. At the start of make period temperature of reaction is 650 degrees centigrades and it drops to 550 degrees centigrades by the end make period and before switching to regeneration.

Pressure is low 120 to 150 mm absolute to force the reaction to the right. So, this is one of the important thing because we wanted the reaction to progress towards the positive direction or right direction for that you need to maintain the low pressure.

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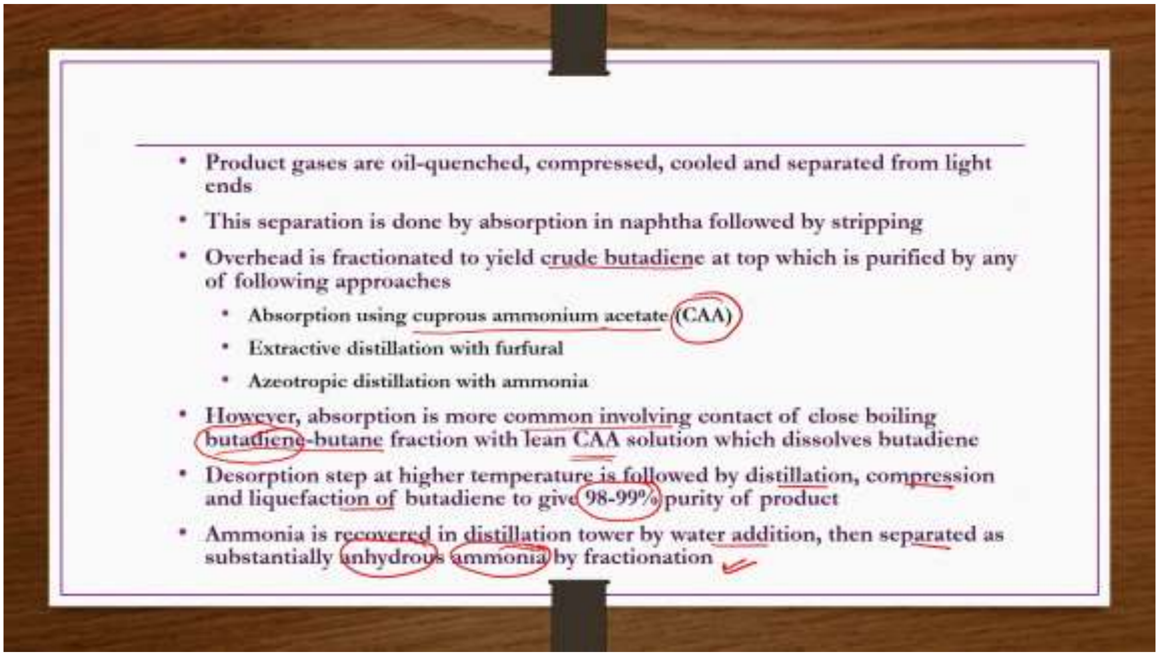

- Product gases are oil-quenched, compressed, cooled and separated from light ends
- This separation is done by absorption in naphtha followed by stripping
- Overhead is fractionated to yield crude butadiene at top which is purified by any of following approaches
  - Absorption using cuprous ammonium acetate (CAA)
  - Extractive distillation with furfural
  - Azeotropic distillation with ammonia
- However, absorption is more common involving contact of close boiling butadiene-butane fraction with lean CAA solution which dissolves butadiene
- Desorption step at higher temperature is followed by distillation, compression and liquefaction of butadiene to give 98-99% purity of product
- Ammonia is recovered in distillation tower by water addition, then separated as substantially anhydrous ammonia by fractionation

Product gases are oil quenched compressed cooled and separated from light ends. This separation is done by absorption in naphtha followed by stripping. Overhead is fractionated to yield crude butadiene at the top which is purified by any of the following approaches.

Absorption using cuprous ammonium acetate, extractive distillation with perforal or azeotropic distillation with ammonia any of the 3 methods can be utilized. However, absorption is more common involving contact of close boiling butadiene butane fraction with lean cuprous ammonium acetate solution which dissolves butadiene. The solution is selected because in this solution actually butadiene is dissolved in more percentages compared to the butylenes. So, whatever the butylene impurities are also there along with the unreacted butane etcetera, they will be less dissolvable in this cuprous ammonium acetate solution. So, most of the butadiene will get into the solution cuprous ammonium acetate solution and then after that what you do, you do the stripping of this butadiene from the solution and then recycle the solution and then whatever the butadiene that you get that you can utilize for the further purification under the butadiene purification section of distillation.

Using the butadiene column you can further purify the butadiene percentage and then increase it to the 98 or more percentage. Desorption step at higher temperature is followed by distillation, compression and liquefaction of butadiene to give 98 to 99 percent purity of product. So, this we have already discussed in the flowchart. Ammonia is recovered in distillation tower by water addition then separated as substantially anhydrous ammonia by fractionation. So, that ammonia solution itself you can recycle or what you can do you can purify the ammonia solution to get the anhydrous ammonia and then you recycle it back to the mixer settler column.

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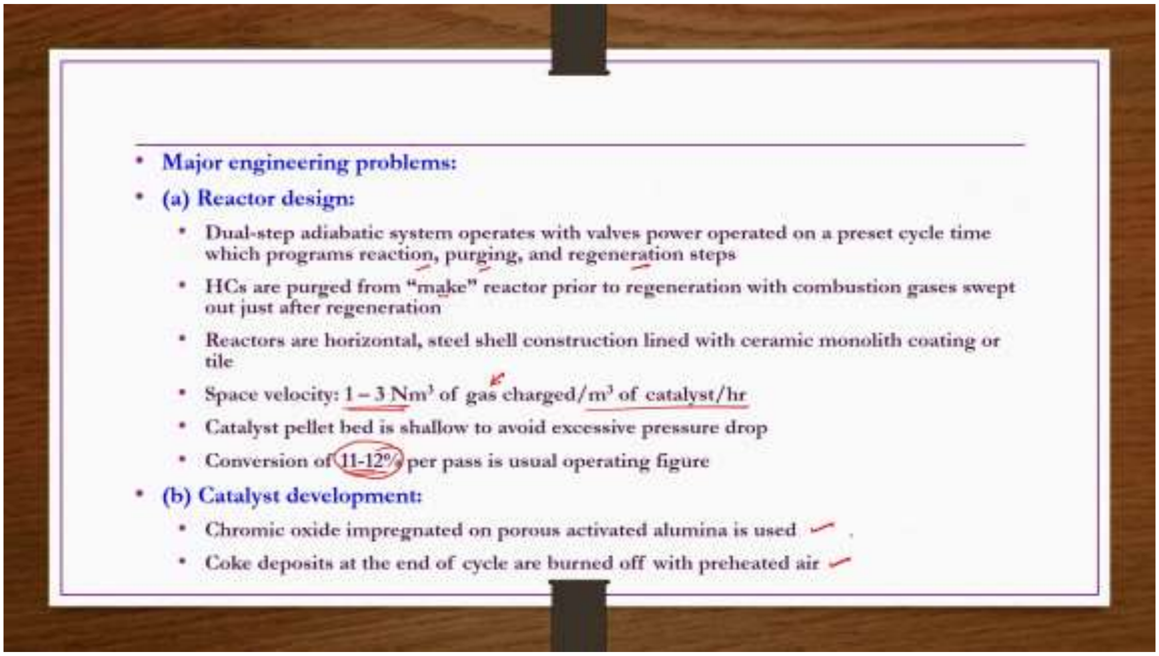

- **Major engineering problems:**
- **(a) Reactor design:**
  - Dual-step adiabatic system operates with valves power operated on a preset cycle time which programs reaction, purging, and regeneration steps
  - HCs are purged from "make" reactor prior to regeneration with combustion gases swept out just after regeneration
  - Reactors are horizontal, steel shell construction lined with ceramic monolith coating or tile
  - Space velocity: 1 – 3 $Nm^3$ of gas charged/$m^3$ of catalyst/hr
  - Catalyst pellet bed is shallow to avoid excessive pressure drop
  - Conversion of 11-12% per pass is usual operating figure
- **(b) Catalyst development:**
  - Chromic oxide impregnated on porous activated alumina is used
  - Coke deposits at the end of cycle are burned off with preheated air

Major engineering problems of this particular method are provided here. The reactor design is one of the important thing because here you have to make sure that make period and then regeneration period. Dual step adiabatic system operates with walls power operated on a preset cycle time which programs the reaction, purging and regeneration steps. So, most of them are automated in general. Hydrocarbons are purged from make reactor prior to the regeneration with combustion gases swift out just after the regeneration.

Reactors are horizontal steel shell construction lined with ceramic monolith coating or tiles. Space velocities that is maintained in the process is 1.3 normal cubic meters of gas charged to the reactor per meter cube of catalyst per hour. Catalyst pellet bed is shallow to avoid excessive pressure drop. Conversion of 11 to 12 percent only purpose is usual operating figure that is the reason lot of recycling is required here.

Catalyst development, chromic oxide impregnated on porous activated alumina is used. Coke deposits at the end of cycle are burned off with the preheated aid and then whatever the energy released because of the combustion that would be utilized to maintain the temperature in the make period reactor.

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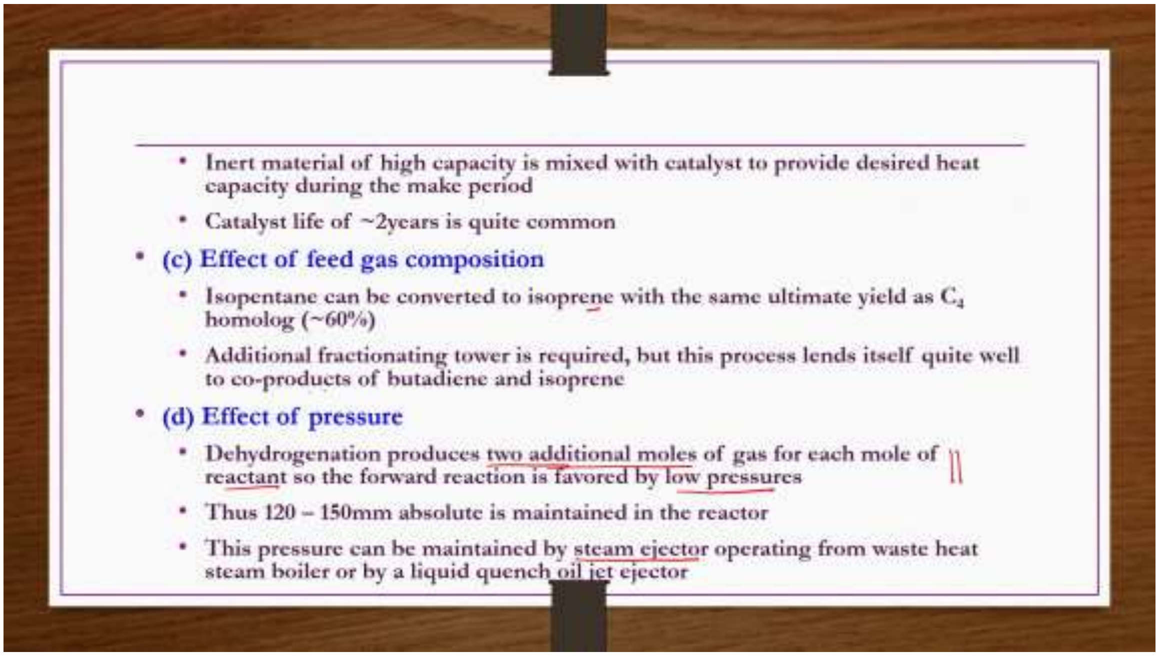

- Inert material of high capacity is mixed with catalyst to provide desired heat capacity during the make period
- Catalyst life of ~2years is quite common

- (c) Effect of feed gas composition
  - Isopentane can be converted to isoprene with the same ultimate yield as $C_4$ homolog (~60%)
  - Additional fractionating tower is required, but this process lends itself quite well to co-products of butadiene and isoprene
- (d) Effect of pressure
  - Dehydrogenation produces two additional moles of gas for each mole of reactant so the forward reaction is favored by low pressures
  - Thus 120 – 150mm absolute is maintained in the reactor
  - This pressure can be maintained by steam ejector operating from waste heat steam boiler or by a liquid quench oil jet ejector

Inert material of high capacity is mixed with catalyst to provide desired heat capacity during the make period. Catalyst life is approximately 2 years and which is very quite common. Effect of feed gas composition, isopentane can be converted to isoprene with the same ultimate yield as $C_4$ homolog of approximately 60 percent.

Additional fractionating tower is required, but this process lends itself quite well to coproducts to butadiene and isoprene and effect of pressure. Dehydrogenation produces 2 additional moles of gas for each mole of reactant. So, the forward reaction is favored by the low pressure. So, that is the reason 120 to 150 mm absolute pressure is maintained. This pressure can be maintained by steam ejector operating from waste heat steam boiler or by a liquid bench oil jet ejector.

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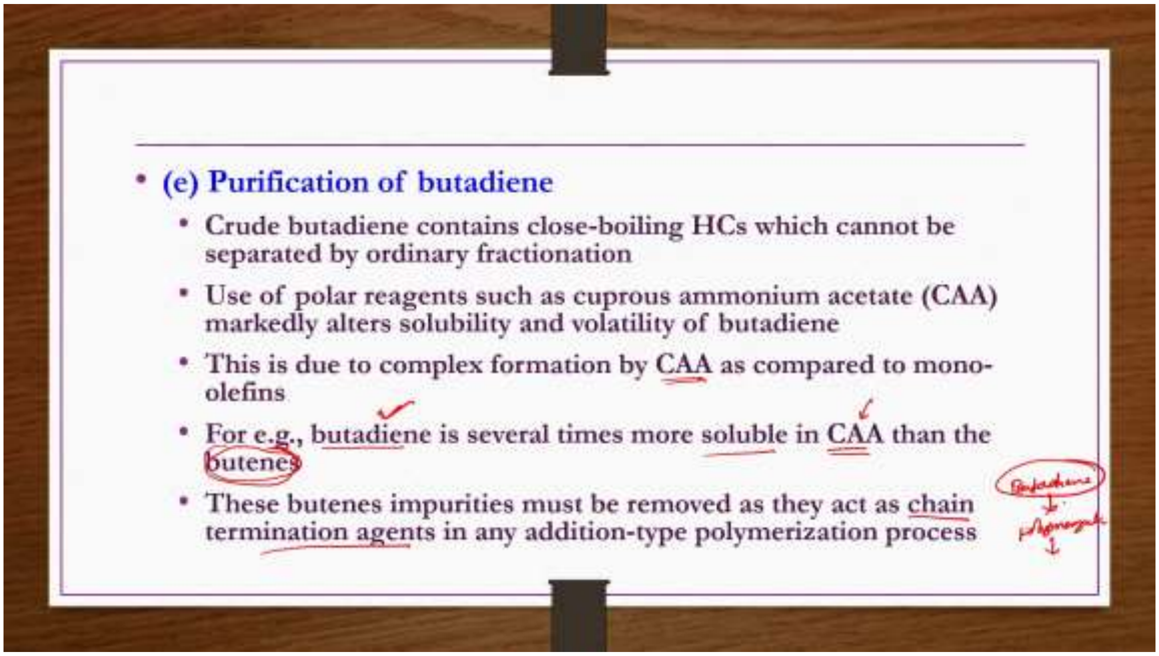

- **(e) Purification of butadiene**
  - Crude butadiene contains close-boiling HCs which cannot be separated by ordinary fractionation
  - Use of polar reagents such as cuprous ammonium acetate (CAA) markedly alters solubility and volatility of butadiene
  - This is due to complex formation by CAA as compared to mono-olefins
  - For e.g., butadiene is several times more soluble in CAA than the butenes
  - These butenes impurities must be removed as they act as chain termination agents in any addition-type polymerization process

Butadiene
↓
Polymerizat
↓

Last important engineering problem is the purification of butadiene because in the mixture so many other components like butylenes, unreacted butane and then because of the absorption some kind of naphtha and so many things are there. So, we have seen after the reaction the purification for the purification so many unit operations are involved in the flowchart. So, purification of butadiene from the reaction mixture is also very important part in fact very important engineering problem. Crude butadiene contains close boiling hydrocarbons which cannot be separated by ordinary fractionation for that reason you have to go either extractive distillation or azeotropic distillation. Use of polar reagents such as cuprous ammonium acetate markedly alter solubility and volatility of butadiene.

This is due to the complex formation by CAA as compared to mono olefins. For example, butadiene is several times more soluble in this particular cuprous ammonium acetate reagent than the butene. So, butenes will be dissolved very less. So, after the absorption in the solution primarily you will be having butadiene which you can release by stripping after the absorption unit. These butenes impurities must be removed as they act as chain termination agents in any addition type polymerization process because the purpose of butadiene that we are producing so that to do the polymerization.

So, this polymerization can be effective if the butadiene is as much pure as possible or very high purity is required. In fact, high purity is required rather saying as much as purity. So, if the butenes are present along with this butadiene they will be leading to chain termination reactions. In polymerization you want chain to propagate not to terminate. So, that is all about the production of a butadiene by dehydrogenation of butane.

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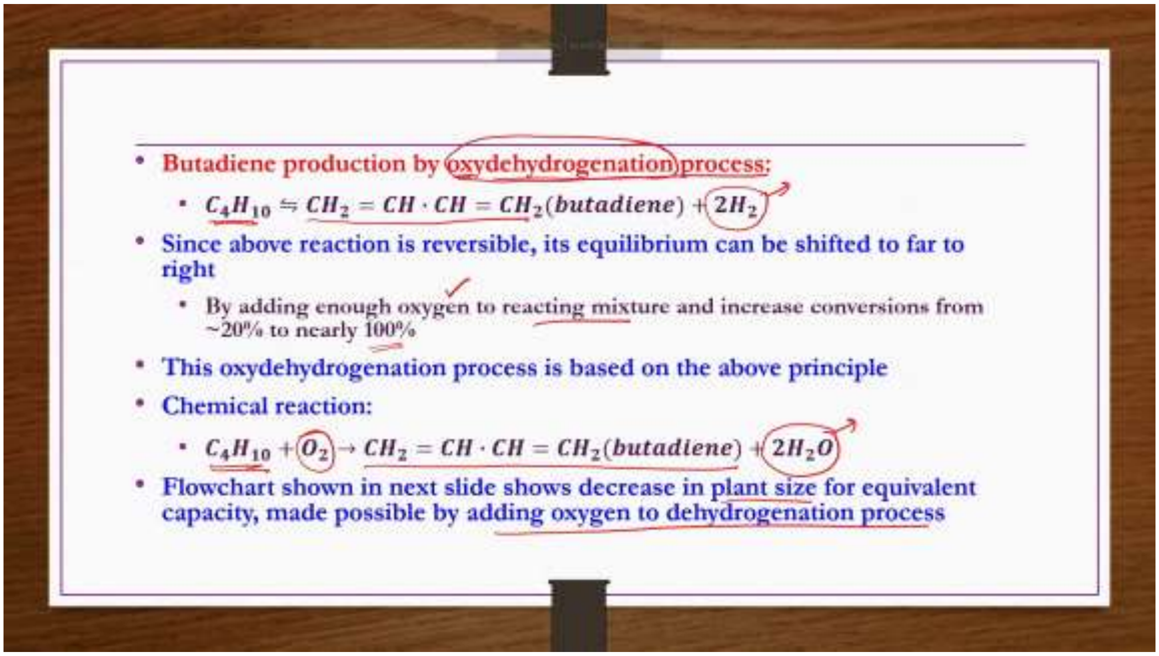

- Butadiene production by oxydehydrogenation process:
  - $\underline{C_4H_{10}} \leftrightharpoons CH_2 = CH \cdot CH = CH_2(butadiene) + \boxed{2H_2}$
- Since above reaction is reversible, its equilibrium can be shifted to far to right
  - By adding enough oxygen to reacting mixture and increase conversions from ~20% to nearly 100%
- This oxydehydrogenation process is based on the above principle
- Chemical reaction:
  - $\underline{C_4H_{10}} + \boxed{O_2} \rightarrow CH_2 = CH \cdot CH = CH_2(butadiene) + \boxed{2H_2O}$
- Flowchart shown in next slide shows decrease in plant size for equivalent capacity, made possible by adding oxygen to dehydrogenation process

But now with little modification same process we discuss once again that is butadiene production by oxo dehydrogenation process. So, that means, we have to see the reaction again. So, whatever this butane is there that undergoes reversibly to butadiene by dehydrogenation reaction releasing hydrogen here. Now this reaction has to move forward positive direction right direction then only it is better, but that is not easy for that purpose you are maintaining low pressure and then in order to maintain the low pressure you are using ejectors, etc. So, your equipment cost and all that increasing, but there is another alternative.

If you add excess oxygen to the reactants then what happens this reaction moves forward in the positive direction. So, that is what the principle of this particular process and then that is what the name also modified as oxydehydrogenation process rather just dehydrogenation process. Since above reaction is reversible its equilibrium can be shifted too far to right by adding enough oxygen to reacting mixture whatever the butane, isopentane and recycle gas mixture is there to that if you add enough oxygen, then this reaction moves towards the right and increases conversion from roughly 20% to nearly 100%. In the dehydrogenation process, the conversion was very less that is the reason we had several times recycling and all that, but here by simply adding oxygen to the reactant mixtures, not only the reaction progresses more towards the right, but also increases conversion to nearly 100%.

Such good is the advantage of this process. This oxydehydrogenation process is based on the above principle. Chemical reaction if you see now simply in the left hand side you are also adding oxygen to the butane you are adding oxygen to get the butadiene product plus water rather getting the $H_2$ you are getting now water $H_2O$. Flow chart shown in next slide shows decrease in plant size for equipment capacity and it is made possible by adding oxygen to dehydrogenation process. Previous flow chart on dehydrogenation of butane we have seen after the reaction so many steps are required to do the purification and all that. Now here just by adding oxygen to the reactant mixture, you can see the plant size has substantially decreased by comparison in this particular flow chart.

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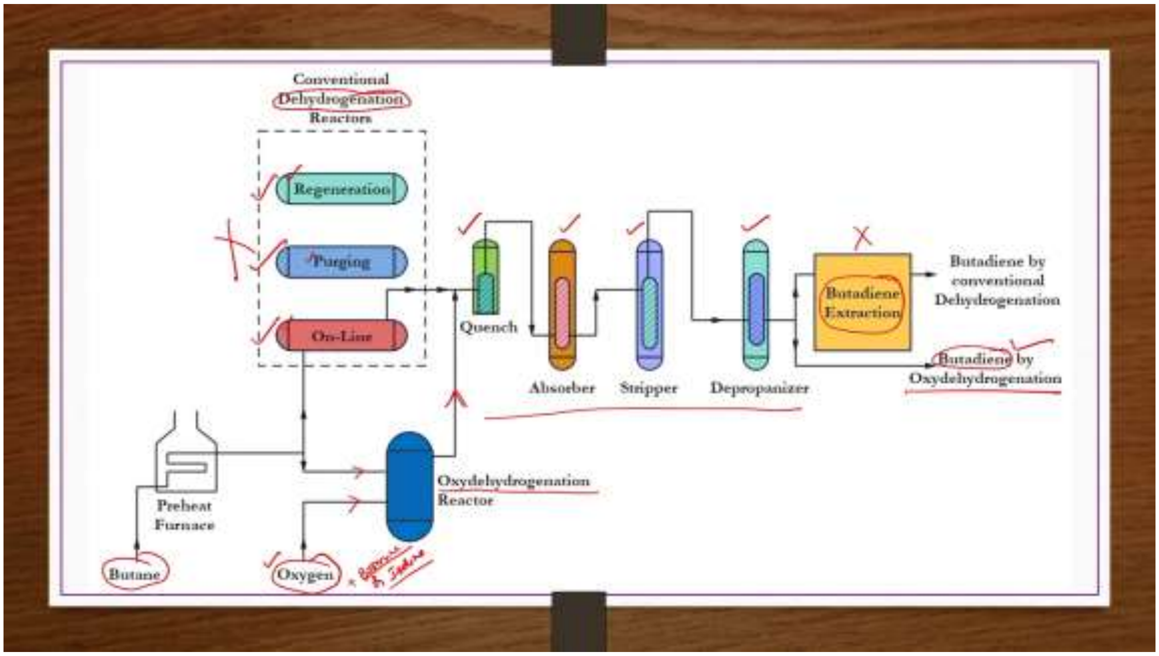

So, here this is the flow chart not only for oxydehydrogenation process, but also a comparison is shown with the conventional dehydrogenation process as well. So, let us say in the conventional process what you take, what you do or what we have done and just concluded topic. We have taken butane and then preheated it by using preheat furnace and then passed it through reactors having adiabatic cycle of make period and regeneration period using dehydrogenation reactors. There you have online programming, purging, regeneration all these steps are there and then after that the squinching, absorption stripping are there and then this butadiene extraction are there. But now along with the butane if you also add oxygen plus some promoters like bromine or iodine to the reactor.

So, now butane you are preheating and then supplying to the oxydehydrogenation reactor and then to that reactor you also supply the oxygen along with some promoters like bromine and iodine halogens. Then what happens directly you get the butadiene of sufficient purity with high conversion and then that can be directly done quenched to reduce the temperature of the product mixture then do the absorption in CAA and then stripping and then finally do the depropanizer if at all some propanes are formed and then finally you get the butadiene product. So now whatever these steps required in the conventional dehydrogenation reactors process is not required in this process and then whatever this butadiene extraction liquefaction, etc. that we have done that is also not required in the oxydehydrogenation process. So, what you can understand that the plant size also sufficiently reduced by this oxydehydrogenation process.

So, obviously your capital cost is decreased as well as you are maintaining operational cost would also be decreased because you may also be giving some funds to maintain and then operate these additional unit operations which are not required in the case of oxydehydrogenation process. So, this is a comparison between the dehydrogenation of butane and then oxydehydrogenation of butane processes.

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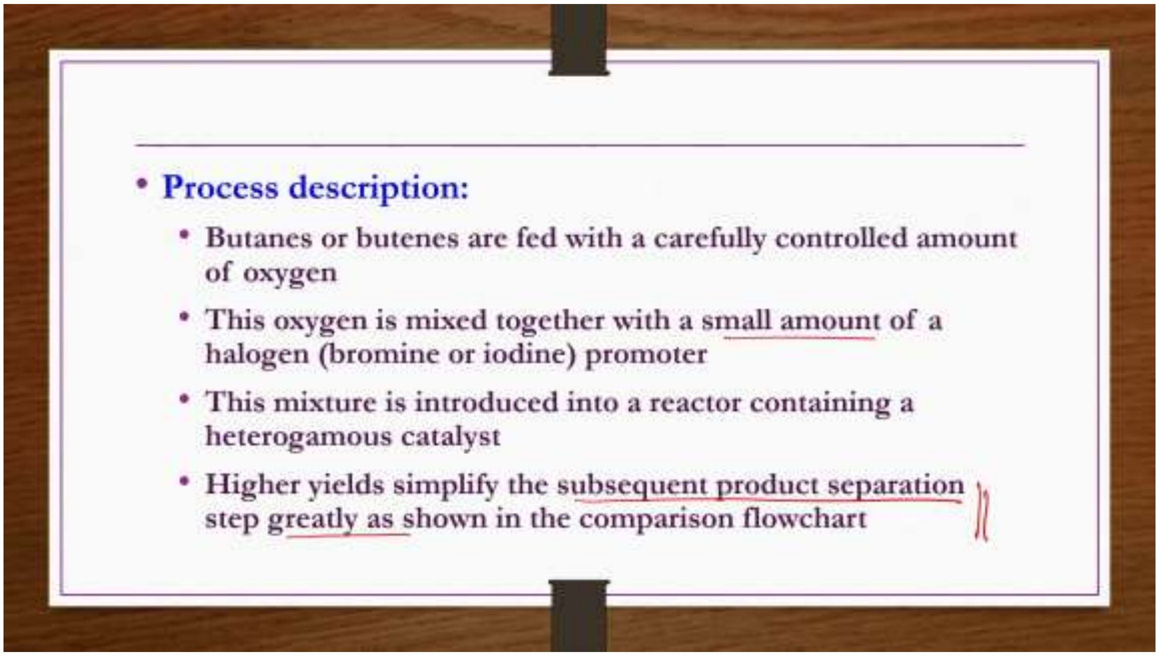

- **Process description:**
  - Butanes or butenes are fed with a carefully controlled amount of oxygen
  - This oxygen is mixed together with a small amount of a halogen (bromine or iodine) promoter
  - This mixture is introduced into a reactor containing a heterogamous catalyst
  - Higher yields simplify the subsequent product separation step greatly as shown in the comparison flowchart

Process description of oxydehydrogenation of butane process is provided here. Butanes or butanes are fed with a carefully controlled amount of oxygen that is essential. This oxygen is mixed together with a small amount of a halogen either bromine or iodine promoter.

This mixture is introduced into a reactor containing heterogeneous catalyst. Higher yields simplify the subsequent product separation step greatly as shown in the comparison flow chart because the yield is higher so then purification steps are not complicated or a little fewer number of equipment or unit operations are required for the separation of butadiene from the reaction product mixture.

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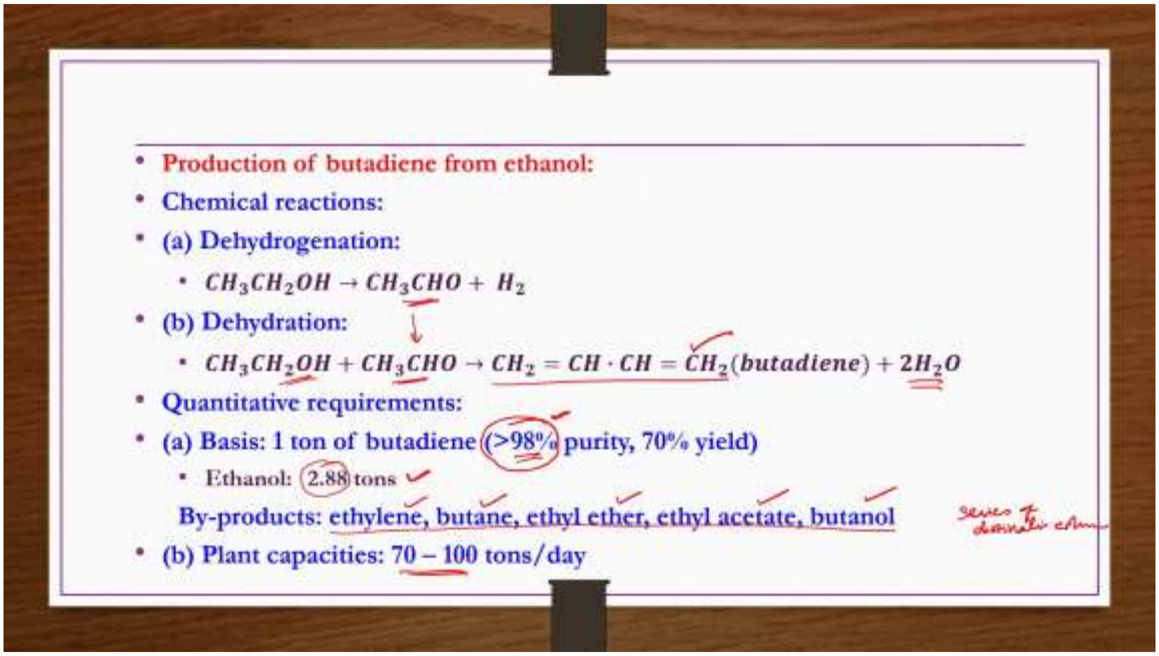

- Production of butadiene from ethanol:
- Chemical reactions:
- (a) Dehydrogenation:
  - $CH_3CH_2OH \rightarrow CH_3CHO + H_2$
- (b) Dehydration:
  - $CH_3CH_2OH + CH_3CHO \rightarrow CH_2 = CH \cdot CH = CH_2 (butadiene) + 2H_2O$
- Quantitative requirements:
- (a) Basis: 1 ton of butadiene (>98% purity, 70% yield)
  - Ethanol: 2.88 tons

  By-products: ethylene, butane, ethyl ether, ethyl acetate, butanol

  series of distillation colum
- (b) Plant capacities: 70 – 100 tons/day

Now, we discussed the third process that is production of butadiene from ethanol which is primarily used in India. Here we have 2 steps ethanol first you have to do the dehydrogenation to get the acetaldehyde then that acetaldehyde will react with excess ethanol to undergo dehydration step to produce butadiene. So, those reactions if you see first is dehydrogenation of ethanol to produce acetaldehyde.

Second reaction is the dehydration of ethanol where ethanol or excess ethanol reacting with the so called just now produced acetaldehyde to produce butadiene and then water. Quantitative requirements if you wanted to produce 1 ton of butadiene more than 98 percent purity 70 percent yield then ethanol requirement is 2.88 tons. This is the only you know reactant that is there and then this is undergoing dehydrogenation and dehydration reactions to get the butadiene.

Byproducts ethylene, butane, ethyl ether, ethyl acetate, butanol, etc. would be forming so many byproducts are there. So, you need series of distillation columns to separate them and it is essential also because this butadiene whatever is there that we primarily utilizing for the polymerization to get the rubber. But if the impurities are there they may be acting as inhibitors for the polymerization reactions which is not good. That is the reason high purity butadiene is required and then for that separation of all byproducts or coproducts is very essential. Plant capacity 70 to 100 tons per day.

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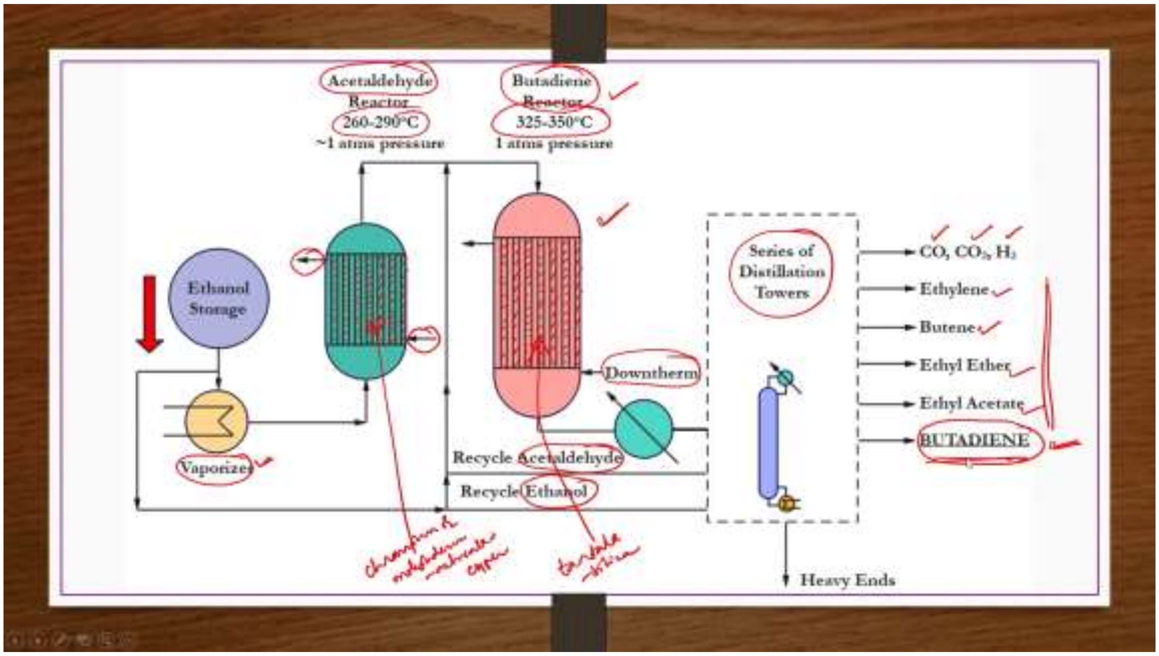

This is the flowchart here. So, from the ethanol storage you take ethanol and do the vaporization using the steam or heat exchangers then send it to a tubular reactor which is the first reactor which also known as the acetaldehyde reactor because in this reactor only dehydrogenation of ethanol takes place to produce acetaldehyde. So, we have a tubular reactors like this different tubes are there and then these tubes are filled with a catalyst. Through these tubes, in these tubes only the catalyst is fed, packed and then through these catalyst packed tubes the reactant which is vaporized ethanol is passing through. When vaporized ethanol pass through this catalytic bed then dehydrogenation of ethanol takes place and then you get acetaldehyde. The temperature required is 260 to 290 degrees integrates and then one atmospheric pressure is there.

What catalyst we use here in these tubes usually chromium or molybdenum activated copper catalyst is used in general here to get the acetaldehyde. So, in order to control the temperature of the dehydrogenation reactor there is a provision to supply the heat transfer fluids as well or the flue gases if you wanted to heat them. Now whatever the acetaldehyde that is been produced by the first reactor that would be mixed with ethanol vapors and then send it to the second reactor which is nothing but the butadiene reactor because in this reactor ethanol and acetaldehyde will react and then undergo dehydration reaction to produce butadiene. So, this reactor is also tubular reactor actually.

Different tubes are there of certain length and diameter. Length usually high like 6 meters, 5 meters something like that. Diameters but would be some 7, 8 centimeters like that it would be having diameter. So many number of tubes would be there in general like this.

They would be clustered or bundled and then arranged in a shell and then through these tubes only the reactant mixtures are passing through.

Here in this case the tubes are packed with a tantala silica catalyst. So, when the reactant mixture of acetaldehyde and ethanol interact with this catalyst at 325 to 350 degrees centigrade butadiene would be forming and along with the butadiene some kind of impurities byproducts would also be there. In order to maintain the temperature of this reactor here also to the shell of the reactor downtherm fluids are being provided so that to control the temperature. After the dehydration reaction whatever the product mixture is there that is cooled and then passed through a series of distillation towers because n number of distillation towers are required. Let us say 2, 3 components are only there to be separated.

So, we can show 3 distillation column. In the first distillation column highest volatile component would be separated out as top product. In the second distillation column intermediate volatile component would be separated as the top column and then in the last column whichever is the lowest volatile component is there that would be separated like 3 distillation columns you can show. But now here not only you need to separate unreacted acetaldehyde and ethanol but also you have to separate CO, $CO_2$, $H_2$, ethylene, butylene, ethyl, ether, ethyl acetate from the butadiene. So, so many units are required so rather showing so many units we are simply writing series of distillation towers to purify butadiene. Whereas the unreacted acetaldehyde and ethanol are there, they will be recycled back to the second reactor which is nothing but the butadiene reactor.

Process is simple but only thing that for the purification you need so many unit operations or distillation columns because so many byproducts are present along with the butadiene.

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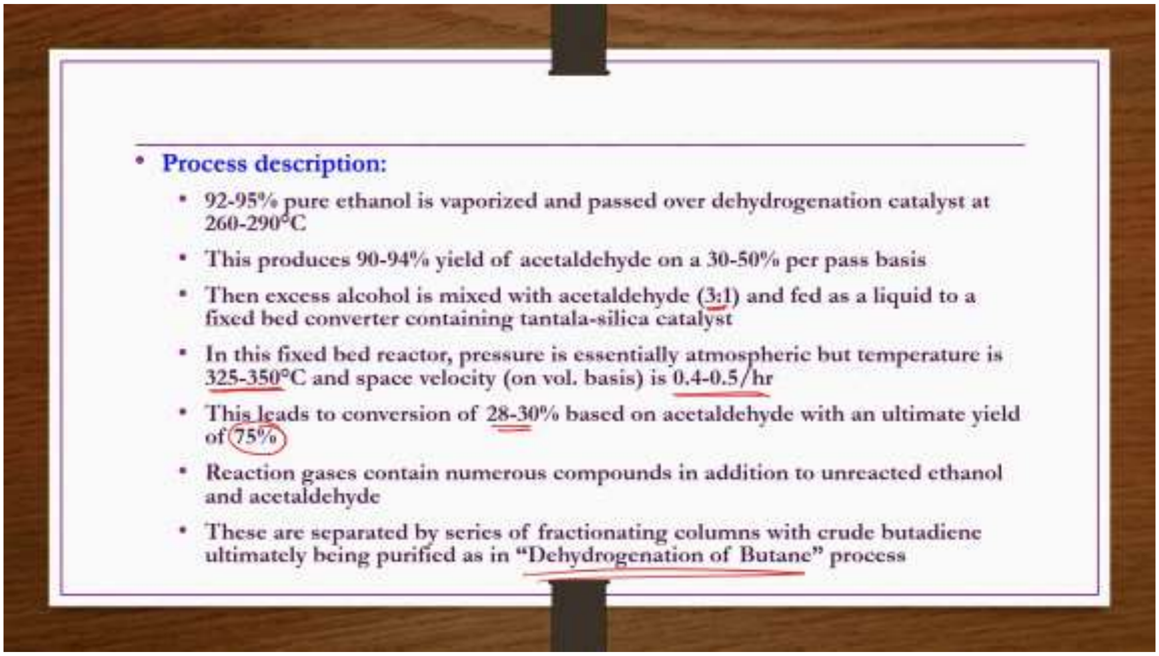

- **Process description:**
  - 92-95% pure ethanol is vaporized and passed over dehydrogenation catalyst at 260-290°C
  - This produces 90-94% yield of acetaldehyde on a 30-50% per pass basis
  - Then excess alcohol is mixed with acetaldehyde (3:1) and fed as a liquid to a fixed bed converter containing tantala-silica catalyst
  - In this fixed bed reactor, pressure is essentially atmospheric but temperature is 325-350°C and space velocity (on vol. basis) is 0.4-0.5/hr
  - This leads to conversion of 28-30% based on acetaldehyde with an ultimate yield of 75%
  - Reaction gases contain numerous compounds in addition to unreacted ethanol and acetaldehyde
  - These are separated by series of fractionating columns with crude butadiene ultimately being purified as in "Dehydrogenation of Butane" process

Process description 92 to 95 percent pure ethanol is vaporized and passed over dehydrogenation catalyst at 260 to 290 degree centigrade. This produces 90 to 94 percent yield of acetaldehyde on a 30 to 50 percent per pass basis. Then excess alcohol is mixed with acetaldehyde at 3 to 1 ratio and fed as a liquid to a fixed bed converter containing tantala silica catalyst. In this fixed bed reactor pressure is essentially atmospheric but temperature is 325 to 350 degrees centigrade and space velocity is usually 0.4 to 0.5 hour inverse which is on volume basis. This leads to conversion of 28 to 30 percent based on acetaldehyde with an ultimate yield of 75 percent because ultimate yield because 2 steps of reactions are there. Reaction gases contain numerous compounds in addition to unreacted ethanol and acetaldehyde. These are separated by series of fractionating columns with crude butadiene ultimately being purified using the similar separation purification steps as we have discussed in the dehydrogenation of butane process.

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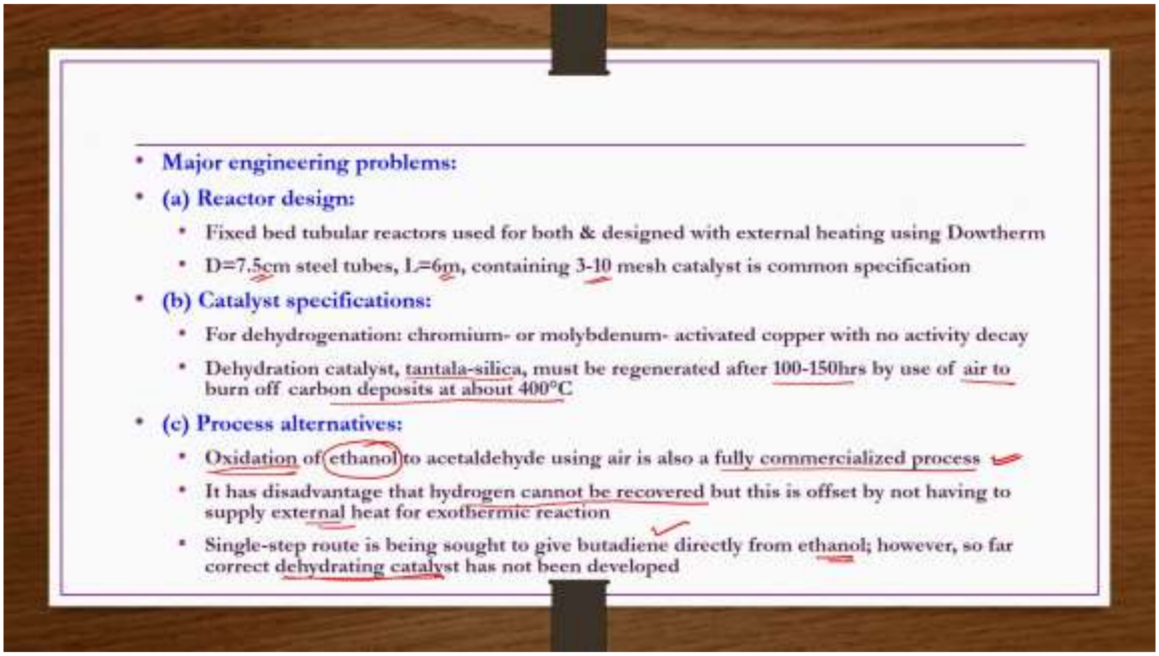

- **Major engineering problems:**
- **(a) Reactor design:**
  - Fixed bed tubular reactors used for both & designed with external heating using Dowtherm
  - D=7.5cm steel tubes, L=6m, containing 3-10 mesh catalyst is common specification
- **(b) Catalyst specifications:**
  - For dehydrogenation: chromium- or molybdenum- activated copper with no activity decay
  - Dehydration catalyst, tantala-silica, must be regenerated after 100-150hrs by use of air to burn off carbon deposits at about 400°C
- **(c) Process alternatives:**
  - Oxidation of ethanol to acetaldehyde using air is also a fully commercialized process
  - It has disadvantage that hydrogen cannot be recovered but this is offset by not having to supply external heat for exothermic reaction
  - Single-step route is being sought to give butadiene directly from ethanol; however, so far correct dehydrating catalyst has not been developed

Coming to the major engineering problems reactor design is very essential. Fixed bed tubular reactors are used for both acetaldehyde reactor as well as the butadiene reactor and these are designed with external heating using downtherm.

Tubes which are present in the reactors having the diameter of only 7.5 centimeters but length of 6 meters and they contain 3 to 10 mesh size catalyst. So, the catalyst are chromium or molybdenum activated copper in the acetaldehyde reactor whereas in the butadiene reactor it is tantala silica catalyst. Catalyst specifications for dehydrogenation chromium or molybdenum activated copper with no activity decay kind of catalyst are used whereas for the dehydration reaction between ethanol and acetaldehyde to produce butadiene you use tantalosilica catalyst and that must be regenerated after every 100 to 150 hours by use of air to burn off carbon deposits at about 400 degrees centigrade. Process alternatives oxidation of ethanol to acetaldehyde using air is also a fully commercialized process. We have discussed only the one you know dehydrogenation and dehydration of ethanol process only but there is another alternative which is nothing but oxidation of ethanol but however it is having disadvantage that in this process hydrogen cannot be recovered because in the oxidation of ethanol when you do to produce butadiene hydrogen is being produced that cannot be recovered.

But however, this is offset by not having to supply external heat for exothermic reaction of oxidation. Single step route is being sought to give butadiene directly from ethanol however for that purpose whatever the required dehydrating catalyst is there. So, the correct dehydrating catalyst has not been developed until now. With this we complete the chapter on synthetic chemicals production from C3 and C4 chemicals.

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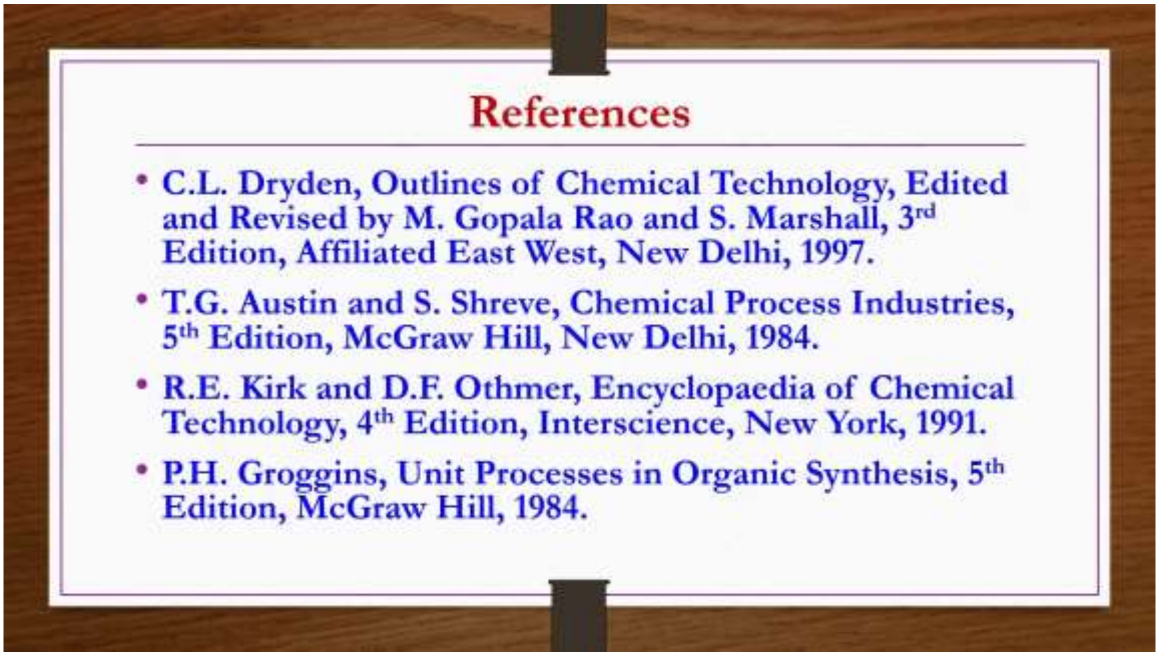

## References

- 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.

References for today's lecture are provided here. Outlines of chemical technology by Dryden edited and revised by Gopal Rao and Marshall third edition. Chemical process industries by Austin and Shreve fifth edition. Encyclopedia of chemical technology by Kirk and Othmer fourth edition. Unit processes in organic synthesis by Groggins fifth edition. Thank you.