Organic Chemical Technology
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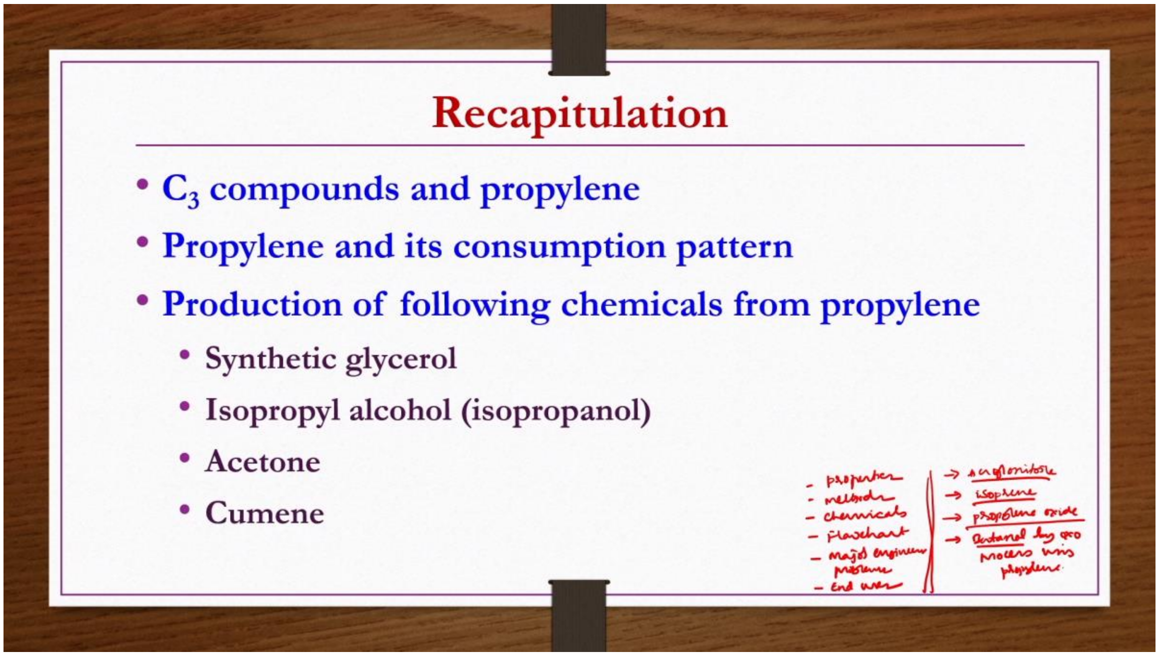
Lecture - 27
Chemicals from C3 Compounds – 2

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is chemicals from C3 compounds part 2. In this lecture, we will be discussing about production of 4 different types of chemicals derived from propylene C3 compound, right? What are they? Acrylonitrile, isoprene monomer, propylene oxide and then butanol by oxo process using propylene raw material, right? So, for these processes also we are going to discuss details of you know properties of a given compound that we are going to produce. Then methods that are available for production of such compounds, associated chemical reactions then process flowchart and then description followed by major engineering problems or alternatives etc., those things we are going to discuss, right? So, in addition to that we also going to see end uses or consumption pattern of such chemicals, okay? However, before going to the details of today's lecture, we have a recapitulation of what we have discussed in the previous lecture. In the previous lecture, we started discussion on the C3 compounds and then we selected propylene because of the different types of chemicals that we can produce from the propylene. (Refer Slide Time: 03:46)



Recapitulation

- C_3 compounds and propylene
- Propylene and its consumption pattern
- Production of following chemicals from propylene
  - Synthetic glycerol
  - Isopropyl alcohol (isopropanol)
  - Acetone
  - Cumene

- properties
- methods
- chemicals
- flowchart
- major engineering problems
- End uses

→ acrylonitrile
→ isoprene
→ propylene oxide
→ butanol by oxo process using propylene.

We have seen that the ethylene is the best compound amongst the olefins because it can be converted into the different types of chemicals both intermediate as well as the end chemicals can be produced from ethylene. After the ethylene, propylene is the one which can be utilized to produce different types of intermediates and chemicals. For that reason, we have selected propylene under C3 compounds category, right? Then we have discussed properties of propylene etc. and then how it can be produced. We have seen that steam cracking of hydrocarbons if you do, we can produce ethylene, acetylene, propylene, propane, butane, etc., these kind of products. So, we have to do this operation to get the propylene as we have already discussed with the help of a flow chart. Then we have realized it is important in terms of different types of intermediates and end chemicals can be produced from the propylene through the consumption pattern and then that we have seen by a flow chart, by a schematic diagram as well. Then we have discussed the production of different types of chemicals from propylene which included synthetic glycerol by 2 processes and then isopropyl alcohol or isopropanol, then acetone, then cumene, okay? Now, we are going to start today's lecture on production of acrylonitrile, right?

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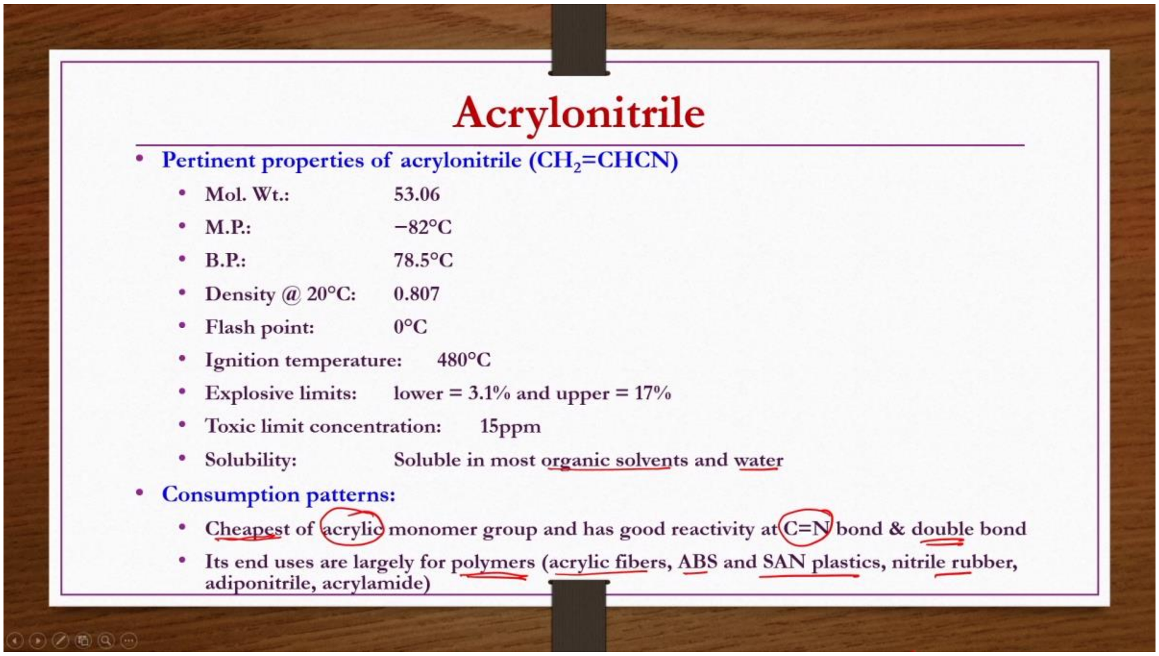

Acrylonitrile

- Pertinent properties of acrylonitrile (CH_2=CHCN)
  - Mol. Wt.: 53.06
  - M.P.: −82°C
  - B.P.: 78.5°C
  - Density @ 20°C: 0.807
  - Flash point: 0°C
  - Ignition temperature: 480°C
  - Explosive limits: lower = 3.1% and upper = 17%
  - Toxic limit concentration: 15ppm
  - Solubility: Soluble in most organic solvents and water
- Consumption patterns:
  - Cheapest of acrylic monomer group and has good reactivity at C=N bond & double bond
  - Its end uses are largely for polymers (acrylic fibers, ABS and SAN plastics, nitrile rubber, adiponitrile, acrylamide)

So, before going into the methods of production and associated chemical reactions and flow charts etc., we will have a look at the pertinent properties of this compound. So, we first discuss the properties of acrylonitrile which is nothing but CH2 double bond CHCN, molecular weight 53.06, melting point minus 82 degrees centigrade, boiling point 78.5degrees centigrade, density at 20 degrees centigrade is 0.807 gram per cc, flash point is 0 degrees centigrades, ignition temperature is 480 degrees centigrades, explosive limits 3.1 and 17% respectively are lower and upper explosive limits of this particular component. Toxic limit concentration is only 15 ppm, it is very toxic. Solubility, it is soluble in most of the organic solvents as well as in water. Consumption pattern amongst the acrylic compounds category or homologue, it is the most cheapest one, okay? And it has good reactivity at C double bond N as well as the double bond whatever present in the molecular structure. It is having end use for the production of different types of polymers that is the main purpose of this particular monomer. It is used for production of acrylic fibers, ABS and SAN plastics, nitrile rubbers, adiponitrile, acrylamides etc.

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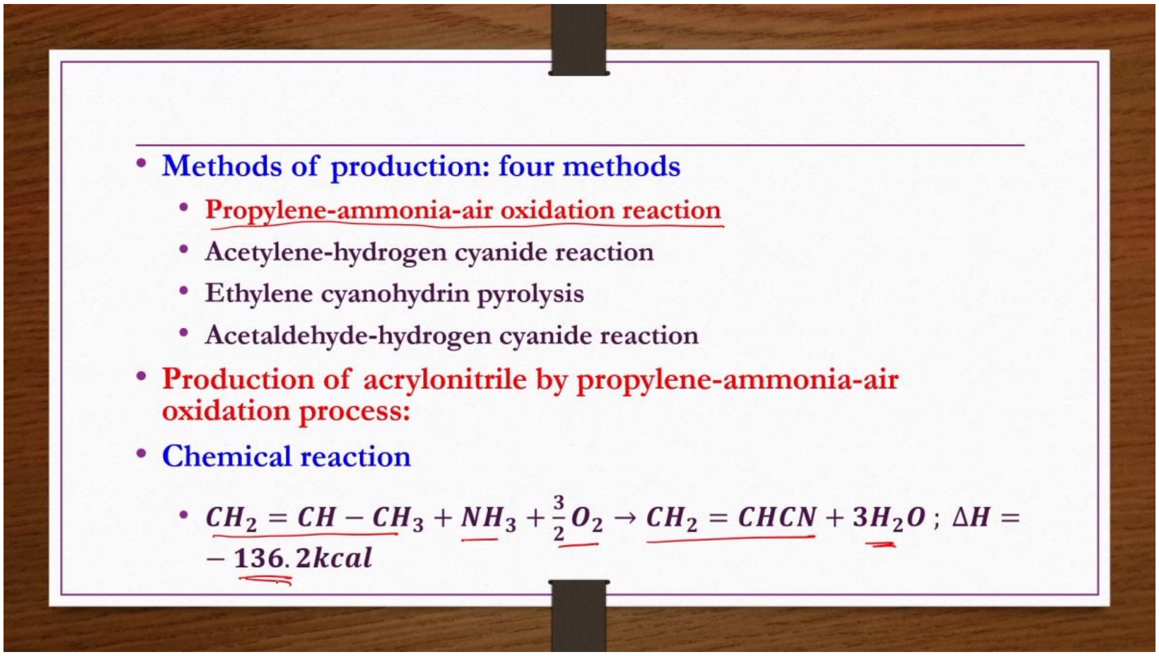

- Methods of production: four methods
  - Propylene-ammonia-air oxidation reaction
  - Acetylene-hydrogen cyanide reaction
  - Ethylene cyanohydrin pyrolysis
  - Acetaldehyde-hydrogen cyanide reaction
- Production of acrylonitrile by propylene-ammonia-air oxidation process:
- Chemical reaction
  - $\underline{CH_2 = CH - CH_3} + \underline{NH_3} + \frac{3}{2}\underline{O_2} \rightarrow \underline{CH_2 = CHCN} + 3\underline{H_2}O\ ;\ \Delta H = -\underline{136}.2kcal$

Coming to the methods of production, 4 methods are there. First one is the propylene ammonia air oxidation reaction. Second one is acetylene hydrogen cyanide reaction. Third one is ethylene cyanohydrin pyrolysis. Fourth one is acetaldehyde hydrogen cyanide reaction, right? We will be taking the first process that is a propylene ammonia air oxidation reaction. So, this is one of the rarest of the commercial reaction where 3 reactants are reacting in the presence of a catalyst and then producing one liquid product, okay? Chemical reactions if you see, propylene is reacting with ammonia and then oxygen to produce acrylonitrile along with the water and it is highly exothermic reaction.

Quantitative requirements if you wanted to produce 1 ton of more than 99% pure acrylonitrile with 80%yield, then propylene you required 0.996 tons, ammonia 0.45 tons required, air 5.2 tons or 4000 normal cubic meters are required. In this process byproducts like acetonitrile are also produced which is nothing but approximately 0.09 tons and then hydrogen cyanide is also produced which is produced at 0.08 tons. Plant capacities vary in general 50 to 125 tons per day.

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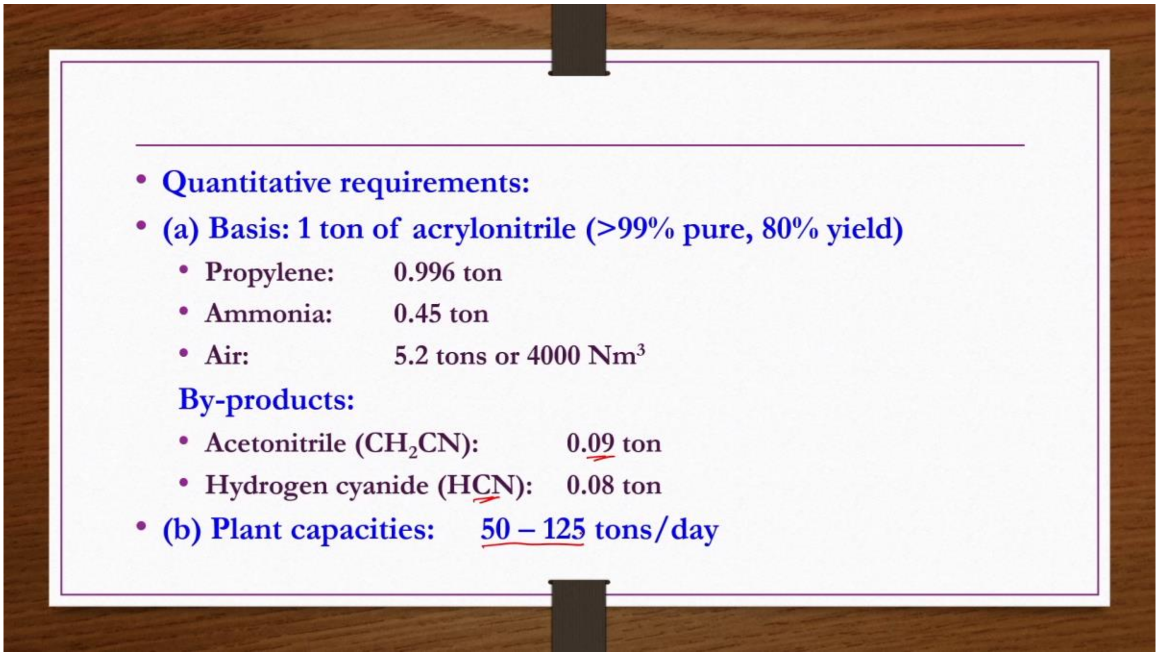

- **Quantitative requirements:**
- **(a) Basis: 1 ton of acrylonitrile (>99% pure, 80% yield)**
  - Propylene: 0.996 ton
  - Ammonia: 0.45 ton
  - Air: 5.2 tons or 4000 Nm^3

  By-products:
  - Acetonitrile (CH_2CN): 0.09 ton
  - Hydrogen cyanide (HCN): 0.08 ton
- **(b) Plant capacities: 50 – 125 tons/day**

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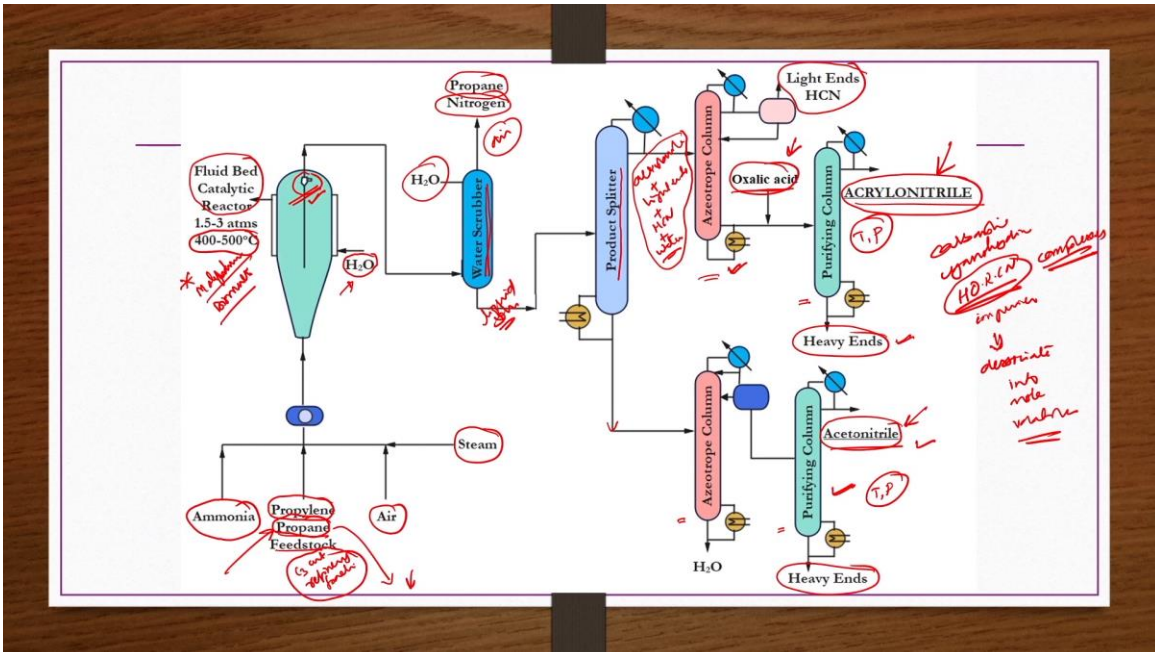

Now, we have a flowchart here, right? So, that to discuss the production of acrylonitrile commercially, right? So, here what we have? We have a C3 cut refinery fraction. So, that means we will not be having only propylene in general. In this one propane would also be there that is what mean by you know propylene propane feedstock, okay? So, that is nothing but C3 cut refinery fraction. So, it may not if it is pure then good enough otherwise some kind of other ingredients may also be there. This material propylene along with the propane will be mixed with ammonia and then air if required some steam is also added and then it would be compressed to 200 atmosphere and then fed to a fluid catalytic reactor, right? So, in this fluid bed catalytic reactor actually we need a catalyst which is nothing but you can have a molybdenum and then bismuth as well or both. Temperature is maintained between 400 to 500 degrees centigrade and pressure is 1.323 atmosphere. Since the reaction we have seen that it is highly exothermic with delta H minus 136 kilocalories, you know you need to have a proper cooling facility also. So, what we do? This reactor heating zone whatever is there that is usually you know fitted with a jacketed provision so that cold water may be circulated along the surface of the reactor so that to maintain the temperature within the range. So that temperature should not shoot out for that purpose this cooling is required, right? This is external cooling, right? So, now whatever the products that are formed they would be water scrubbed.

Why water scrubbed? Because here in this reaction some propane whatever is there that may not be reacting in fact that will not be reacted and then in the air nitrogen would also be there. So, those things we can separate out by water scrubbing. So, how these will be separated by water scrubber rather separating this whatever the products are there that is acetonitrile and then acrylonitrile are there they will be mixed with the water and then liquid solution of products would be formed, okay? And then this product would be this liquid solution whatever is there which is having primarily this mixture of acrylonitrile and acylonitrile that would be taken to a product stripper because out of these 2 products acrylonitrile and acetonitrile, acrylonitrile is the more volatile one and then acetonitrile would be the less volatile one. So, more volatile acrylonitrile would be taken as a top product and then purified subsequently whereas the low volatile acetonitrile product mixture whatever is there that is collected from the bottom of this product stripper and then subsequently purified, right? So, how they are purified? They are purified by azeotrope column as well as the conventional distillation column both of them are used for purifying both of these products. So, what does it mean by here from the top you get acrylonitrile plus some light ends plus some hydrogen cyanide plus water these things would be mixed in the mixture, right? So, when you do the azeotropic separation what will happen whatever the light ends and then HCN would be there, they would be separated as a lighter ones from the top because they are lighter than the acrylonitrile, right? So, here in this mixture there is no acetonitrile. So, mostly acrylonitrile and then impurities are there. Acrylonitrile is the heavier one compared to the other components like HCN and light ends. So, that acrylonitrile would be formed at the bottom of the azeotropic column that you take it and then purify in purifying column. But what happens here some carbonylic cyanohydrines would be forming, they will be having structures generalized structure something like HORC and something like this. These impurities actually these impurities would be there along with this acrylonitrile. This is the generalized one some kind of a carbonylic cyanohydrines would be there. So, what they will do, they will actually dissociate and then get into more volatiles, right? But we want more volatiles only acrylonitrile. So, what we do this mixture before purifying whatever the acrylonitrile or crude acrylonitrile solution is there that would be treated with oxalic acid so that this oxalic acid would form complex some kind of complexes it will be forming with cyanohydrines. So that they will become heavier and then they will be forced to get into the heavier ends right and then you get only acrylonitrile in the top column of the purifying distillation section that is the purpose of using this oxalic acid here. Now, here bottom of product stripper primarily having the acetonitrile with some kind of heavy end impurities and water. So, what we do that mixture we take to azeotropic column and then try to separate out the lighter acetonitrile because here now this acetonitrile is lighter because it is in this one impurities whatever are there they are much heavier than the acetonitrile. Compared to the acrylonitrile, acetonitrile is the heavier one, but there are impurities which are much heavier than acetonitrile. So, in this section what happens acetonitriles will come as the top products and then heavy ends would be taken as the bottom products. How it is possible the temperature, pressure etc. you have to maintain such a way that such kind of separation takes place. So, now here you not only have the acrylonitrile product but also co-product acetonitrile also you are getting. Now, coming to this catalyst, the catalyst is having a very good resistance for the abrasion etc. but however, some fine should be forming. So, what we do these fines in fact this molybdenum, bismuth are expensive. So, what you do you try to recover them by cyclone separators located within the fluid bed catalytic reactor itself. So, that to avoid loss of the catalyst. So, now, this is one of the engineering problem a recovering of the catalyst fines within the fluid catalytic cracker and then using oxalic acids to form complexes with the cyanohydrines and then forcing them to the heavy ends of this particular section. And then another engineering problem is that this propane whatever is there in the feedstock, it is better to separate out you know before the reaction, why because if it is separated after the reaction using the water scrubber here, what happens if this gaseous mixture whatever is there if it is having too much of air or nitrogen then it is become then it becomes very difficult to separate the propane. So, that is the reason it is better to separate out the propane before the reaction itself.

The description of the process is provided here, mixture of a C3 refinery stream, ammonia and air is introduced into a fluidized bed catalytic reactor via spargers, pressure of 1.3 atmosphere and temperature of 400 to 500 degrees centigrades and the contact time of several seconds only maintained in the reactor. The contact between the catalyst and then the reactant mixture should be few seconds only the fluidizing medium velocity etc has to be maintained such a way that the contact is only for the smaller time. Effluents from the reactor are scrubbed with water to remove desired products in an aqueous solution what happens here light ends etc would be separated out whereas the acetonitrile and acrylonitrile would be dissolved into the water. This solution is fractionated to get wet acrylonitrile and acetonitrile and then both are further purified by isotropic and conventional distillation as we have discussed in the flowchart.

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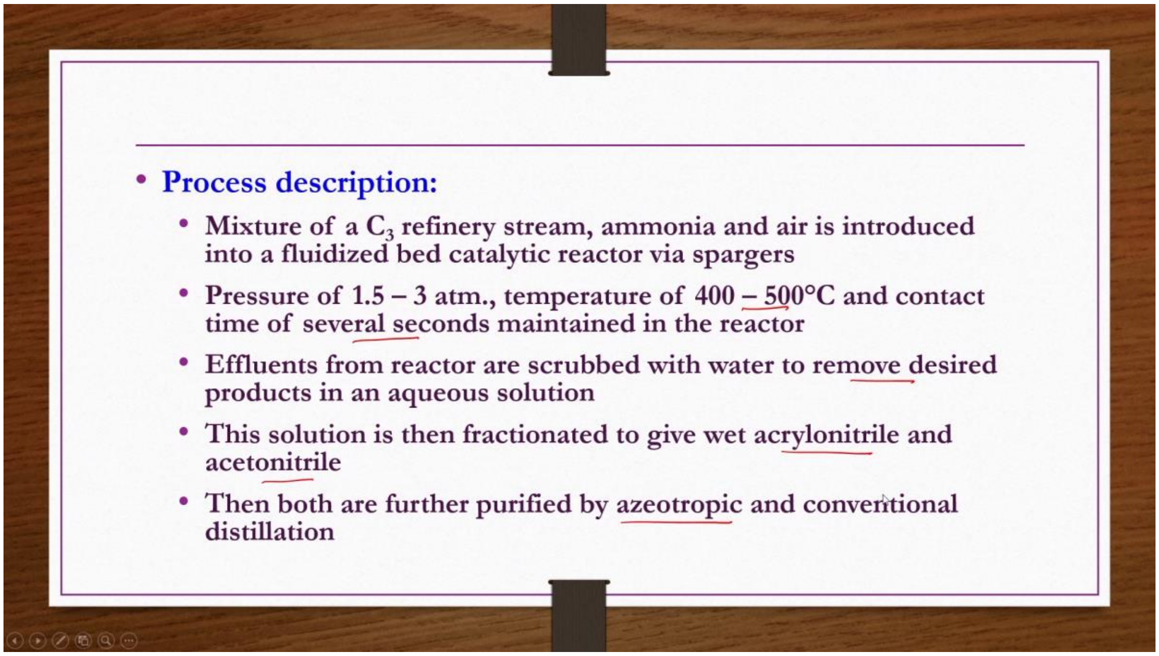

- **Process description:**
  - Mixture of a C_3 refinery stream, ammonia and air is introduced into a fluidized bed catalytic reactor via spargers
  - Pressure of 1.5 – 3 atm., temperature of 400 – 500°C and contact time of several seconds maintained in the reactor
  - Effluents from reactor are scrubbed with water to remove desired products in an aqueous solution
  - This solution is then fractionated to give wet acrylonitrile and acetonitrile
  - Then both are further purified by azeotropic and conventional distillation

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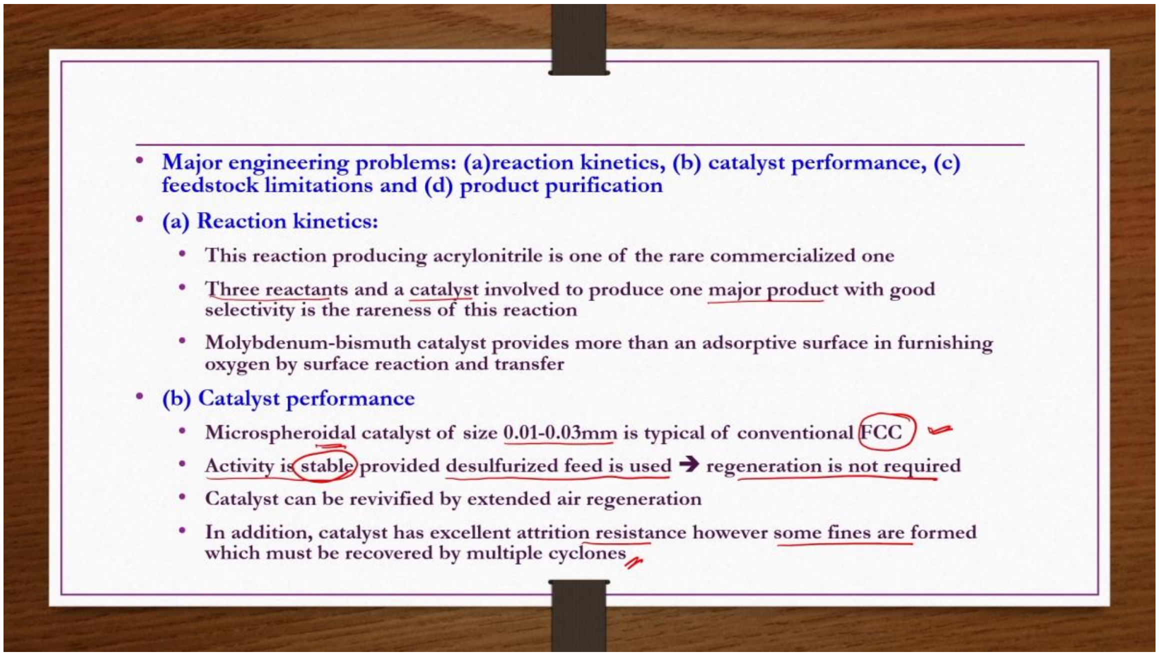

- **Major engineering problems: (a)reaction kinetics, (b) catalyst performance, (c) feedstock limitations and (d) product purification**
- **(a) Reaction kinetics:**
  - This reaction producing acrylonitrile is one of the rare commercialized one
  - Three reactants and a catalyst involved to produce one major product with good selectivity is the rareness of this reaction
  - Molybdenum-bismuth catalyst provides more than an adsorptive surface in furnishing oxygen by surface reaction and transfer
- **(b) Catalyst performance**
  - Microspheroidal catalyst of size 0.01-0.03mm is typical of conventional FCC
  - Activity is stable provided desulfurized feed is used ➔ regeneration is not required
  - Catalyst can be revivified by extended air regeneration
  - In addition, catalyst has excellent attrition resistance however some fines are formed which must be recovered by multiple cyclones

Coming to the engineering problem reaction kinetics is the one other one is the catalyst performance feedstock limitation is the third one and then product purification is the last engineering problem which are essential to realize in this plant where we are producing acrylonitrile. Reaction kinetics this reaction producing acrylonitrile is one of the rare commercialized one because 3 reactants and a catalyst involved to produce one major products and then these 3 reactants are gaseous reactants and this catalyst is a solid catalyst whereas the major product whatever acrylonitrile you are getting that is a liquid product. Such a kind of a rare situation is there about this in a process. Molybdenum bismuth catalyst provides more than an adsorptive surface in furnishing oxygen by surface reaction and transfer. Second problem is the catalyst performance. Micro spheroidal catalyst of size 0.01 to 0.03mm are typical for in general for conventional FCCs fluid catalytic crackers and then same is suitable here in this case as well. And then if you are desulphurizing the feed before feeding into the reactor then activity is very much stable because of that one regeneration is not required. So, it is better to remove the sulphur from the C3 cut refinery whatever stream you have taken. Catalyst can be re-vivified by extended air regeneration. In addition, catalyst has excellent attrition resistance. However, some fines are formed which must be recovered by multiple cyclones within the fluid catalytic cracker as shown in the flow chart. If the fines are too many then we can have cyclone separators out of the fluid bed catalytic cracker and then after passing through the cyclone and then after collecting the catalyst particle then only scrubbing with water is to be done.

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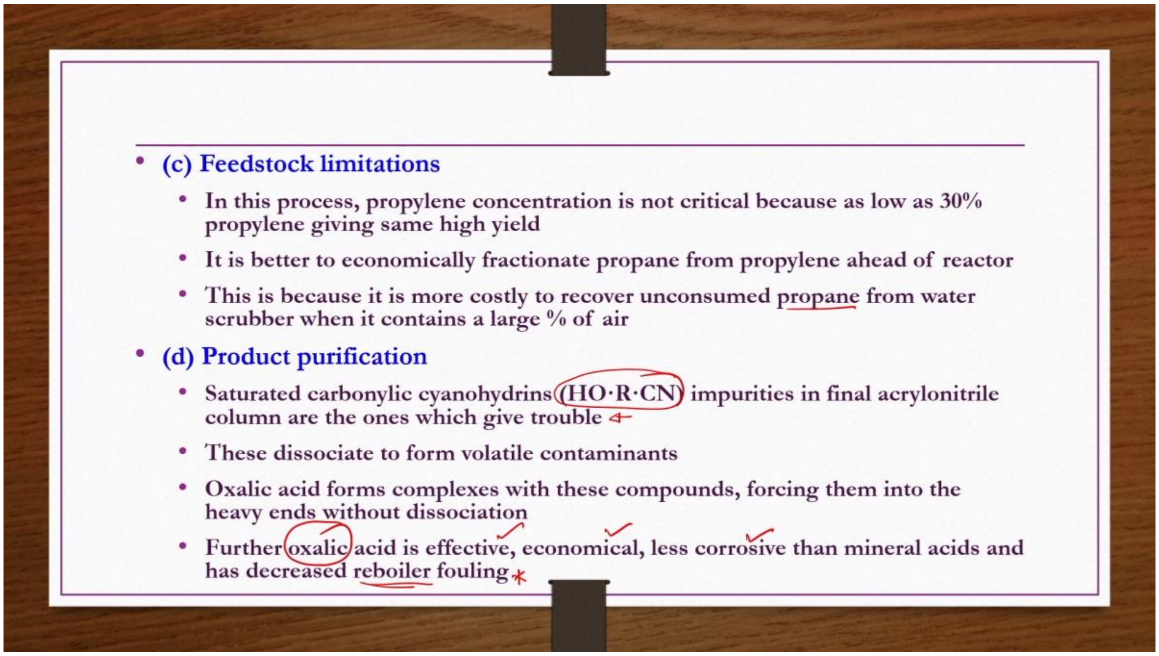

- **(c) Feedstock limitations**
  - In this process, propylene concentration is not critical because as low as 30% propylene giving same high yield
  - It is better to economically fractionate propane from propylene ahead of reactor
  - This is because it is more costly to recover unconsumed propane from water scrubber when it contains a large % of air
- **(d) Product purification**
  - Saturated carbonylic cyanohydrins (HO·R·CN) impurities in final acrylonitrile column are the ones which give trouble
  - These dissociate to form volatile contaminants
  - Oxalic acid forms complexes with these compounds, forcing them into the heavy ends without dissociation
  - Further oxalic acid is effective, economical, less corrosive than mineral acids and has decreased reboiler fouling

Feedstock limitations in this process propylene concentration is not critical because as low as 30 percent propylene giving same high yield of whatever 80 percent yield required. So, it is better to economically fractionate propane from propylene ahead of the reactor because it is more costly to recover unconsumed propane from water scrubber when it contains a large percent of air. So, because of economics reason, it is better to separate the propane from the C3 feed mixture before the reaction. Product purification, saturated carbonylic cyanohydrines are impurities in final acrylonitrile column and these are the ones which give the trouble. If we do not separate them then what happens they will dissociate and then get into the high volatiles and then along with the acrylonitrile they may be present because of that one, you know what we do? Oxalic acid we use to form complexes with these compounds and force them into the heavy ends without dissociation. We do not allow them to dissociate and then get into the product acrylonitrile by using the oxalic acid. Why oxalic acid? Why not the other ones? Because oxalic acid is effective, economical, less corrosive than mineral acids and has decreased reboiler falling also. That is also important advantage of having oxalic acid to form complexes with cyanohydrin sand then forcing them into the heavy ends rather going into the lighter ends where acrylonitrileis collected as product. That is all about acrylonitrile.

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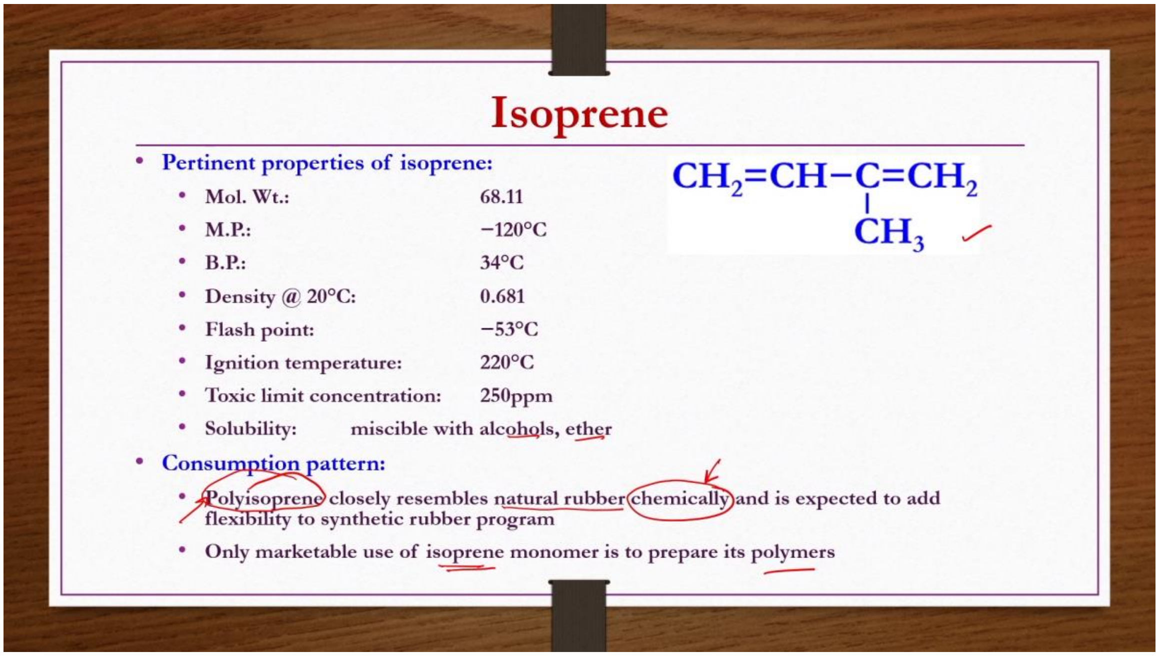

Isoprene

- **Pertinent properties of isoprene:**

Mol. Wt.:	68.11
M.P.:	−120°C
B.P.:	34°C
Density @ 20°C:	0.681
Flash point:	−53°C
Ignition temperature:	220°C
Toxic limit concentration:	250ppm
Solubility:	miscible with alcohols, ether

$$CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

- **Consumption pattern:**
  - Polyisoprene closely resembles natural rubber chemically and is expected to add flexibility to synthetic rubber program
  - Only marketable use of isoprene monomer is to prepare its polymers

Now, we discuss about isoprene. Isoprene is a monomer and then most important application of this isoprene is nothing but for polymerization to get polyisoprene right? Because polyisoprene whatever are there chemically they are much closer to the natural rubber, right? So, because of that one it is primarily used for the polymerization and then used in the rubber industries, okay? Isoprene structure is given here. First, we see its properties then we discuss about methods of production and then flowchart chemical reaction, etc. Pertinent properties of isoprene, molecular weight 68.11, melting point minus 120 degrees centigrade, boiling point 34 degrees centigrade, density at 20 degrees centigrade is 0.681, flash point is minus 53 degrees centigrade, ignition temperature is 220 degrees centigrade, toxic limit concentration is 250 ppm, solubility it is miscible with alcohols and ethers. Consumption pattern, polyisoprene whichever formed by using pure isoprene you can get polyisoprenes by using certain polymerization techniques which we will be discussing in the 11th chapter of the course, okay? This polyisoprene resembles closely with natural rubber but chemically if you compare the chemical properties of natural rubber and then polyisoprene, there are so much of resemblance and is expected to add flexibility to synthetic rubber program. So, because of that one only marketable use of isoprene monomer is to prepare its polymers.

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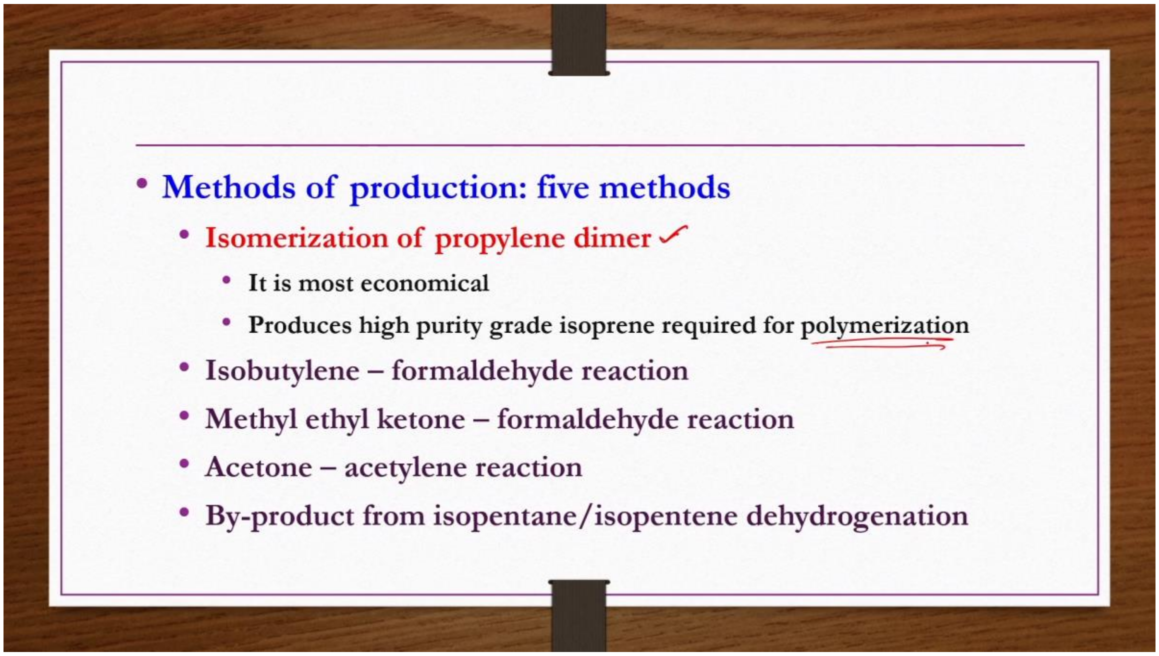

- Methods of production: five methods
  - Isomerization of propylene dimer ✓
    - It is most economical
    - Produces high purity grade isoprene required for polymerization
  - Isobutylene – formaldehyde reaction
  - Methyl ethyl ketone – formaldehyde reaction
  - Acetone – acetylene reaction
  - By-product from isopentane/isopentene dehydrogenation

So, because of production, several methods are there, 5 important methods are isomerization of a propylene dimer, second one is isobutylene formaldehyde reaction, third one is methyl-ethyl-ketone formaldehyde reaction, fourth one is acetone-acetylene reaction, fifth one is byproduct from isopentane-isopentane dehydrogenation reaction. However, we select this process isomerization of a propylene dimer because it is more economical or the most economical process amongst all 5 methods. Further, it produces the high purity isoprene. High purity isoprene is very much required for its polymerization. Impurities if are present in the isoprene, corresponding polymers may not be having good properties.

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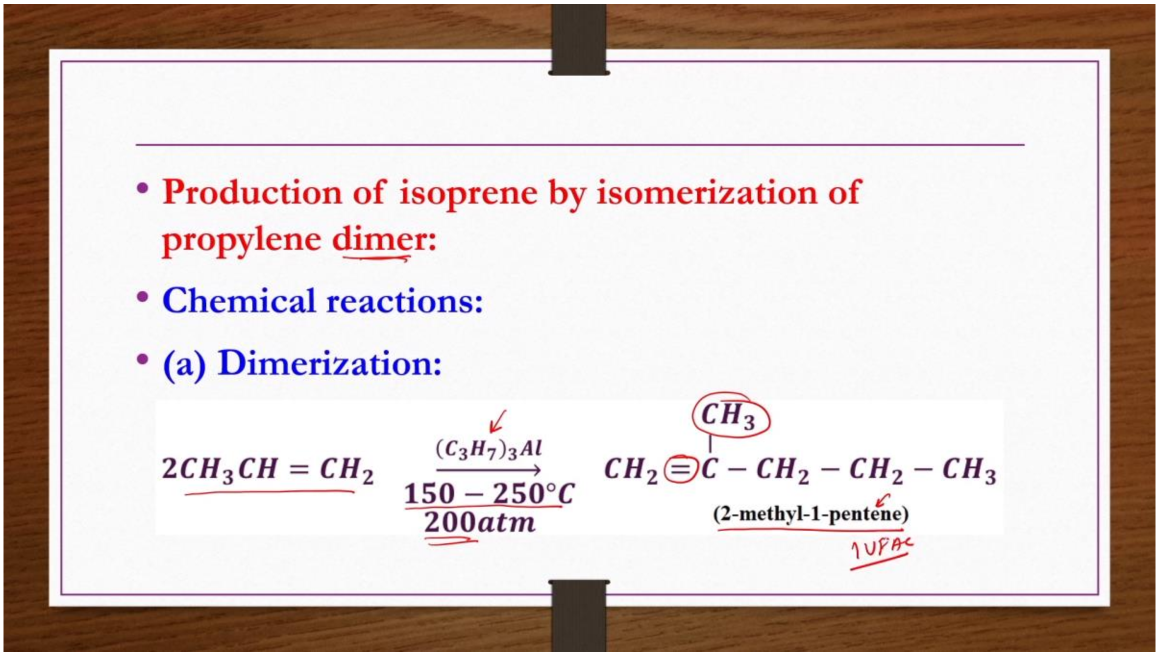

- **Production of isoprene by isomerization of propylene dimer:**
- **Chemical reactions:**
- **(a) Dimerization:**

$$2CH_3CH = CH_2 \xrightarrow[\substack{150-250^\circ C \\ 200atm}]{(C_3H_7)_3Al} CH_2 = \overset{CH_3}{\overset{|}{C}} - CH_2 - CH_2 - CH_3$$

(2-methyl-1-pentene)

IUPAC

So, let us discuss production of isoprene by isomerization of a propylene dimer, okay? So, propylene dimer is there that by title what does it mean? Propylene whatever is there, first you have to take and then do the dimerization. Once you do the dimerization, then you have to do the isomerization followed by the pyrolysis to get the so-called isoprene, okay? So, chemical reactions, first dimerization reaction where 2 moles of propylene reacts in the presence of a tri-propyl aluminum catalyst at 150 to 250 degrees centigrade and 200 atmospheric pressure. So product 2-methyl-1-pentene, why we call it 2-methyl-1-pentene? Because for the second carbon atom, methyl functional group is attached and then whatever the pentene that means double bond is there, the double bond is there after the first carbon atom. So, that is the reason it is known as 2-methyl-1-pentene, it is nothing but IUPAC name of the compound, okay?

Then this dimer whatever 2-methyl-1-pentene is formed by the dimerization that would be undergoing isomerization reaction in the presence of acid catalyst at 150 to 300 degrees centigrade to produce an isomer which is nothing but 2-methyl-2-pentene. Why 2-methyl-2-pentene? To the second carbon methyl group is attached and then whatever the pentene that means double bond is there, so that is there after the second carbon atom. So, because of that one it is 2-methyl-2-pentene, right? Now, this 2-methyl-2-pentene undergo pyrolysis in the presence of hydrogen bromide catalyst at 650 to 800 degrees centigrades to produce isoprene monomer along with the methane, okay? So, 3 steps reaction here, so obviously 3 reactors are required for your plant, so that to do dimerization followed by the purification followed by the isomerization followed by purification followed by the pyrolysis followed by the purification. So, 3 reactors and soon several purification steps would be there and then that we will be discussing in the flow chart.

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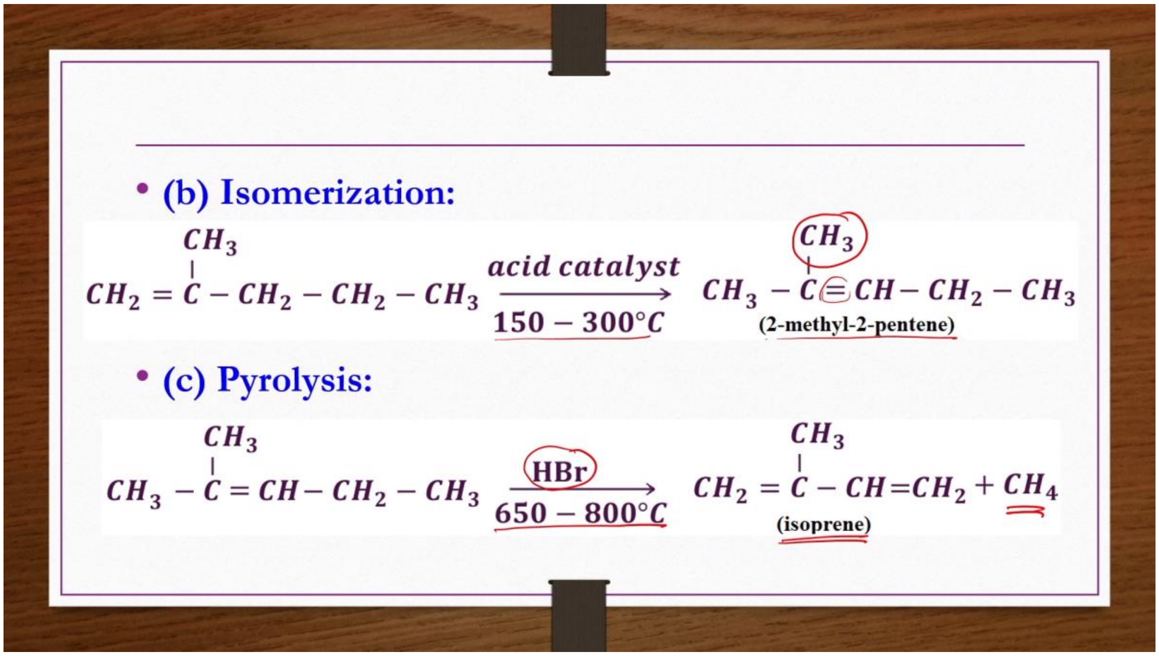

- **(b) Isomerization:**

$$CH_2 = \overset{CH_3}{\overset{|}{C}} - CH_2 - CH_2 - CH_3 \xrightarrow[150 - 300°C]{acid\ catalyst} CH_3 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 - CH_3$$

(2-methyl-2-pentene)

- **(c) Pyrolysis:**

$$CH_3 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 - CH_3 \xrightarrow[650 - 800°C]{HBr} CH_2 = \overset{CH_3}{\overset{|}{C}} - CH = CH_2 + CH_4$$

(isoprene)

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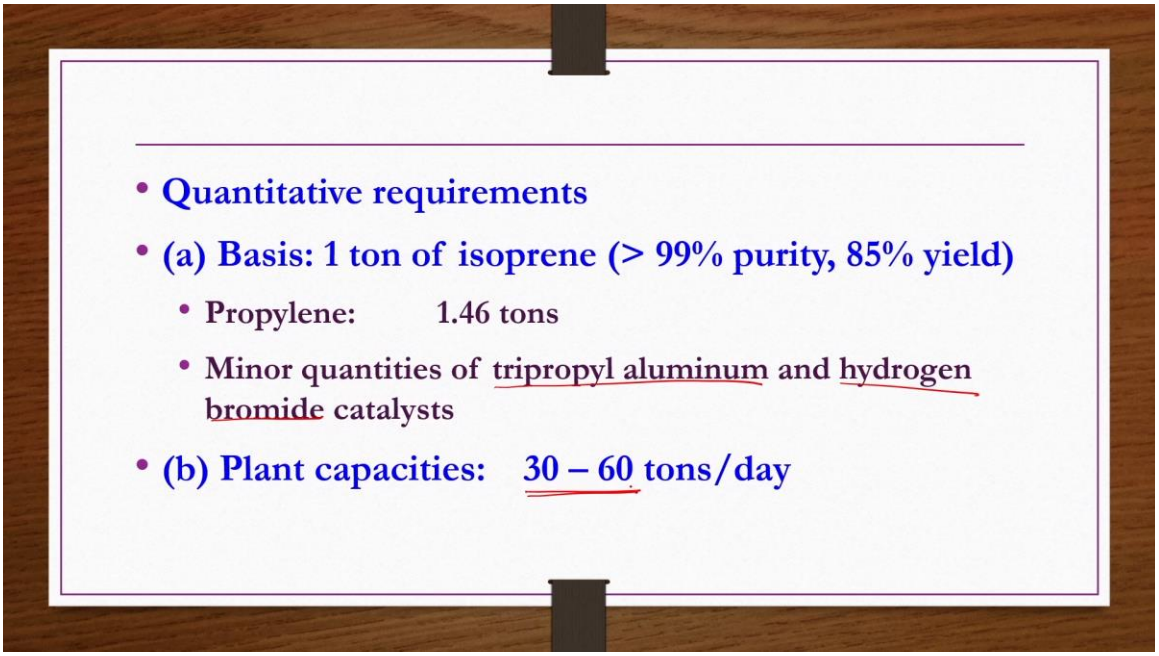

- **Quantitative requirements**
- **(a) Basis: 1 ton of isoprene (> 99% purity, 85% yield)**
  - Propylene: 1.46 tons
  - Minor quantities of tripropyl aluminum and hydrogen bromide catalysts
- **(b) Plant capacities: 30 – 60 tons/day**

Coming to the quantitative requirements, basis if you take 1 ton of isoprene having more than 99 percent purity with 85 percent yield, propylene you required 1.46 tons and then catalyst tri-propyl aluminum catalyst is required for the dimerization and then hydrogen bromide catalyst is required for the pyrolysis. So, these are required in the minor quantities only. Plant capacities usually 30 to 60 tons per day.

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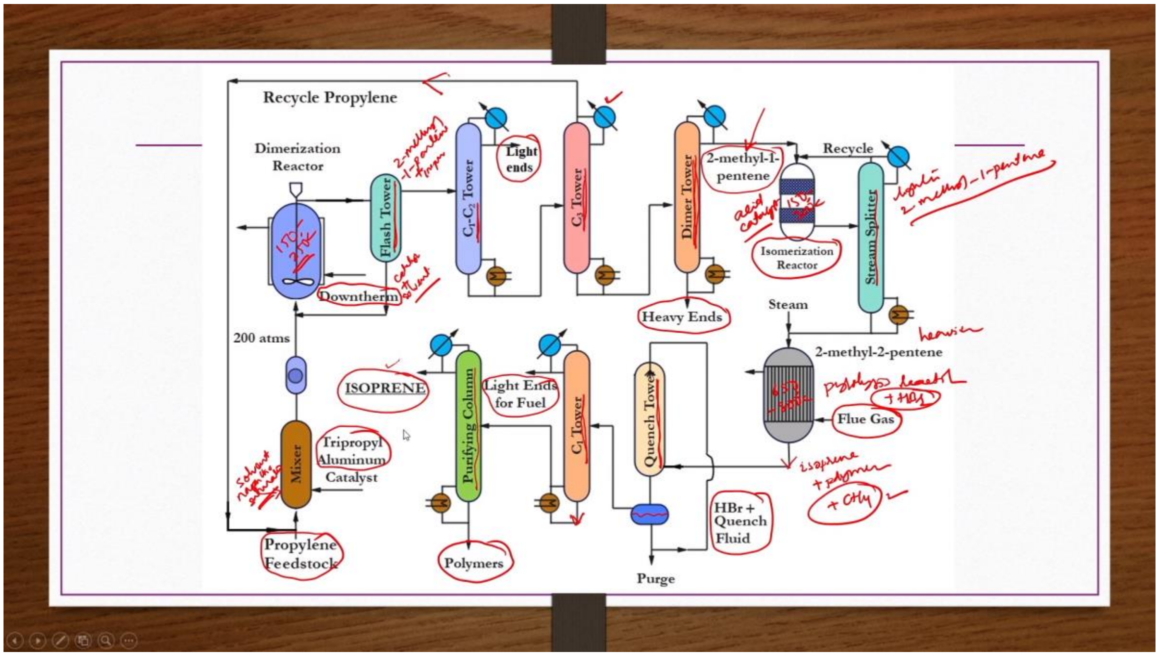

So, this is the flow chart to discuss so that to get isoprene monomer product from the propylene. So, what you do? You take propylene feedstock along with the tri-propyl aluminum catalyst, you mix them in a mixer. Then actually you can also add some solvents which are nothing but naphtha saturates that means naphtha grade products, but they should not have any double bond, they should be having only single bonds and then they are saturated. This mixture you take to the reactor at 200 atmosphere and then inside the reactor you maintain the temperature of 150 to 250 degrees centigrade. Actually, here absorption of these chemicals are taking place so that to form the required dimers, okay? Required dimers can be formed here, okay? So, now here what happens? This reaction is also exothermic as we have seen the reactions. Now, to the outside of the reactor, jackets are provided so that one can supply the heat transfer fluids to control the temperature as per the required temperature only, right? Then what you do? This reaction mixture you take to flash tower by suddenly reducing the pressure what happens? Whatever the catalyst is there that is tri-propyl aluminum catalyst plus solvent etc. are there, they would be separated at the bottom and then they can be recycled back to the reactor. Whereas from the top you will be getting 2 methyl, 1 pentene product plus impurities. Impurities because the propylene feedstock pure you may not be having, right? So, and then you are also taking some solvent, naphtha saturates also, right? So, because of that one there would be some impurities like light ends and then unreacted propylene etc. may also be there. So, this mixture you take to C1 to C3 tower, right? So, where what you do? Lighter products like methane etc. would be separated out from the top as the light ends. Whereas the heavier one which are including the 2 methyl, 1 pentane dimer along with the unreacted propylene etc. would be taken to C3 tower. C3 tower in the sense this tower the temperature, pressure conditions are maintained such a way that unreacted propylene whatever is there that would be collected from the top as the top product and then recycled back to the reactor mixture, okay? Whereas from the bottom you will be having the heavy ends plus 2 methyl, 1 pentene mixture. So that you take to the dimer tower, right? So, dimer purification takes place. This 2 methyl, 1 pentene is nothing but the so called the dimer of the propylene, right? So that would be purified and then obtained as the top product from the dimer tower whereas the heavy ends are separated out from the bottom. So until now what we have done? We have done the dimerization and then purification of the dimer that has been produced, right? So now this dimer 2 methyl, 1 pentene whatever is there that you take to isomerization reactor where acid catalyst is used because this dimerization reaction does not take place without acid catalyst that we have seen and then required temperature also 150 to 300 degree centigrade is maintained. So that what happens? This 2 methyl, 1 pentene will be converted into 2 methyl, 2 pentene which is nothing but the isomer of the 2 methyl, 1 pentene, right? So, but the reaction may not be complete obviously. So, then what we do? We take the reaction mixture to stream stripper where the lighter 2 methyl, 1 pentene is separated from the top and then recycled back to the isomerization reactor whereas the heavier 2 methyl, 2 pentene whatever is there that is collected from the bottom and then sent to a pyrolysis reactor to which steam is also being supplied. Here in this reactor temperature requirement is 650 to 800 degree centigrade. So, in order to get such high temperature you need to have the flue gas and then combust it and then get the required energy, right? This pyrolysis reactor is a tubular reactor, okay? So here whatever the required catalyst you know hydrogen bromide is also present in the reactor, right? So now whatever the pyrolysis effluents are there, they will be taken to a quench tower, right? In order to reduce the temperature because in this reactor what happened? Already whatever this 2 methyl, 2 pentene is there that is being converted to isoprene and then of course there may be polymers also be present or there may be some kind of methane. In fact, methane would also be there because of the pyrolysis reaction that we have seen. So, this mixture is taken to the quencher, cooled down and then passed through a separator where we separated out the hydrogen bromide and then quench fluid whatever used for the quenching purpose and then recycled. After separating the catalyst and quench fluid whatever the mixture is there that is taken to the C1 tower so that to remove the methane and other light ends from the top and then can be taken as or used as fuel whereas the bottom one should be primarily isoprenes and then any polymers. So, what we do? This mixture we take to purifying column which is again distillation column. Here again temperature, pressure, conditions you maintain such a way that the lighter isoprene would be purified and collected as the top product whereas the heavier polymers would be collected as a bottom waste.

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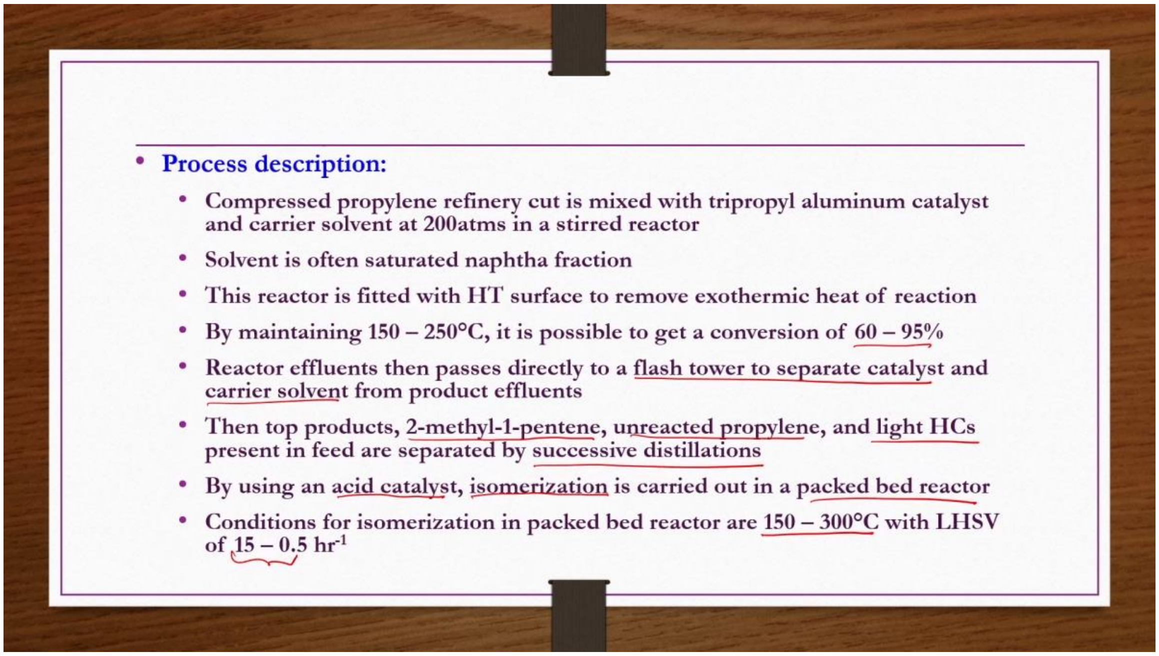

- **Process description:**
  - Compressed propylene refinery cut is mixed with tripropyl aluminum catalyst and carrier solvent at 200atms in a stirred reactor
  - Solvent is often saturated naphtha fraction
  - This reactor is fitted with HT surface to remove exothermic heat of reaction
  - By maintaining 150 – 250°C, it is possible to get a conversion of 60 – 95%
  - Reactor effluents then passes directly to a flash tower to separate catalyst and carrier solvent from product effluents
  - Then top products, 2-methyl-1-pentene, unreacted propylene, and light HCs present in feed are separated by successive distillations
  - By using an acid catalyst, isomerization is carried out in a packed bed reactor
  - Conditions for isomerization in packed bed reactor are 150 – 300°C with LHSV of 15 – 0.5 hr^{-1}

So, this is the process. Description if you see, compressed propylene refinery cut is mixed with tripropyl aluminum catalyst and carrier solvent at 200atmospheres in a stirred reactor. Solvent is often saturated in a naphtha fraction. This reactor is fitted with heat transfer surface to remove exothermic heat of reaction by maintaining 150 to 250 degrees centigrade. It is possible to get a conversion of 60 to 95%. Reactor effluents then passes directly to a flash tower to separate catalyst and then carrier solvent from product effluents and then recycle back to the reactor mixture. Then top products from the flash tower which includes 2 methyl, 1 pentene, unreacted propylene and then light hydrocarbons, they will be separated by successive distillations as we have seen in the flow chart. By using an acid catalyst, isomerization of 2 methyl, 1 pentene is carried out in a packed bed reactor by using 150 to 300 degrees centigrade temperature and then the material has been sent to the reactor or the dimers are fed to the reactor at the LHSV of 15 to 0.5 hour inverse.

Subsequent fractionation and recycling of a dimer is required to obtain 98 to 99% ultimate yield. Final step is pyrolysis of 2 methyl, 2 pentene to isoprene which is carried out as below. Pyrolysis is carried out in a tubular cracking furnace. Hydrogen bromide is used as catalyst and steam is used as diluent in the furnace. Conditions in furnace for pyrolysis are 650 to 800 degrees centigrades and then contact time is very small 0.3 to 0.5 seconds that is fast pyrolysis is taking place.

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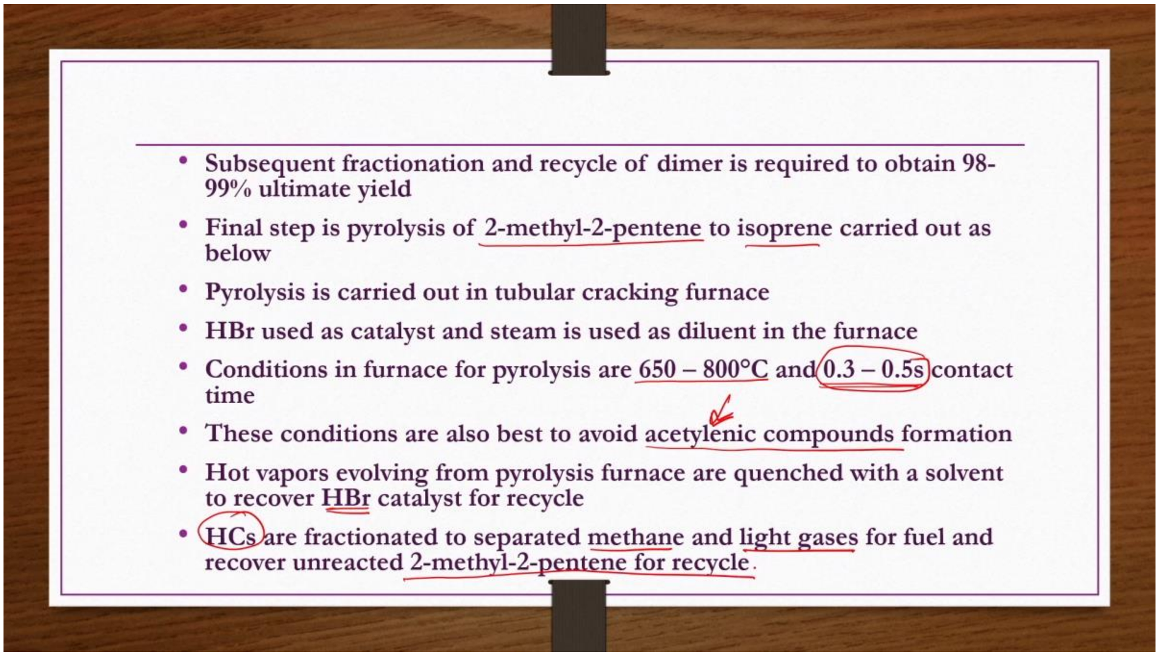

- Subsequent fractionation and recycle of dimer is required to obtain 98-99% ultimate yield
- Final step is pyrolysis of 2-methyl-2-pentene to isoprene carried out as below
- Pyrolysis is carried out in tubular cracking furnace
- HBr used as catalyst and steam is used as diluent in the furnace
- Conditions in furnace for pyrolysis are 650 – 800°C and 0.3 – 0.5s contact time
- These conditions are also best to avoid acetylenic compounds formation
- Hot vapors evolving from pyrolysis furnace are quenched with a solvent to recover HBr catalyst for recycle
- HCs are fractionated to separated methane and light gases for fuel and recover unreacted 2-methyl-2-pentene for recycle.

These conditions are also best to avoid acetylenic compounds formation because of the very small contact time other impurities, other products will not form which are not desired from the isoprene formation point of view. Hot vapors evolving from pyrolysis furnace are quenched with a solvent to recover hydrogen bromide catalyst for recycle and then hydrocarbons are fractionated to separate methane and light gases for fuel and recover unreacted 2 methyl,2 pentene for recycle.

Coming to the major engineering problems obviously 2 important ones are there. First one is the dimerization step, second one is the isomerization step. How effectively are you doing this process? The product yield and quality would be accordingly you know effective because pyrolysis having a little role in the product quality. Dimerization step, tri-propyl aluminum is extremely active towards polar solvents thus these compounds must be removed from the feed so that to avoid excessive loss of expensive catalyst. Low concentrations of propylene in feed will work satisfactory so you do not need to go for high purity propylene thus there is economic balance of reactor size versus a prior fractionation. High pressure of 200 atmosphere requires an expensive reactor and it is better to run with high propylene concentrations. New vapor phase dimerization solid catalyst system has been developed which removes necessity of high purity feed and then recycling of a liquid phase catalyst as well. Coming to the isomerization step associated problems, catalyst deterioration occurs on acid carrier surface by carbon or polymer formation. Required revivification is possible by oxidative regeneration of fixed bed. So, this is all about isoprene manufacturing process.

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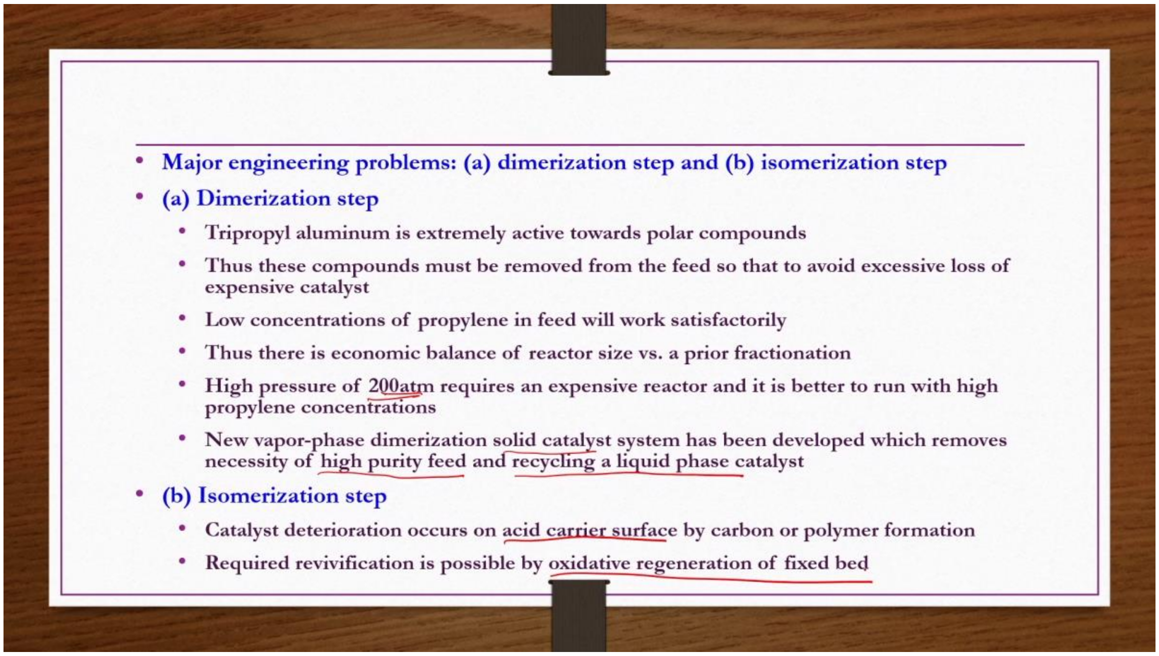

- **Major engineering problems: (a) dimerization step and (b) isomerization step**
- **(a) Dimerization step**
  - Tripropyl aluminum is extremely active towards polar compounds
  - Thus these compounds must be removed from the feed so that to avoid excessive loss of expensive catalyst
  - Low concentrations of propylene in feed will work satisfactorily
  - Thus there is economic balance of reactor size vs. a prior fractionation
  - High pressure of 200atm requires an expensive reactor and it is better to run with high propylene concentrations
  - New vapor-phase dimerization solid catalyst system has been developed which removes necessity of high purity feed and recycling a liquid phase catalyst
- **(b) Isomerization step**
  - Catalyst deterioration occurs on acid carrier surface by carbon or polymer formation
  - Required revivification is possible by oxidative regeneration of fixed bed

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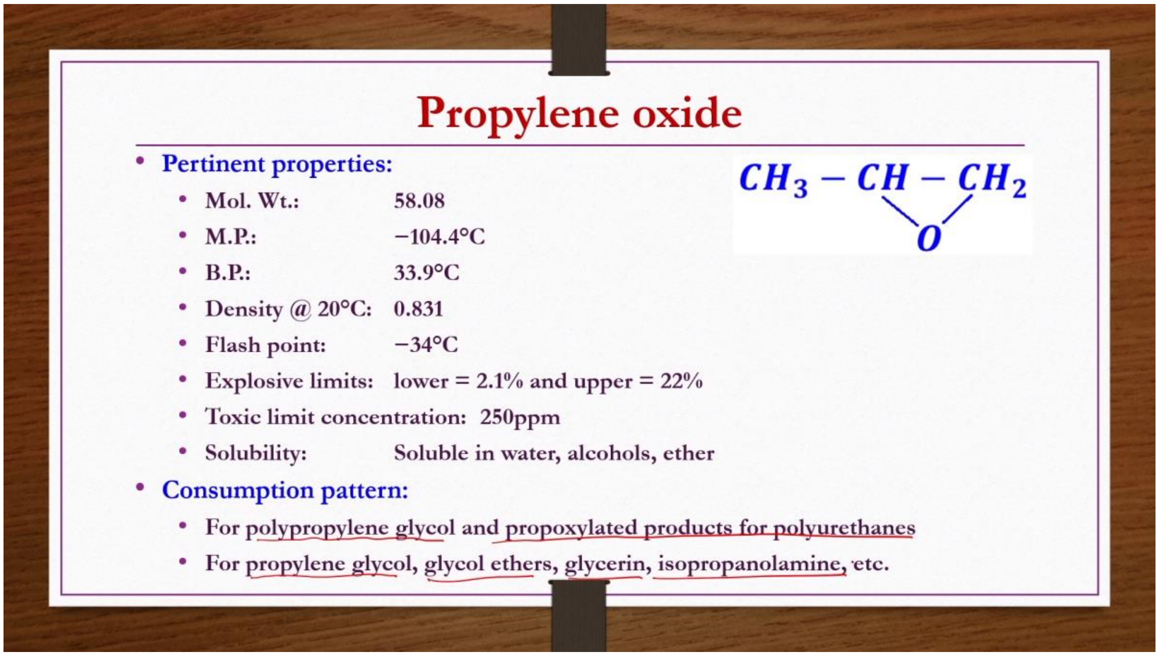

Propylene oxide

- **Pertinent properties:**
  - Mol. Wt.: 58.08
  - M.P.: −104.4°C
  - B.P.: 33.9°C
  - Density @ 20°C: 0.831
  - Flash point: −34°C
  - Explosive limits: lower = 2.1% and upper = 22%
  - Toxic limit concentration: 250ppm
  - Solubility: Soluble in water, alcohols, ether
- **Consumption pattern:**
  - For polypropylene glycol and propoxylated products for polyurethanes
  - For propylene glycol, glycol ethers, glycerin, isopropanolamine, etc.

$$CH_3 - CH - CH_2 \quad (\text{CH and } CH_2 \text{ bridged by } O)$$

Now, we discuss about propylene oxide, its molecular structure is provided here. First we see its pertinent properties, molecular weight 58.08, melting point minus 104.4 degrees centigrade, boiling point 33.9 degrees centigrade, density at 20 degrees centigrade is 0.831gram per cc, flash point is minus 34 degrees centigrade, explosive limits are 2.1 and 22percent respectively lower and upper limits. Toxic limit is 250 ppm, solubility it is soluble in water, alcohols and ether, consumption pattern it is used for several products like you know especially from the polymers point of view like polypropylene glycol, propoxylated products for polyurethanes and then propylene glycol, glycol ethers, glycerin, isopropanol amines etc. are prepared using the propylene oxide.

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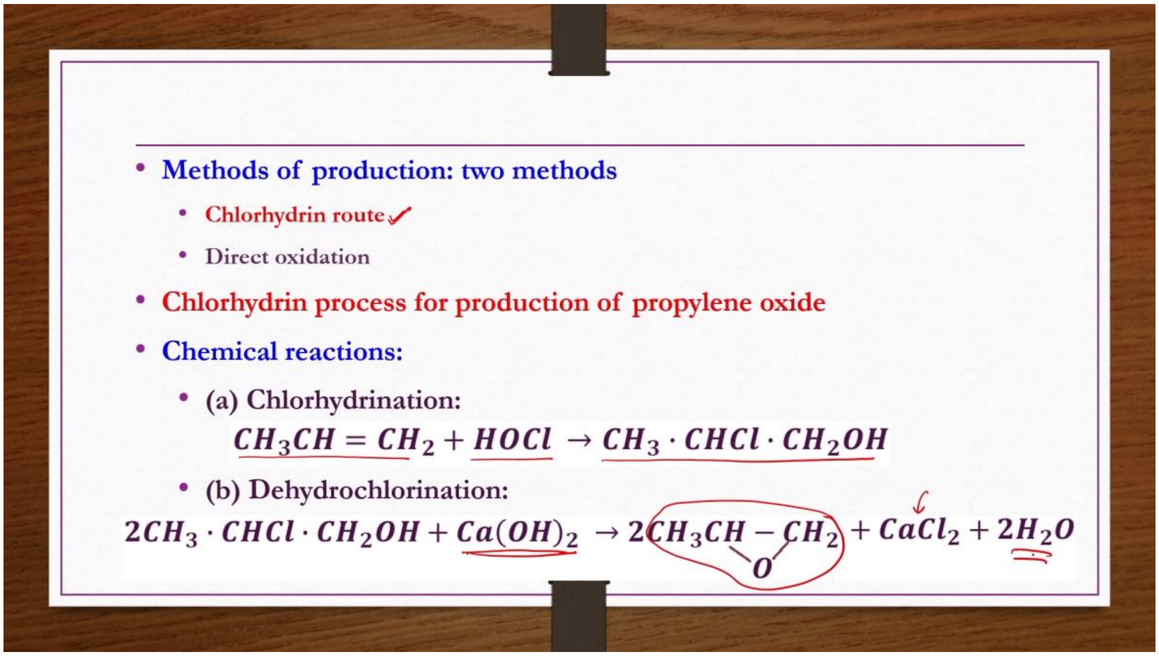

- **Methods of production: two methods**
  - Chlorhydrin route ✓
  - Direct oxidation
- **Chlorhydrin process for production of propylene oxide**
- **Chemical reactions:**
  - (a) Chlorhydrination:

$$\underline{CH_3CH = CH_2} + \underline{HOCl} \rightarrow \underline{CH_3 \cdot CHCl \cdot CH_2OH}$$

  - (b) Dehydrochlorination:

$$2CH_3 \cdot CHCl \cdot CH_2OH + \underline{Ca(OH)_2} \rightarrow 2\boxed{CH_3CH \underset{O}{-} CH_2} + \overset{\downarrow}{CaCl_2} + 2\underline{\underline{H_2O}}$$

Coming to the methods of production, 2 important methods are there, one is the chlorhydrin route, another one is the direct oxidation route. We select this chlorhydrin route. If we look at the reactions associated with this process, first we have chlorhydrination reaction where propylene reacts with hypochlorous acid to form chlorhydrin. This will undergo dehydrochlorination by using calcium hydroxide to produce propylene oxide and then calcium chloride along with water, okay?

Quantitative requirements, if you wanted to produce 1 ton of propylene oxide having more than 99 percent purity with 80 percent yield, propylene requirement is 0.91 tons, chlorine requirement is 2.0 tons, lime 100 percent CaO, calcium oxide requirement is 1.6 tons, electricity is 150 kilowatt hours, steam requirement 12 tons, water requirement 240 tons, byproducts also there which are used 0.97 tons of calcium chloride. If you cannot find market for it, lot of waste may be accumulated, okay? Other byproduct is that you know propylene dichloride which is produced at 0.1 to 0.15 tons. Plant capacities usually 30 to 200 tons per day.

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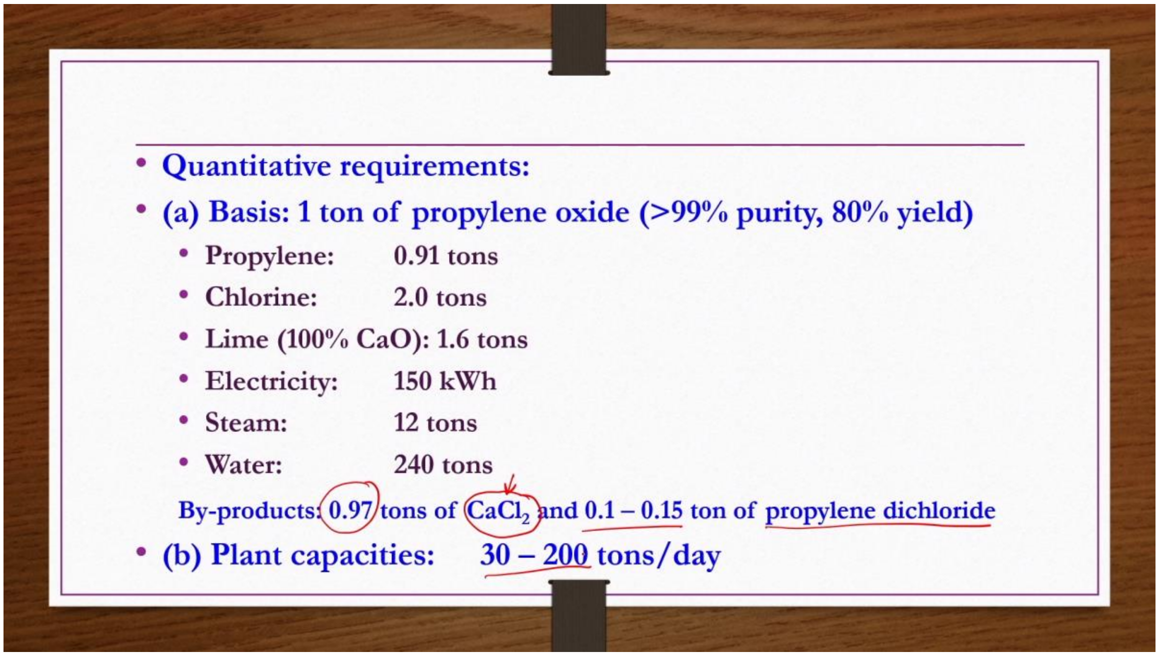

- **Quantitative requirements:**
- **(a) Basis: 1 ton of propylene oxide (>99% purity, 80% yield)**
  - **Propylene:** 0.91 tons
  - **Chlorine:** 2.0 tons
  - **Lime (100% CaO):** 1.6 tons
  - **Electricity:** 150 kWh
  - **Steam:** 12 tons
  - **Water:** 240 tons

  By-products: 0.97 tons of $CaCl_2$ and 0.1 – 0.15 ton of propylene dichloride
- **(b) Plant capacities:** 30 – 200 tons/day

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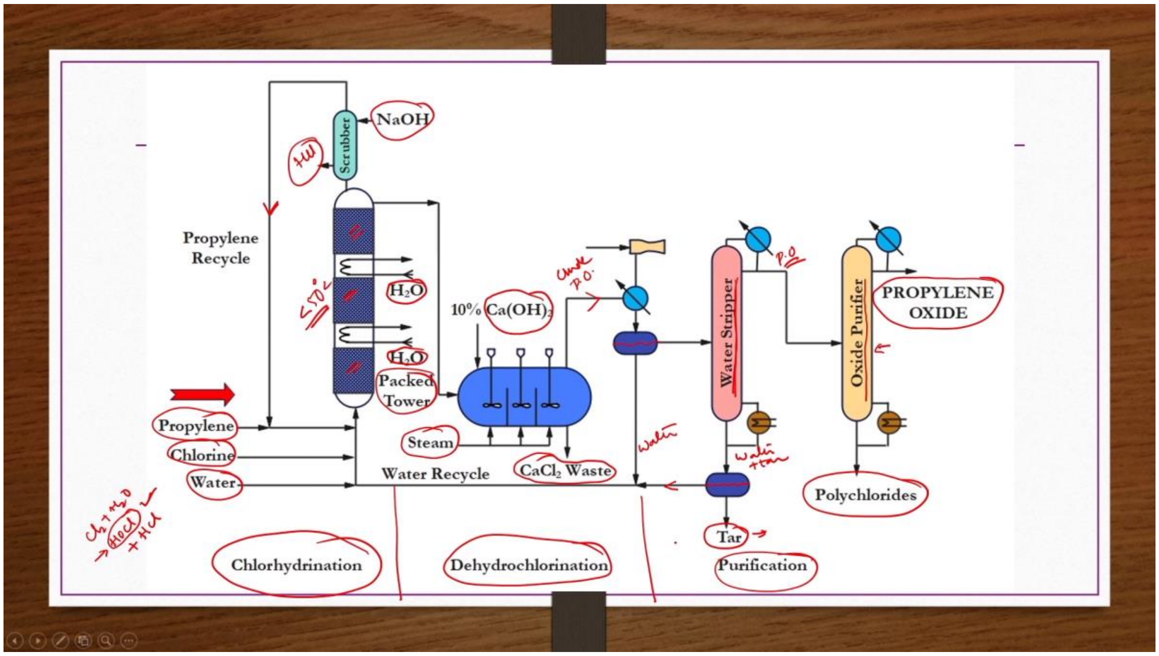

Now, we first discuss the flowchart for this process. Here what we do? Water, chlorine, propylene are mixed and then sent to the bottom of a packed bed reactor, right? So, here what happens within the reactor, this chlorine and water react together to give hypochlorous acid plus HCl, right? So, whatever the catalyst required for the reaction to take place that is HOCl, we are not supplying directly but we are supplying chlorine and water and then within the reactor we are making sure that this catalyst is formed. Using this catalyst what happen? Propylene chlor hydrogenation takes place and then you get chlorhydrene product, intermediate infact. Along with this one this HCl is also there. So, this reaction mixture what happens? It has to be taken to a scrubber where caustic is used to scrub out the HCl, right? And then spent NaOH would be there, okay? So, after separating out the HCl whatever the unreacted propylene is there that is recycled back to the bottom of the reactor along with the feed, okay? Now, this reactor what you have? You have a stage wise packing like this and then in between water supplier are also provided. What do you mean by this? This is not the supply of water to the reactor directly. It may be used to cool down the temperature because it is highly exothermic reaction. So, then temperature has to be maintained maximum up to 50 degrees centigrade only, okay? Then after separating out the HCl and then recycling propylene to the bottom of the reactor whatever the mixture is there that would be reacting with calcium hydroxide and then it will be giving you the so called propylene oxide, crude propylene oxide. And then in this reaction what happens calcium chloride is also forming that you have to collect as a waste or you know finds appropriate market. For this reaction to occur steam is also provided, okay? This crude propylene oxide what you do? You cool it down and then send it to a separator, right? Where water whatever is there that you can separate out whatever you can separate and then recycle it, but you cannot separate out the water completely. So, then this mixture you take to water stripper so that lighter propylene oxide would be collected from the top whereas the heavier water plus tar would be collected from the bottom as a heavy product, right? And then they would be separated out this tar is collected separately and discarded whereas the water is recycled back to the reactor as a water requirement as per the calculations, okay? This crude propylene oxide still we are calling crude because it may be having some polychlorides also. So, those are removed in a purifier or oxide purifier which is also a distillation column. Again, you maintain temperature, pressure or such a way that you know propylene oxide lighter compound would be collected from the top as a product whereas the heavier polychloride should be collected from the bottom of the reactor, okay? So, now here this flowchart if you look at up to this step you know you have chlor hydrination reaction and then dehydrochlorination reaction by using calcium hydroxide to form the propylene oxide, calcium chloride and then water along with the polychlorides and then other impurities. So, subsequent steps are the purification steps. So, that is what you know a kind of separation of the flowchart is shown like this.

Process description in order to form chlorhydrin, propylene, chlorine and then water are introduced into the bottom of a packet tower. Reaction mechanism is formation of hypochlorous acid by reacting between chlorine and water so that which reacts rapidly with propylene and then forms required chlorhydrin.

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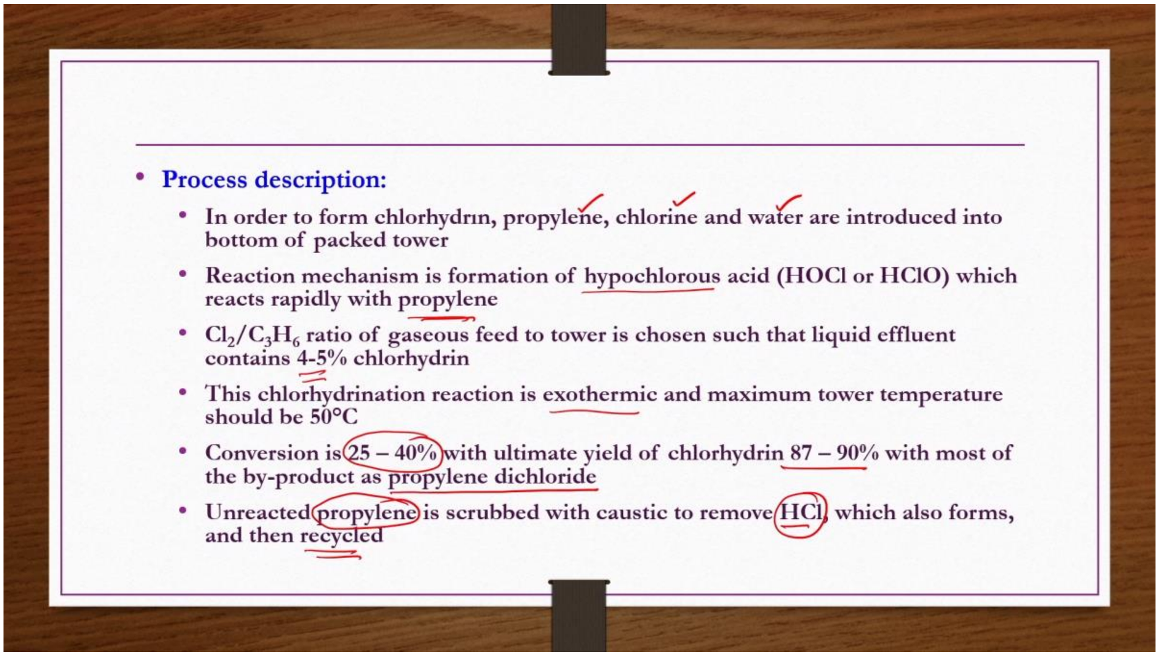

- **Process description:**
  - In order to form chlorhydrin, propylene, chlorine and water are introduced into bottom of packed tower
  - Reaction mechanism is formation of hypochlorous acid (HOCl or HClO) which reacts rapidly with propylene
  - Cl_2/C_3H_6 ratio of gaseous feed to tower is chosen such that liquid effluent contains 4-5% chlorhydrin
  - This chlorhydrination reaction is exothermic and maximum tower temperature should be 50°C
  - Conversion is 25 – 40% with ultimate yield of chlorhydrin 87 – 90% with most of the by-product as propylene dichloride
  - Unreacted propylene is scrubbed with caustic to remove HCl, which also forms, and then recycled

Chlorine to propylene ratio of gases feed to tower is chosen such that liquid effluent contains for at least 4 to 5 percent of chlorhydrin. This chlorhydrination reaction is exothermic and maximum tower temperature should not be more than 50 degrees centigrade. Conversion is 25 to 40 percent with ultimate yield of chlorhydrin between 87 to 90 percent with most of the byproduct as propylene dichloride. Unreacted propylene is scrubbed with caustic to remove HCl which also forms when this hypochlorous acid is formed within the reactor and then recycle whatever the propylene is there that is recycled after washing the mixture with the NaOH to separate out HCl. Once HCl is separated out by treating with NaOH you get the pure unreacted propylene that you can recycle back to the reactor.

Major engineering problems obviously because of the chlorine presence corrosion would be there and then chlorine losses would be there so that you have to reduce and then what about calcium chloride product, how are you utilizing? So, these are the 3 important problems of this process. Corrosion it occurs because of wet chlorine and calcium chloride at 50 to 100 degrees centigrade in the process. Thus, requires material of construction such as DuClor, Durimet, Haveg, ceramic or glass materials. Chlorine losses relatively high cost of chlorine forces and optimization of HOCl, hypochlorous acid concentration versus tower reaction capacity. Chlorine is ultimately lost to calcium chloride or free chlorine so that you have to make sure as minimum as possible. Then calcium chloride byproduct, use of lime to neutralize HCl and aid in rapid dehydrochlorination creates calcium chloride waste as steam as per the reaction that we have seen.

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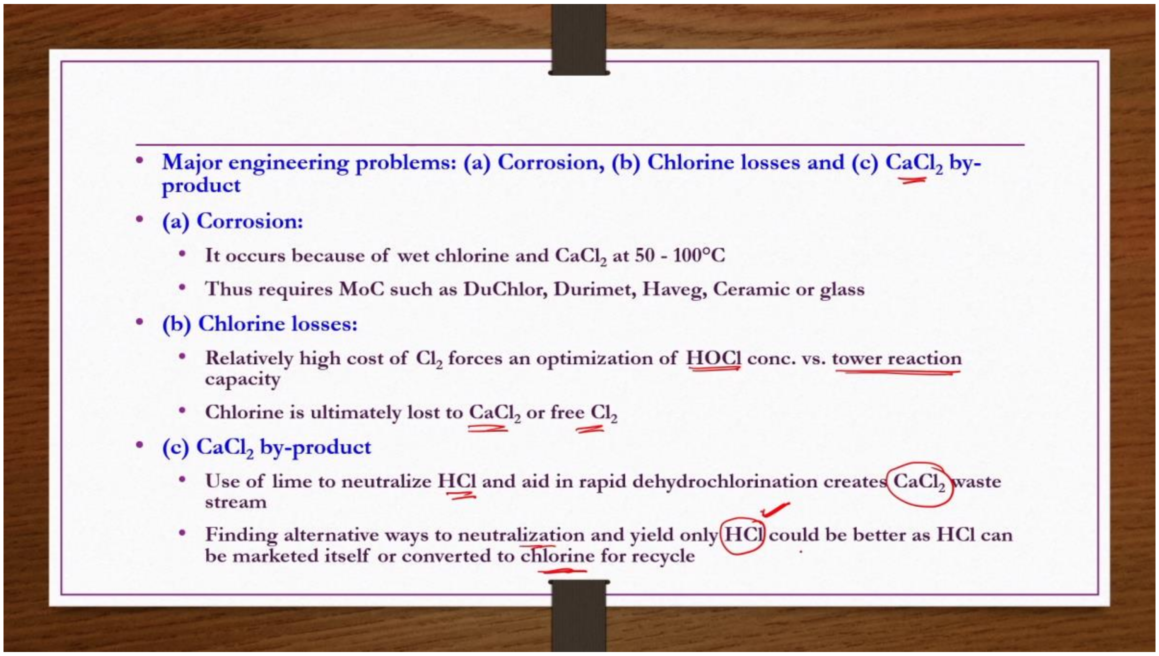

- **Major engineering problems: (a) Corrosion, (b) Chlorine losses and (c) $CaCl_2$ by-product**
- **(a) Corrosion:**
  - It occurs because of wet chlorine and $CaCl_2$ at 50 - 100°C
  - Thus requires MoC such as DuChlor, Durimet, Haveg, Ceramic or glass
- **(b) Chlorine losses:**
  - Relatively high cost of Cl_2 forces an optimization of HOCl conc. vs. tower reaction capacity
  - Chlorine is ultimately lost to $CaCl_2$ or free Cl_2
- **(c) $CaCl_2$ by-product**
  - Use of lime to neutralize HCl and aid in rapid dehydrochlorination creates $CaCl_2$ waste stream
  - Finding alternative ways to neutralization and yield only HCl could be better as HCl can be marketed itself or converted to chlorine for recycle

So, if you find alternative ways to neutralize it, then what you can do? You can have only HCl yield and then you can find appropriate market for this HCl or this HCl may be converted to the chlorine for recycle also. That is all about production of propylene oxide.

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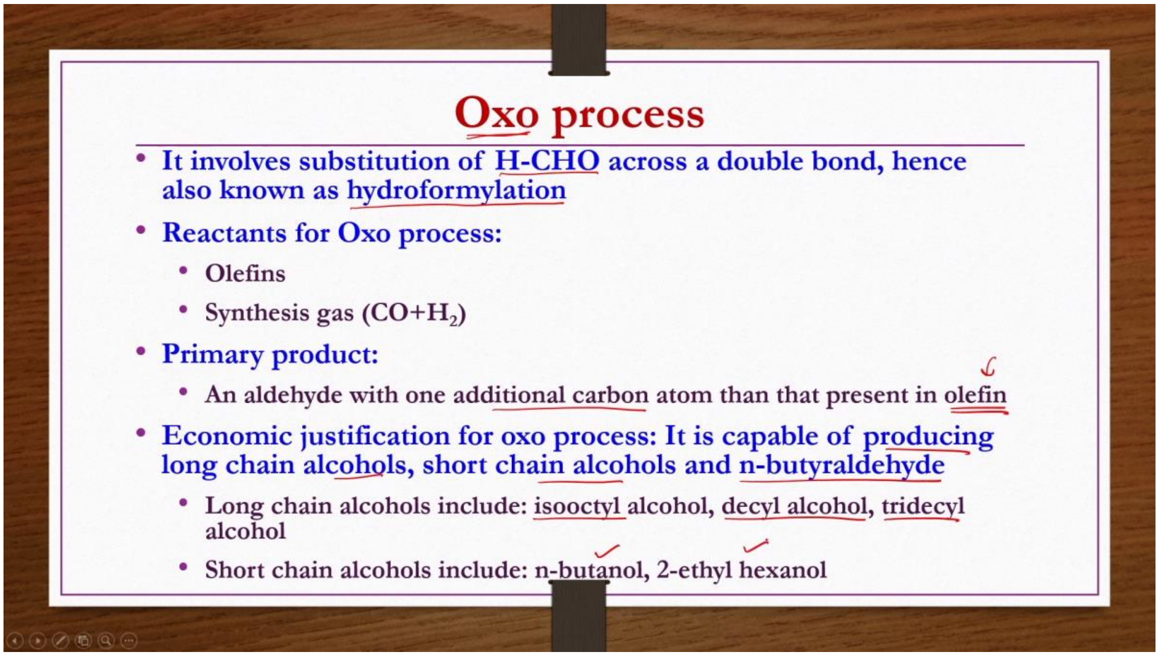

Oxo process

- **It involves substitution of H-CHO across a double bond, hence also known as hydroformylation**
- **Reactants for Oxo process:**
  - Olefins
  - Synthesis gas ($CO+H_2$)
- **Primary product:**
  - An aldehyde with one additional carbon atom than that present in olefin
- **Economic justification for oxo process: It is capable of producing long chain alcohols, short chain alcohols and n-butyraldehyde**
  - Long chain alcohols include: isooctyl alcohol, decyl alcohol, tridecyl alcohol
  - Short chain alcohols include: n-butanol, 2-ethyl hexanol

Now, we discuss about oxo processes. Oxo process it involves substitution of HCHO across a double bond. Hence, it is also known as hydroformylation process as well. What is oxo process? Basically, it is a reaction between an olefin and synthesis gas so that to produce some kind of aldehyde. Aldehyde also one carbon atom more than the whatever the number of carbon atoms were present in the olefins. Let us say if you take propylene, then butyraldehyde you may get and then that butyraldehyde you may also do the hydrogenation to get the butanol. So, this oxo process primarily the product is aldehyde, but that aldehyde may be hydrogenated within the plant to get the corresponding alcohol also. So, reactants for oxo process are nothing but olefins and synthesis gas. Primary product is an aldehyde with one additional carbon atom than that present in the olefin. If you take propylene as a raw material, then whatever the aldehyde that you get that would be get 4 carbon atom aldehyde that is butyraldehyde or isobutyraldehyde you may get. Economic justification for oxo process it is capable of producing long chain alcohols as well as the short chain alcohols and n-butyraldehyde as well. What are the long chain alcohols in general that you can produce by this process are iso-octylalcohol, decyl alcohol, tridecyl alcohol, etc. What are the short chain alcohols you can produce n-butanol, 2-methylhexanol, etc.

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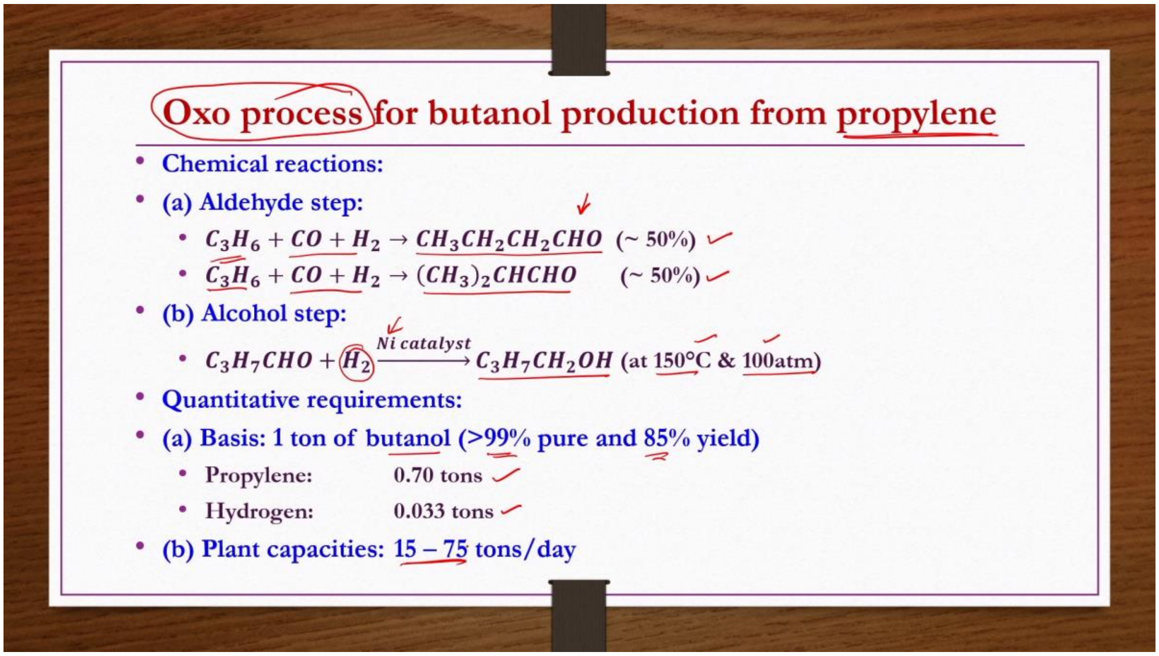

Oxo process for butanol production from propylene

- Chemical reactions:
- (a) Aldehyde step:
  - $C_3H_6 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO$ (~ 50%)
  - $C_3H_6 + CO + H_2 \rightarrow (CH_3)_2CHCHO$ (~ 50%)
- (b) Alcohol step:
  - $C_3H_7CHO + H_2 \xrightarrow{Ni\ catalyst} C_3H_7CH_2OH$ (at 150°C & 100atm)
- Quantitative requirements:
- (a) Basis: 1 ton of butanol (>99% pure and 85% yield)
  - Propylene: 0.70 tons
  - Hydrogen: 0.033 tons
- (b) Plant capacities: 15 – 75 tons/day

Now, we see the oxo process actually oxo process is a generalized one. Actually, this oxo process is a very generalized one. So, you can produce different types of alcohols different types of aldehyde and alcohols that depends on the what type of or what carbon number olefin have you selected. So, now what we do we take propylene as the base or you know propylene from the olefin category and then react with the synthesis gas, try to get the butyraldehyde or iso-butyraldehyde or both of them and then do the hydrogenation of butyraldehyde to get the butanol, okay? That process we are going to discuss. Chemical reactions obviously first step is aldehyde step which is nothing but the reaction between the olefin and then synthesis gas. So, here olefin is the propylene we are selecting synthesis gas CO plus H2 when you do then you can get butyraldehyde approximately 50 percent you may get and then the same composition of the reactants when you take then also you know you get iso-butyraldehyde also you may get. This is butyraldehyde, this is iso-butyraldehyde both of them you may get 50 percent respectively. Second step is alcohol then second step what you do you take this butyraldehyde and do the hydrogenation in the presence of nickel catalyst to get the butanol. Of course, temperature of 150 degrees centigrade and then 100 atmospheric pressure is required for the hydrogenation reaction because hydrogenation reaction does not occur easily. It requires high pressure, moderate temperature and then expensive catalyst like nickel, platinum, etc. Quantitative requirements, basis 1 ton of butanol if you wanted to produce more than 99 percent pure butanol and 85 percent yield then propylene 0.7 tons required and then hydrogen 0.033 tons required. Plant capacities usually 15 to 75 tons per day only.

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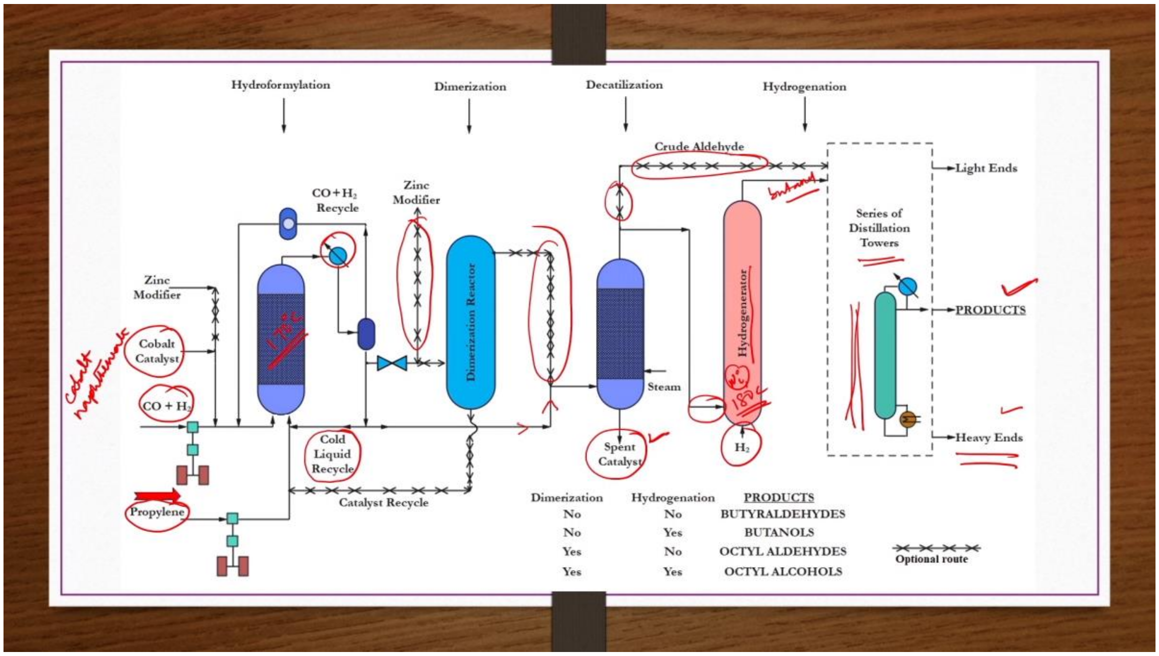

Dimerization	Hydrogenation	PRODUCTS
No	No	BUTYRALDEHYDES
No	Yes	BUTANOLS
Yes	No	OCTYL ALDEHYDES
Yes	Yes	OCTYL ALCOHOLS

Now this is the flow chart what we have here we have synthesis gas and then propylene separately we are compressing and then sending to the reactor. To the reactor we also send cobalt, here what we are taking cobalt, naphthenates we are taking and then sending along with the propylene and then synthesis gas to the reactor. In this packed bed reactor what happens the required hydroformylation reaction takes place and then you get a butyraldehyde, isobutyraldehyde as products actually. So, this product mixture is cooled down and then gaseous mixture whatever CO, H2 which is non-condensable they are taken back to the reactor as a recycle. Whereas the cold product some of it you take it back to the reactor in order to maintain the temperature of the reactor within the limits of required temperatures. So, here you do not want the temperature to go more than 150 to 170 degrees centigrade. So, then what you do some of the cold product whatever is there liquid product especially that is fed back to the reactor to maintain the temperature. This will also aid increase in the conversion and then more production of the aldehydes. This product mixture now you have the alternative options whatever these lines depicted this formula they are options. You can have or you cannot if you do not want products you do not need to have you do not need to go further like that. Let us say if you are happy with the butyraldehyde producing from the propylene and then synthesis gas reaction then you do not need to go for this dimerization step etc. So, this process this you make sure you take and then remove this spent catalyst in the decatalization unit and then after that what you do you take it to the purification step that is series of distillation towers would be there. There you can do the purification and get the butyraldehyde isobutyraldehydes as the product. Let us say if you wanted to produce alcohols which we are discussing then what we do this aldehydes whatever butyraldehyde isobutyraldehyde are there you pass through a decatalyzer unit to remove the spent catalyst and then send them to the recycle. After removing the catalyst you send it to the hydrogenator which is a packed bed reactor using the nickel catalyst and then reactor temperature is maintained at 180 degrees centigrade to this reactor hydrogen and then the butyraldehydes are supplied. When the reaction completes you can get the products butanol and then some heavy ends. So, those mixtures you can take to the series of distillation towers to get the butanol products at the top and then heavy ends at the bottom. So, oxo process is very generalized one so that is the reason very generalized way we have discussed here.

Propylene is compressed to 250 atmosphere and cobalt naphthenate added to give 0.5 to 1 percent CO in solution cobalt in solution. Then this stream is passed co-currently through a packed tower containing a porous carrier with 2 percent metallic cobalt deposited. Reaction is highly exothermic and 170 degrees centigrade is controlled by recycle of a portion of product stream after cooling. Liquid fraction is mixed with steam at 180 degrees centigrade and relatively low pressures of 20 atmosphere. This is to decompose cobalt carbonyl and naphthenate depositing the cobalt on a porous carrier as oxide so that it can be used as a catalyst. This cobalt is dissolved periodically in an acid wash and converted to naphthenate for reuse. Unconverted synthesis gas from oxo converter is recompressed and recycled.

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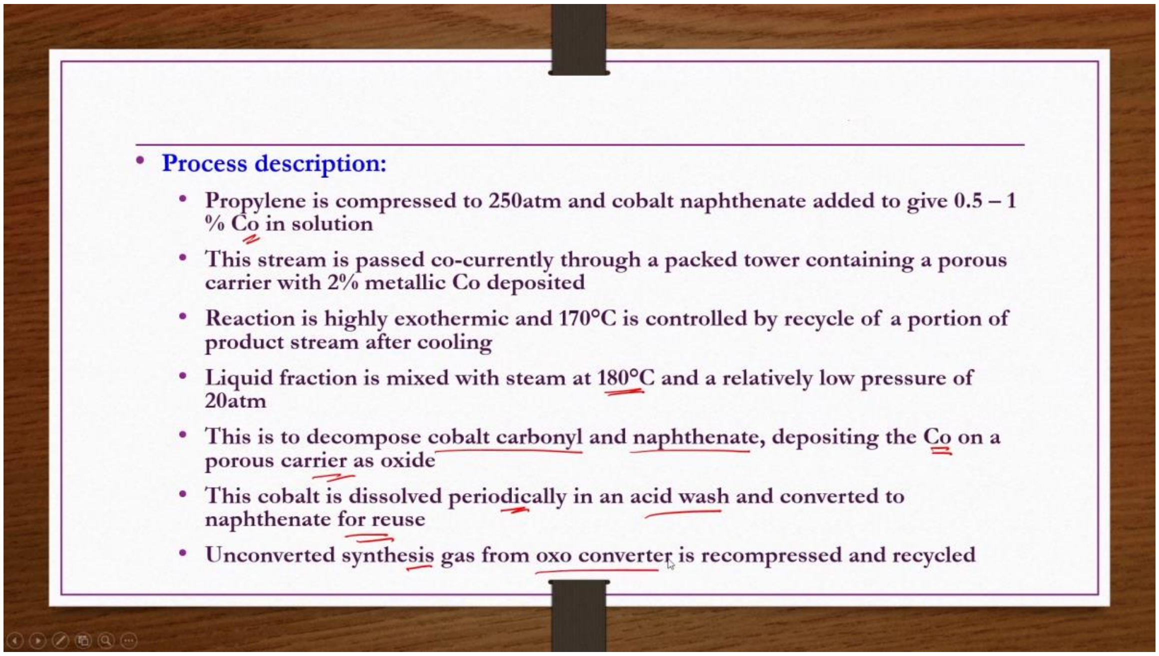

- **Process description:**
  - Propylene is compressed to 250atm and cobalt naphthenate added to give 0.5 – 1 % Co in solution
  - This stream is passed co-currently through a packed tower containing a porous carrier with 2% metallic Co deposited
  - Reaction is highly exothermic and 170°C is controlled by recycle of a portion of product stream after cooling
  - Liquid fraction is mixed with steam at 180°C and a relatively low pressure of 20atm
  - This is to decompose cobalt carbonyl and naphthenate, depositing the Co on a porous carrier as oxide
  - This cobalt is dissolved periodically in an acid wash and converted to naphthenate for reuse
  - Unconverted synthesis gas from oxo converter is recompressed and recycled

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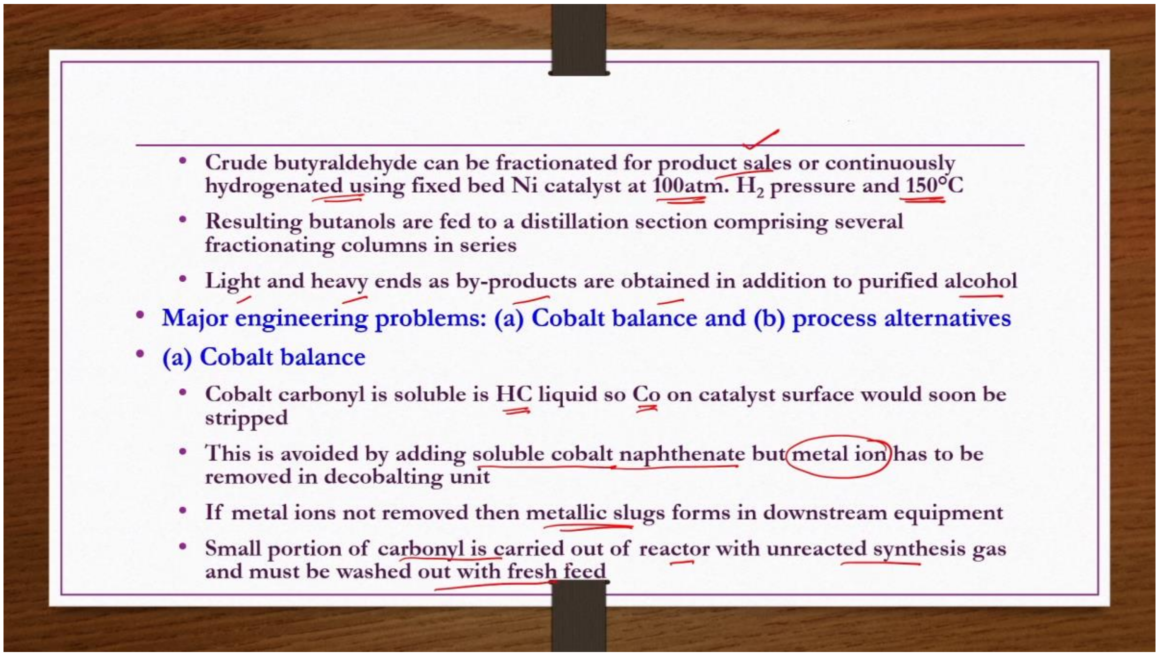

- Crude butyraldehyde can be fractionated for product sales or continuously hydrogenated using fixed bed Ni catalyst at 100atm. H_2 pressure and 150°C
- Resulting butanols are fed to a distillation section comprising several fractionating columns in series
- Light and heavy ends as by-products are obtained in addition to purified alcohol

- **Major engineering problems: (a) Cobalt balance and (b) process alternatives**
- **(a) Cobalt balance**
  - Cobalt carbonyl is soluble is HC liquid so Co on catalyst surface would soon be stripped
  - This is avoided by adding soluble cobalt naphthenate but metal ion has to be removed in decobalting unit
  - If metal ions not removed then metallic slugs forms in downstream equipment
  - Small portion of carbonyl is carried out of reactor with unreacted synthesis gas and must be washed out with fresh feed

Crude butyraldehyde can be fractionated for product sales directly or continuously hydrogenated using fixed bed nickel catalyst at 100 atmosphere hydrogen pressure and 150 to 180 degrees centigrade temperature to get the butanol. Resulting butanols are fed to a distillation section comprising several fractionating columns in series which are required to have the purification. In this series of fractionating columns light ends, heavy ends as byproducts are obtained in addition to purified alcohol. Major engineering problems cobalt balance and process alternatives are 2 important issues to be considered. Under the cobalt balance cobalt carbonyl is soluble in hydrocarbon liquid. So, cobalt on catalyst surface would soon be stripped. This is avoided by adding soluble cobalt naphthenate but metal ion has to be removed in decobalting unit. If you do not remove this metal ions what happen in the downstream equipment metallic slugs would be forming. Small portion of carbonyl is carried out of the reactor with unreacted synthesis gas and must be washed out with fresh feed.

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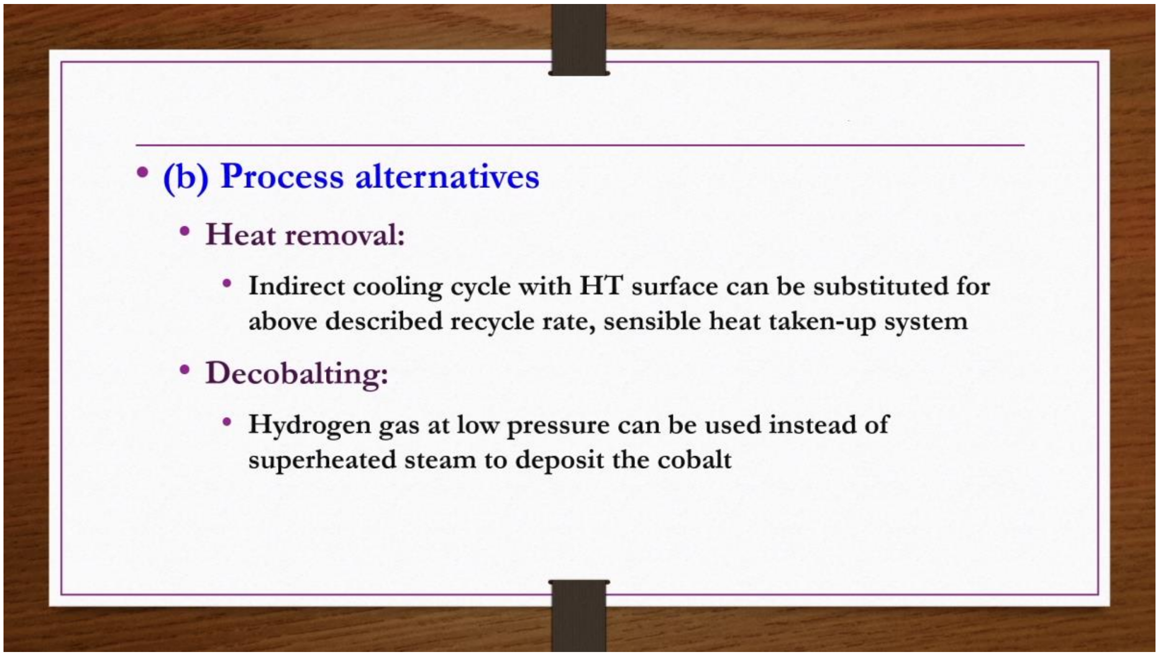

- **(b) Process alternatives**
  - **Heat removal:**
    - Indirect cooling cycle with HT surface can be substituted for above described recycle rate, sensible heat taken-up system
  - **Decobalting:**
    - Hydrogen gas at low pressure can be used instead of superheated steam to deposit the cobalt

Coming to the process alternatives especially with respect to heat removal indirect cooling cycle with heat transfer surface can be substituted for above described recycle rate and sensible heat taken up system. Decobalting is another process alternative where hydrogen gas at low pressure can be used instead of a superheated steam to deposit the cobalt. This is all about production of butyraldehyde and butanol from the propylene by using oxo process.

So, with this we complete the selected chemicals production from a C3 compound that is propylene. We have discussed the production of 8 different types of chemicals from propylene compound. In the next lecture we will be selecting a few C4 compounds and then we try to produce a few chemicals from C4 compounds. References for this particular lecture are provided here. Thank you.

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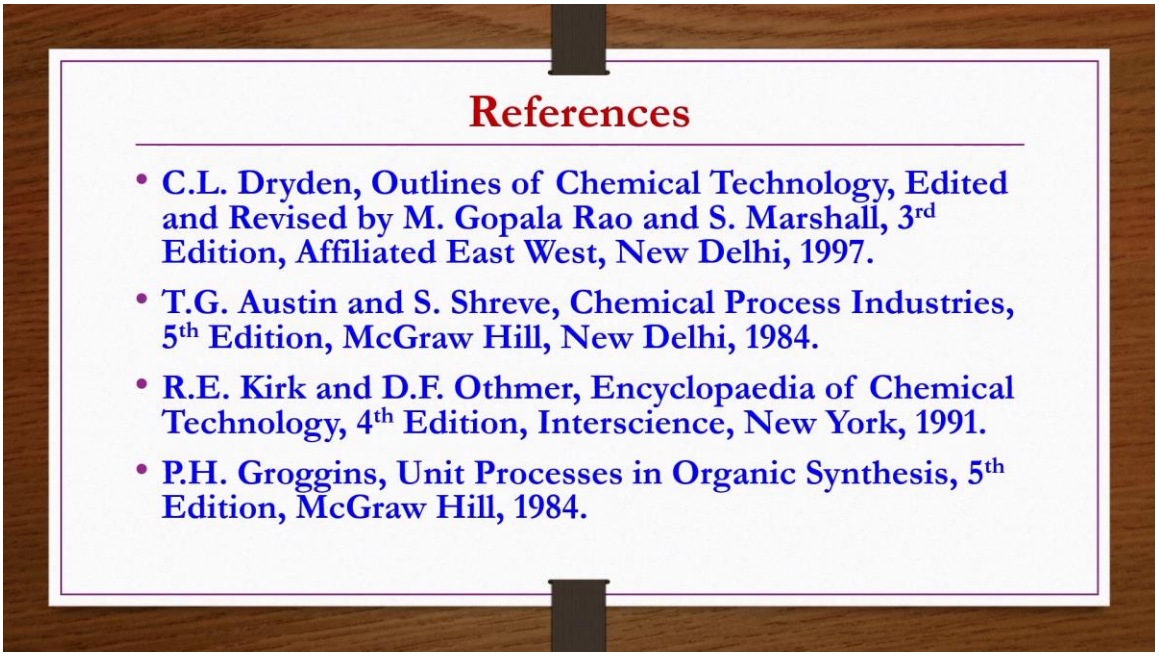

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