Organic Chemical Technology

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Lecture - 26
Chemicals from C3 Compounds

Welcome to the MOOCs course Organic Chemical Technology. The title of today's lecture is chemicals from C3 compounds. In this lecture, we discuss production of different types of chemicals from C3 compounds. Under the C3 compounds, we have taken propylene because in the previous chapter, we have discussed when we do the steam cracking of hydrocarbons to produce ethylene and acetylene, not only ethylene and acetylene, propylene, butylene, propane, butane, etc. So many other compounds are also produced and then we realized that this propylene is produced at least at 50% rate at which the ethylene is produced.

So that much large quantities it is being produced and then also from the application point of view after the ethylene, propylene is the most important olefin that can be utilized to produce different types of chemicals, right? Because of such reasons under the C3 compounds, we consider propylene and then try to produce different types of chemicals. Before getting into the details of productions of different types of chemicals, we see the spectrum of products one can produce from this propylene, okay?

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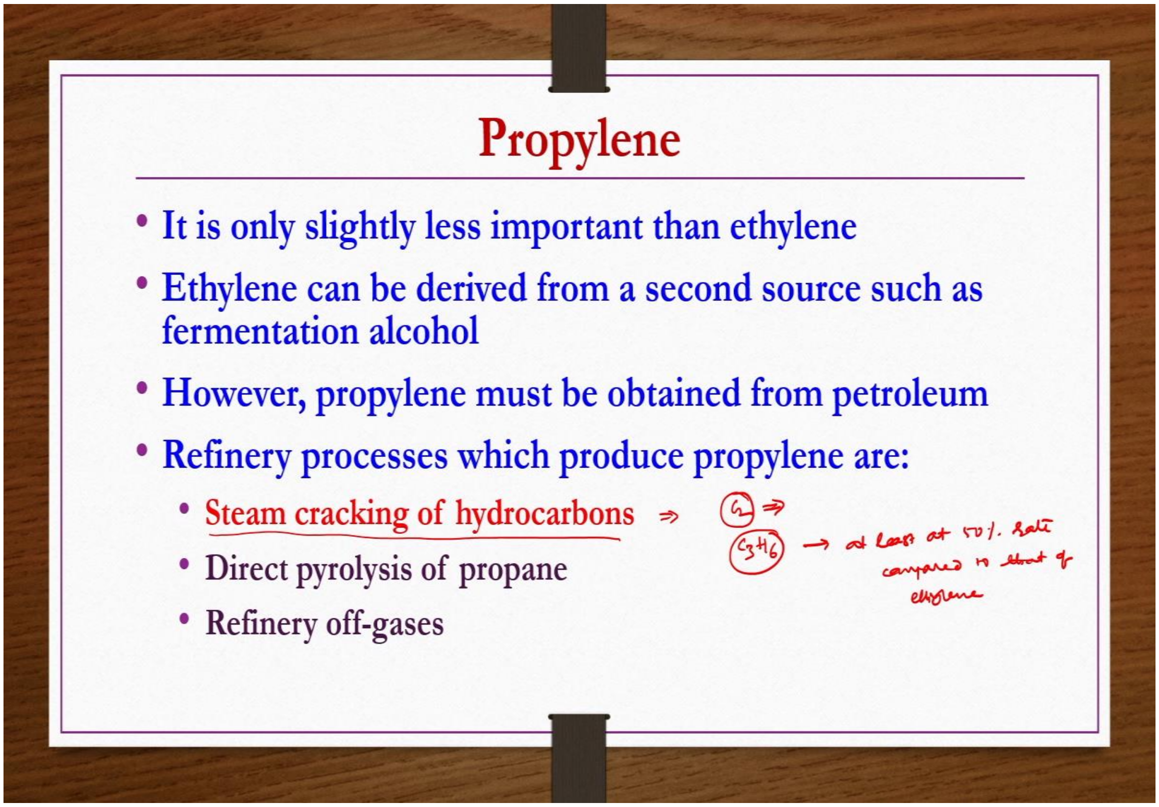

Propylene

- It is only slightly less important than ethylene
- Ethylene can be derived from a second source such as fermentation alcohol
- However, propylene must be obtained from petroleum
- Refinery processes which produce propylene are:
  - Steam cracking of hydrocarbons ⇒ $\boxed{C_2}$ ⇒
  - Direct pyrolysis of propane
  - Refinery off-gases

$\boxed{C_3H_6}$ → at least at 50% rate compared to that of ethylene

Propylene it is only slightly less important than ethylene from the applications point of view or from the end use applications point of view, how it can be utilized to produce different types of intermediate chemicals and then end chemicals, etc. On such basis if you compare it is only slightly less important than the ethylene because ethylene we have discussed in the previous chapter that it is the most important olefin from its applications point of view. So after the ethylene, propylene is such highly important olefin, okay? We have also seen in the previous lecture that ethylene can be produced from the fermentation alcohol as well, right? However, majority of the ethylene is being nowadays produced from the steam cracking of the hydrocarbons, right? So what I mean to say that though you have a secondary source for the production of ethylene that is fermentation alcohol, but in the case of propylene only source of production of propylene is the steam cracking of hydrocarbons. That is propylene must be obtained from petroleum resources only, it cannot be produced from other sources.

Refinery process which produce propylene are listed below, steam cracking of hydrocarbons, direct pyrolysis of propane and then refinery of gases, right? So this method we have already seen in the previous chapter when we were discussing about production of chemicals from C1 and C2 chemicals under which when we discussed production of C2 chemicals, right? First we have produced C2 compounds from the hydrocarbons by steam cracking, then we produce different types of chemical from such C2 compounds like ethylene, acetylene. In such process we have also seen that propylene is being produced at least at 50% rate compared to that of ethylene. So whatever the rate or whatever the mass rate or volumetric rate of ethylene that has been produced in the steam cracking of hydrocarbons, at least 50% of that rate, at that rate, you know, propylene is being produced, such large quantities it is being produced that is what it means to say, right? So not only from the production rate point of view, but also from the applications point of view propylene is very much essential, right?

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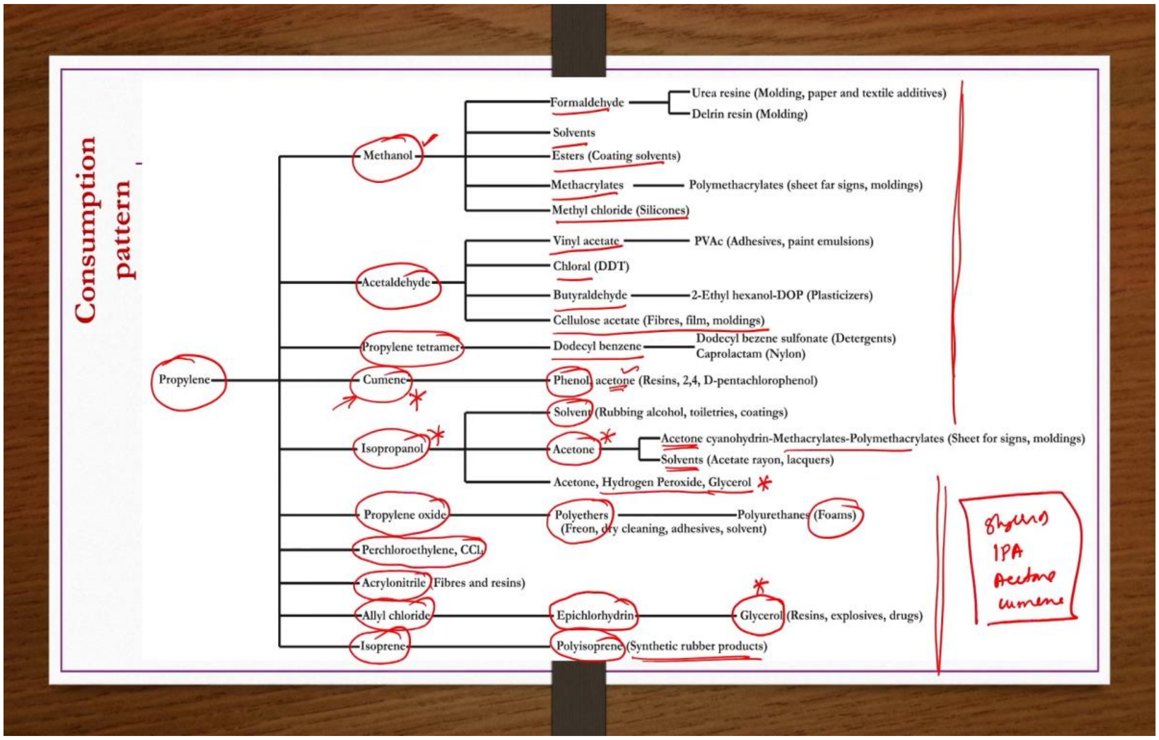

Consumption pattern

- Propylene
  - Methanol
    - Formaldehyde
      - Urea resine (Molding, paper and textile additives)
      - Delrin resin (Molding)
    - Solvents
    - Esters (Coating solvents)
    - Methacrylates
      - Polymethacrylates (sheet far signs, moldings)
    - Methyl chloride (Silicones)
  - Acetaldehyde
    - Vinyl acetate
      - PVAc (Adhesives, paint emulsions)
    - Chloral (DDT)
    - Butyraldehyde
      - 2-Ethyl hexanol-DOP (Plasticizers)
    - Cellulose acetate (Fibres, film, moldings)
  - Propylene tetramer
    - Dodecyl benzene
      - Dodecyl bezene sulfonate (Detergents)
      - Caprolactam (Nylon)
  - Cumene
    - Phenol, acetone (Resins, 2,4, D-pentachlorophenol)
  - Isopropanol
    - Solvent (Rubbing alcohol, toiletries, coatings)
    - Acetone
      - Acetone cyanohydrin-Methacrylates-Polymethacrylates (Sheet for signs, moldings)
      - Solvents (Acetate rayon, lacquers)
    - Acetone, Hydrogen Peroxide, Glycerol
  - Propylene oxide
    - Polyethers (Freon, dry cleaning, adhesives, solvent)
      - Polyurethanes (Foams)
  - Perchloroethylene, CCl_4
  - Acrylonitrile (Fibres and resins)
  - Allyl chloride
    - Epichlorhydrin
      - Glycerol (Resins, explosives, drugs)
  - Isoprene
    - Polyisoprene (Synthetic rubber products)

Glycerol
IPA
Acetone
cumene

So that we can see in this chart. Now, if you see this consumption pattern of propylene, you can understand how much important it is that you can utilize to produce different types of intermediates and then end chemicals. So from the propylene you can produce intermediates like methanol, acetaldehyde, propylene tetramer, cumene, isopropanol, propylene oxide, perchloroethylene, carbon tetrachloride, acrylonitriles, allyl chlorides, isoprene, etc., this you can see. And then using methanol what kind of chemicals we can produce that we have already discussed in the previous chapter. We have also discussed once you have the acetaldehyde, we can produce vinyl acetate, chloral, butyraldehyde, cellulose acetate fibers, etc., those things we have seen. Propylene tetramer can be used for the dodecyl benzene production.

Cumene initially it was produced as a blending for high octane fuels, but nowadays it is primarily utilized to produce phenol. In the production of phenol from the cumene, acetone is also obtained as co-product. Isopropanol is primarily used to produce acetone by dehydrogenation of isopropanol, you can get the acetone and then you know acetone is how much important as solvent. Nowadays acetone is also used for the acetone based chemicals, so many as mentioned here. Isopropanol is also used as solvent for different applications. Isopropanol is also utilized to produce hydrogen peroxide, glycerol, etc., that we are going to see. Propylene oxides can be used for production of polyethers, foams like polyurethanes, etc., whereas allyl chloride can be used to produce intermediate like epichlorhydrin from which you can also get the synthetic glycerol. Isoprene you can utilize to get polyisoprenes which is used for the synthetic rubber products.

Now you can see so many number of products are there, we have listed only few. So from the applications point of view, it is very much important after the ethylene within the olefins category. In this lecture, we are going to discuss the production of glycerol by 2 different ways and then we discuss production of isopropanol and from isopropanol production of acetone we will discuss and then production of cumene we will be discussing. So production of these 4 chemicals that is synthetic glycerol, isopropyl alcohol, acetone and then cumene would be covered in this particular lecture.

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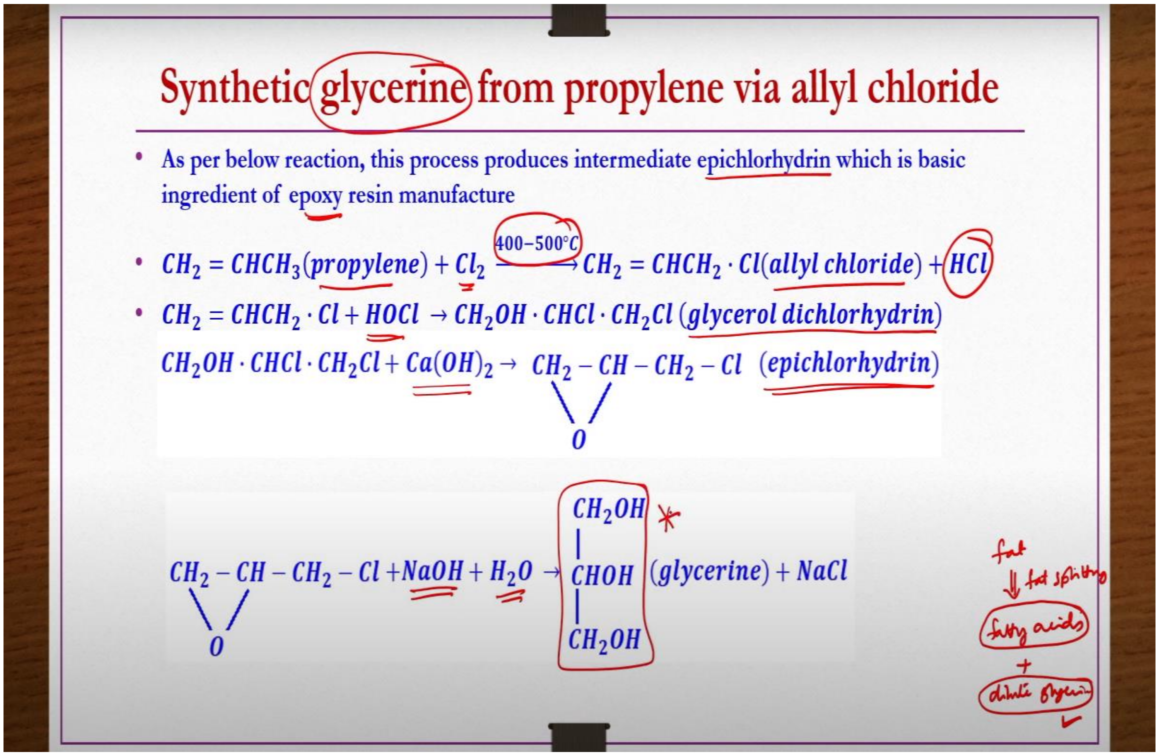

Synthetic glycerine from propylene via allyl chloride

- As per below reaction, this process produces intermediate epichlorhydrin which is basic ingredient of epoxy resin manufacture
- $CH_2 = CHCH_3(propylene) + Cl_2 \xrightarrow{400-500°C} CH_2 = CHCH_2 \cdot Cl(allyl\ chloride) + HCl$
- $CH_2 = CHCH_2 \cdot Cl + HOCl \rightarrow CH_2OH \cdot CHCl \cdot CH_2Cl$ (glycerol dichlorhydrin)

$CH_2OH \cdot CHCl \cdot CH_2Cl + Ca(OH)_2 \rightarrow CH_2 - CH - CH_2 - Cl$ (epichlorhydrin)

$CH_2 - CH - CH_2 - Cl + NaOH + H_2O \rightarrow CH_2OH - CHOH - CH_2OH$ (glycerine) + NaCl

fat
⇓ fat splitting
fatty acids
+
dilute glycerin

Synthetic glycerin from propylene via allyl chloride, so glycerin or glycerol production we are discussing now. Actually we have seen in the natural product industries what we have done, we have taken the fat and then we have done the fat splitting reaction using the high temperature high pressure water so that what you get fatty acids and then dilute glycerin you can get. So this is what we have discussed in the oils and fats industries followed by the soaps and detergents industries. So these fatty acids you can purify and then get as a product or further utilized to produce. Soaps, this dilute glycerin you can do the purification and then get a pure natural glycerol. So the glycerin can also be obtained by synthetic methods using propylene. So glycerin can be produced by synthetic methods using propylene. So there are 2 approaches are there, the first one is via allyl chloride that we discussed first. As per below reaction this process produces intermediate epichlorhydrin which is basic ingredient for epoxy resins manufacture. So where propylene reacts with the chlorine at 400 to 500 degrees centigrade to give allyl chloride plus HCl. This allyl chloride would further react with HOCl to give glycerol dichlorhydrin which is this component and this glycerol dichlorhydrin will further react with calcium hydroxide to give epichlorhydrin which is an intermediate and can be used as ingredient for production of different types of epoxy resins. So this epichlorhydrin can further react with sodium hydroxide and water to produce glycerol. So this is the process. This is one synthetic process.

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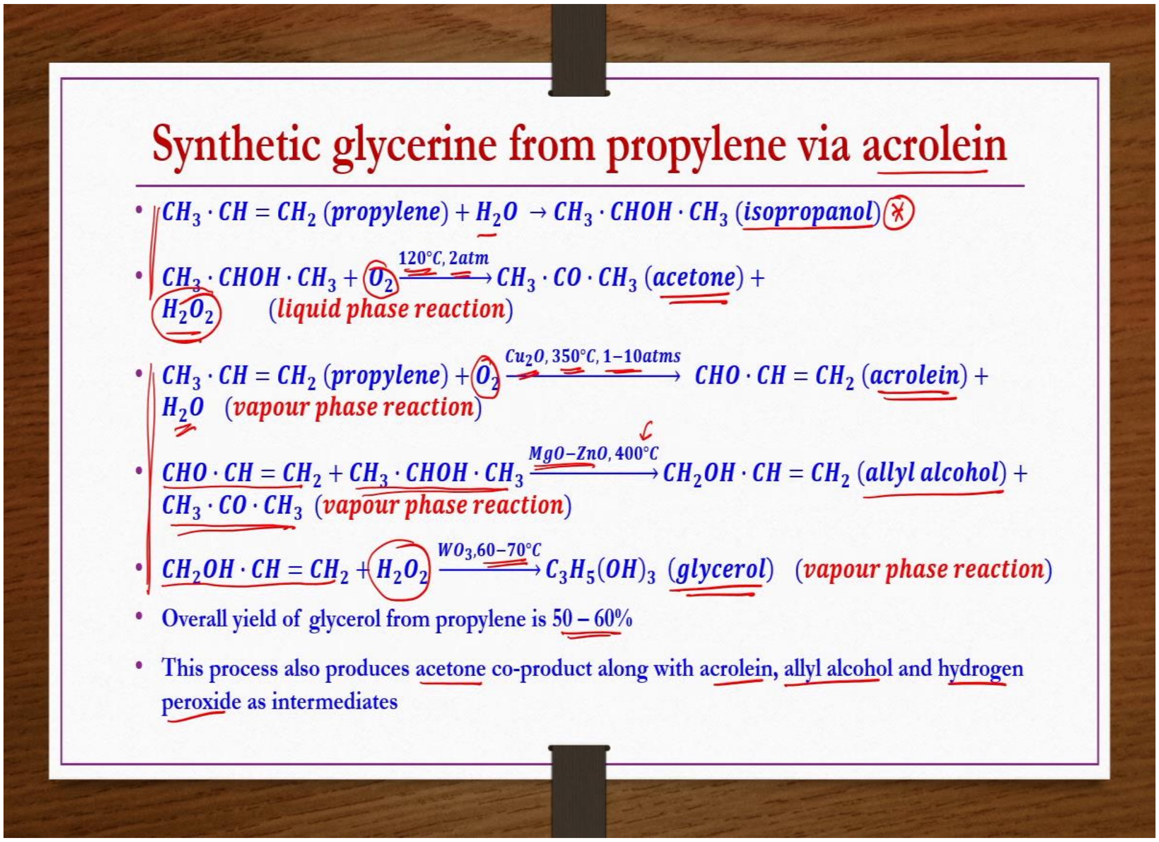

Synthetic glycerine from propylene via acrolein

- $CH_3 \cdot CH = CH_2\ (propylene) + H_2O \rightarrow CH_3 \cdot CHOH \cdot CH_3\ (isopropanol)$
- $CH_3 \cdot CHOH \cdot CH_3 + O_2 \xrightarrow{120°C,\ 2atm} CH_3 \cdot CO \cdot CH_3\ (acetone) + H_2O_2$ (liquid phase reaction)
- $CH_3 \cdot CH = CH_2\ (propylene) + O_2 \xrightarrow{Cu_2O,\ 350°C,\ 1-10atms} CHO \cdot CH = CH_2\ (acrolein) + H_2O$ (vapour phase reaction)
- $CHO \cdot CH = CH_2 + CH_3 \cdot CHOH \cdot CH_3 \xrightarrow{MgO-ZnO,\ 400°C} CH_2OH \cdot CH = CH_2\ (allyl\ alcohol) + CH_3 \cdot CO \cdot CH_3$ (vapour phase reaction)
- $CH_2OH \cdot CH = CH_2 + H_2O_2 \xrightarrow{WO_3, 60-70°C} C_3H_5(OH)_3\ (glycerol)$ (vapour phase reaction)
- Overall yield of glycerol from propylene is 50 – 60%
- This process also produces acetone co-product along with acrolein, allyl alcohol and hydrogen peroxide as intermediates

Another synthetic process to get the glycerol from propylene is via acrolein. Here propylene reacts with water to give isopropanol. In fact, this isopropanol production we are going to discuss with flowchart in this lecture itself. This isopropanol would be oxidized at 120 degrees centigrade and 2 atmospheres to give acetone plus hydrogen peroxide. Then propylene also gets oxidized at 350 degrees centigrade at 1 to 10 atmosphere by using Cu2O catalyst to get acrolein plus water. This acrolein will react with isopropanol to give allyl alcohol. This reaction required 400 degrees centigrade and then catalyst like magnesium oxide and zinc oxide or mixture of both.

This reaction also produces acetone co-product. Now this allyl alcohol would be reacting with the hydrogen peroxide that is produced here using WO3 catalyst at 60 to 70 degrees centigrade to produce glycerol. So out of these 5 reactions, these 3 reactions are vapor phase reactions whereas the remaining are liquid phase reactions. Overall yield of glycerol from propylene is approximately 50 to 60%. This process also produces acetone as co-product along with acrolein, allyl alcohol and hydrogen peroxide as intermediates. So this is the second approach to get synthetic glycerol using propylene.

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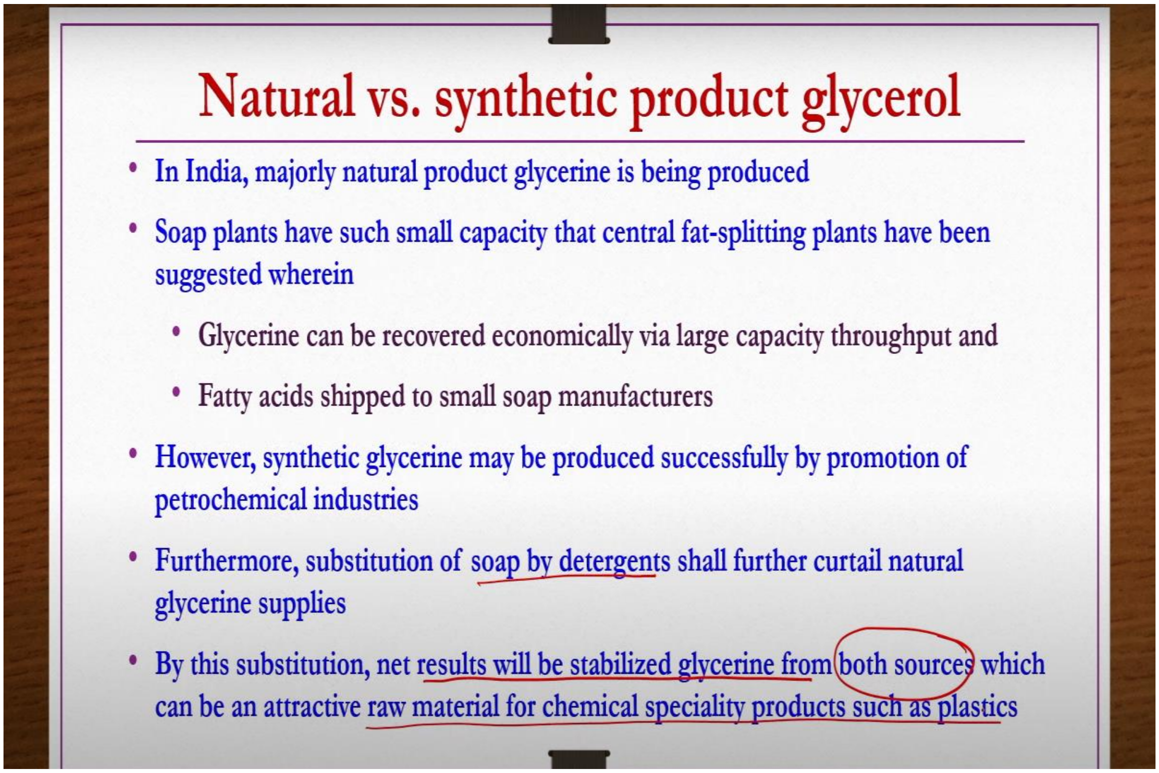

Natural vs. synthetic product glycerol

- In India, majorly natural product glycerine is being produced
- Soap plants have such small capacity that central fat-splitting plants have been suggested wherein
    - Glycerine can be recovered economically via large capacity throughput and
    - Fatty acids shipped to small soap manufacturers
- However, synthetic glycerine may be produced successfully by promotion of petrochemical industries
- Furthermore, substitution of soap by detergents shall further curtail natural glycerine supplies
- By this substitution, net results will be stabilized glycerine from both sources which can be an attractive raw material for chemical speciality products such as plastics

Natural versus synthetic product glycerin if you see, in India majorly natural product glycerin is being produced. Soap plants have such small capacity that central fat splitting plants have been suggested wherein glycerin can be recovered economically via large capacity throughput and then fatty acids shipped to small soap manufacturing units. However, synthetic glycerin may be produced successfully by promotion of petrochemical industries where propylene can be utilized to get a glycerol as per the process just discussed. Further substitution of soap by detergents shall further curtail natural glycerol supplies because of this substitution. Net results will be stabilized glycerin from both sources natural as well as the synthetic sources. So because this glycerol can be attractive raw material for production of different types of speciality chemicals such as plastics, etc.

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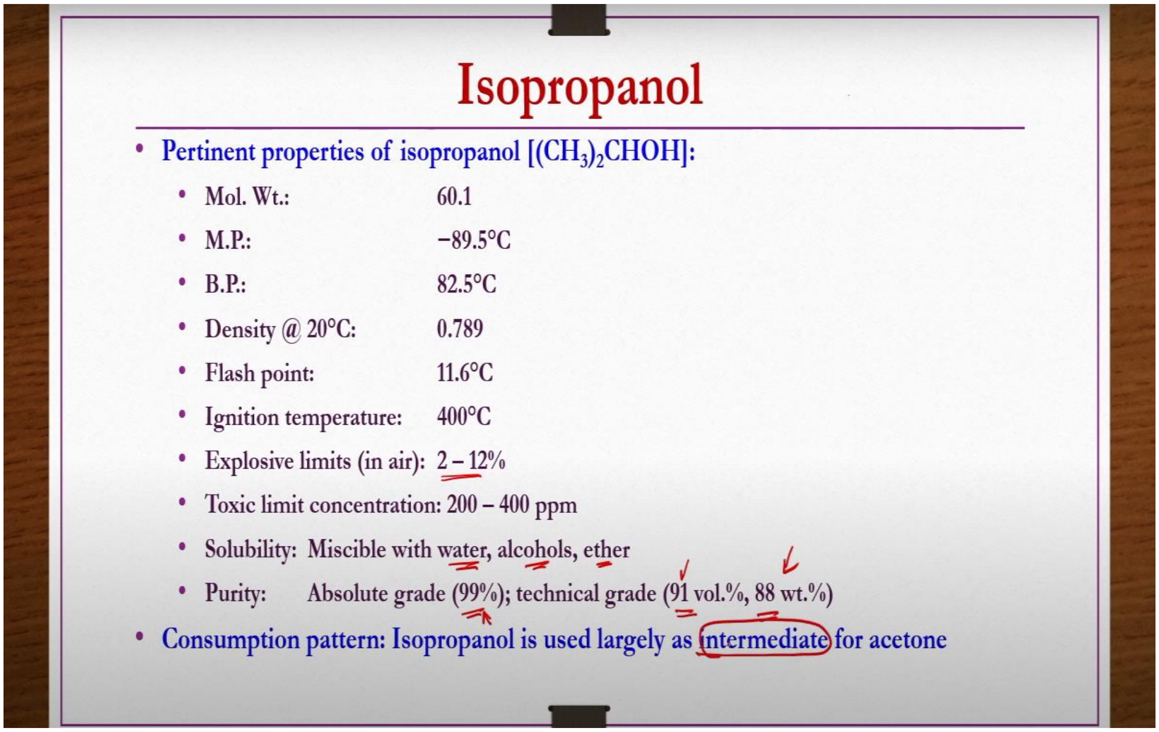

Isopropanol

- Pertinent properties of isopropanol [$(CH_3)_2CHOH$]:
  - Mol. Wt.: 60.1
  - M.P.: −89.5°C
  - B.P.: 82.5°C
  - Density @ 20°C: 0.789
  - Flash point: 11.6°C
  - Ignition temperature: 400°C
  - Explosive limits (in air): 2 – 12%
  - Toxic limit concentration: 200 – 400 ppm
  - Solubility: Miscible with water, alcohols, ether
  - Purity: Absolute grade (99%); technical grade (91 vol.%, 88 wt.%)
- Consumption pattern: Isopropanol is used largely as intermediate for acetone

Now we discuss production of isopropanol. Before going into the production details, we have a pertinent properties of isopropanol here. Molecular weight 60.1, melting point minus 89.5 degrees centigrade, boiling point 82.5 degrees centigrade, density at 20 degrees centigrade is 0.789 gram per cc, flash point is 11.6 degrees centigrade, ignition temperature is 400 degrees centigrade, explosive limits in air is 2 to 12 volume percent, toxic limit concentration is 200 to 400 ppm, it is miscible with water, alcohols and ether, purity 99 percent absolute grade is there and then 91 percent technical grade is there. So these are volume percent, if you measure in terms of weight percent, 88 percent weight percent is equivalent to 91 percent by volume which is a technical grade. Consumption pattern, isopropanol is majorly used as intermediate for production of acetone. So production of acetone also we are going to discuss.

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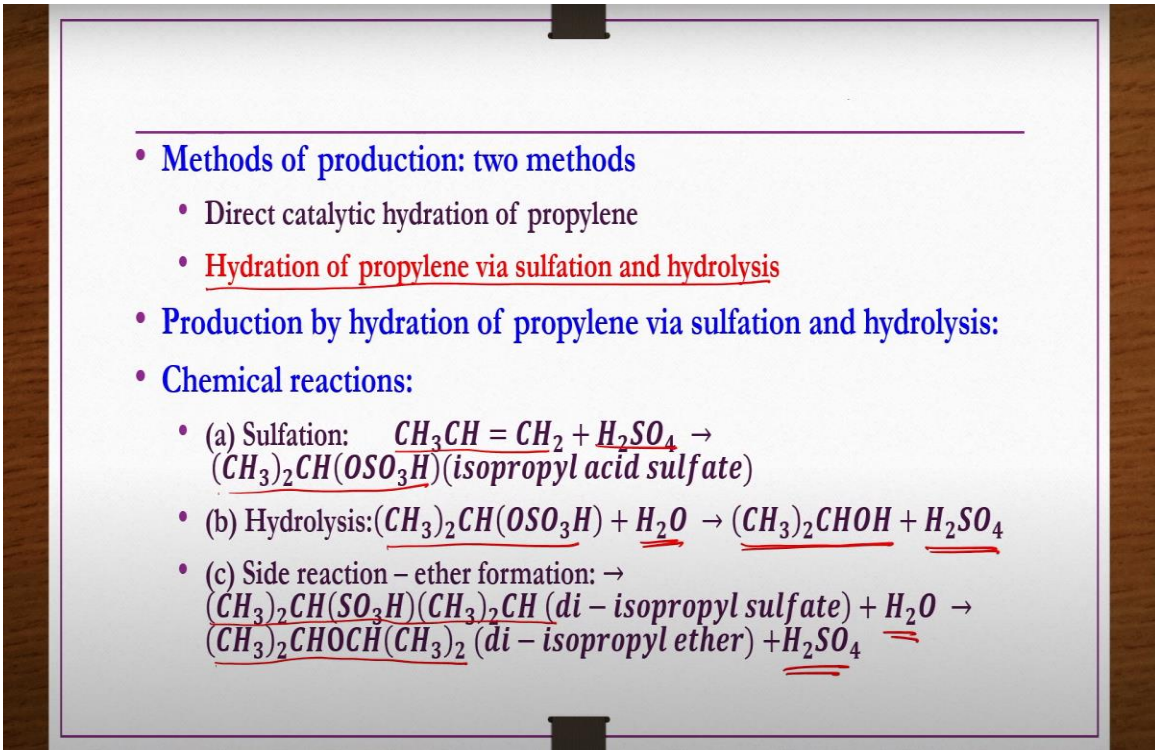

- Methods of production: two methods
  - Direct catalytic hydration of propylene
  - Hydration of propylene via sulfation and hydrolysis
- Production by hydration of propylene via sulfation and hydrolysis:
- Chemical reactions:
  - (a) Sulfation: $CH_3CH = CH_2 + H_2SO_4 \rightarrow (CH_3)_2CH(OSO_3H)(isopropyl\ acid\ sulfate)$
  - (b) Hydrolysis: $(CH_3)_2CH(OSO_3H) + H_2O \rightarrow (CH_3)_2CHOH + H_2SO_4$
  - (c) Side reaction – ether formation: → $(CH_3)_2CH(SO_3H)(CH_3)_2CH\ (di - isopropyl\ sulfate) + H_2O \rightarrow (CH_3)_2CHOCH(CH_3)_2\ (di - isopropyl\ ether) + H_2SO_4$

Methods of production of isopropyl alcohol or isopropanol, two methods are there. One is the direct catalytic hydration of propylene, another one is hydration of propylene via sulfation and hydrolysis. So we are going to discuss this process. First we do the sulfation of propylene and then whatever the compounds intermediate form will be doing the hydrolysis of such compounds to get isopropyl alcohol. Chemical reactions, first sulfation reaction of a propylene with H2SO4 to get isopropyl acid sulfate. This isopropyl acid sulfate would be reacting with water to undergo hydrolysis reaction to produce isopropanol or isopropyl alcohol and then H2SO4 is released. Side reaction, ether formation may take place here where di-isopropyl sulfate whatever is there that would be reacting with water to give di-isopropyl ethers plus H2SO4. So ether maybe sometimes is taken as a product if it is required otherwise the process would be carried out such a way that ether production would be as much less as possible, okay?

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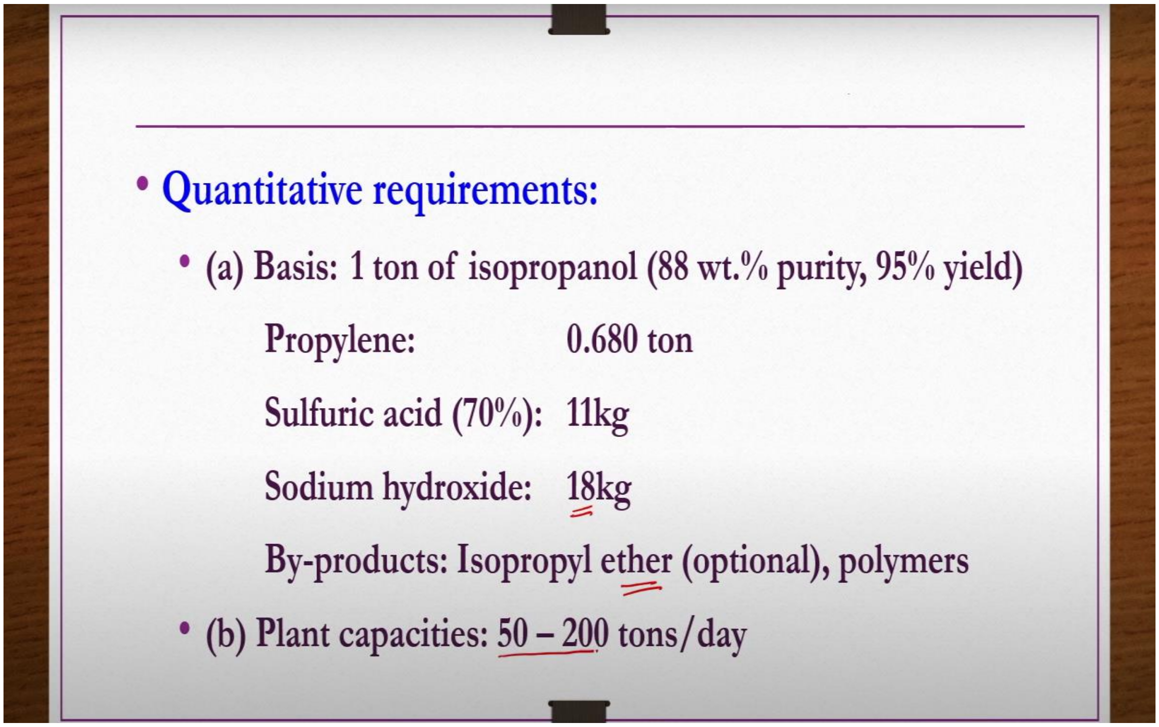

- Quantitative requirements:
  - (a) Basis: 1 ton of isopropanol (88 wt.% purity, 95% yield)

    Propylene: 0.680 ton

    Sulfuric acid (70%): 11kg

    Sodium hydroxide: 18kg

    By-products: Isopropyl ether (optional), polymers
  - (b) Plant capacities: 50 – 200 tons/day

Purity requirements, basis 1 ton of isopropanol that is 88 weight percent purity with 95 percent yield. Propylene is required 0.680 tons, sulfuric acid of 70% or 70 to 80% concentration 11 kgs. Sodium hydroxide is required for the neutralization of the products after the sulfation reaction which is required at 80 kgs to produce 1 ton of isopropanol. Byproducts, isopropyl ethers or polymers are produced, ethers is an optional one. So, process conditions you can tune so that this isopropyl ethers production may be negligible. Plant capacity 50 to 200 tons per day.

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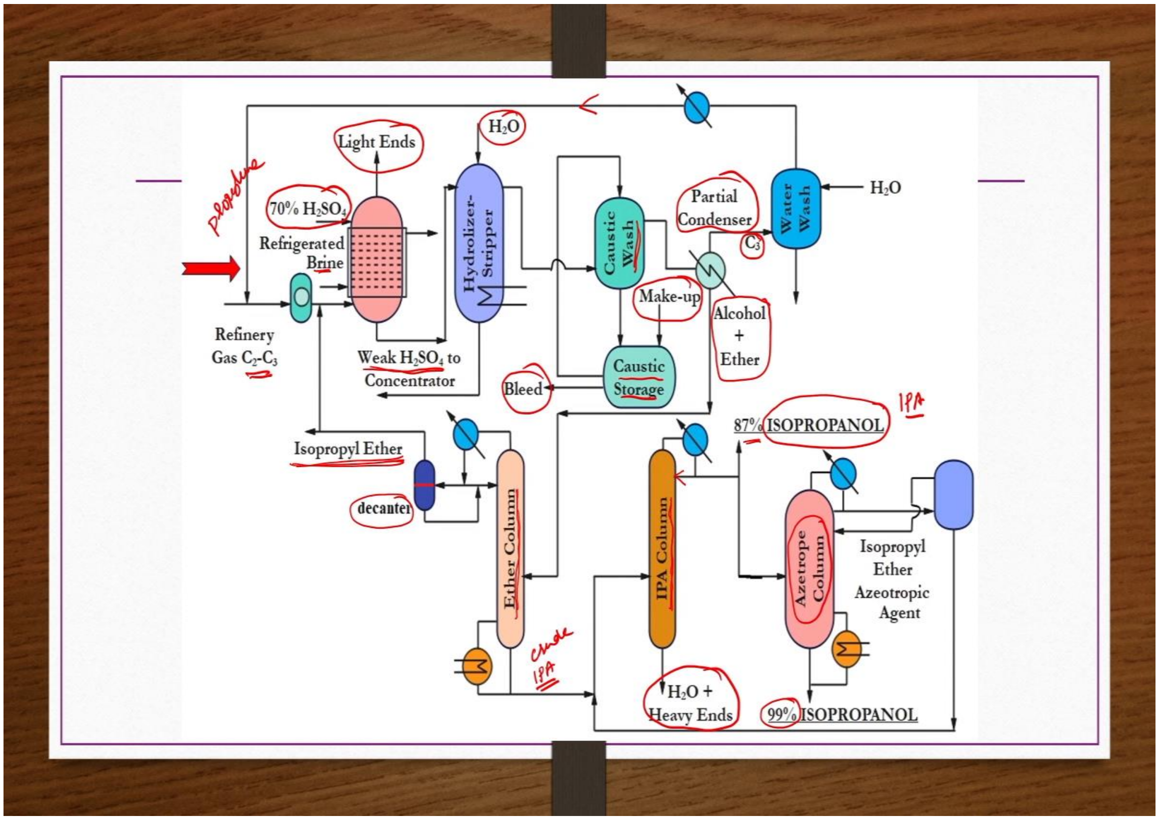

Now we have a flowchart here to discuss the production of isopropanol or isopropyl alcohol, right? So here what we do whatever the propylene is there that is mixed with other C2, C3 compounds then compressed and then sent to a reactor or absorber, packed bed absorber or sieve tray absorber to which 70 to 80% or 70 to 75% H2SO4 is supplied from the top. So here the absorption of gases in H2SO4 takes place. So their sulfation reaction takes place. This reaction is exothermic reaction so that in order to control the temperature of the reaction refrigerated brine is supplied to the exterior of the reactor. So while this absorption is taking place where sulfation reaction also taking place the light ends are being released from the top.

Whereas the products you take to steam stripper where water is being supplied to recover weak H2SO4 from the product mixture and then that can be taken to a H2SO4 plant for the concentration purpose so that it can be reused, right? Then after the steam stripping of the products then mixture is taken to the caustic wash so that to check if at all still traces of

H2SO4 are there in the product they will be washed out with the caustic, right? And then whatever the depleted caustic is there that you can take to the storage after recovering or purifying it. If you cannot recover, purify it then you can take it as a bleed stream and then you have to add new makeup caustic, okay? After caustic wash the products are passed through a partial condenser where non-condensable olefins like propylene, etc., whatever are there, they will be water washed and then recycled back to the reactor along with the refinery C2, C3 gases so that further conversion of this propylene can take place, right? Whereas from the bottom of partial condenser whatever the liquid solution that you get that would be rich in the alcohols and ether that would be taken to the ether column.

So, in the ether column you operate such a way that most of the isopropyl ethers are going as top products and they will be partially condensed. Then whatever the partially condensed solution is there that would be taken to a decanter in which 2 layers would be forming, lighter isopropyl ether layer would be forming at the top that would be taken as a product or can be mixed with the refinery gases and propylene and then send it back to the reactor if you do not want it as a product, okay? Whereas the lower portion of the decanter is primarily having alcohols and then water, etc. So, that would be sent back to the ether column, right? So, from the bottom of the ether column primarily you will be having IPA, isopropyl alcohol or isopropanol plus some heavy ends plus water, etc. would be there. So, here you can call this IPA as crude one.

So, this you can take to IPA column where you do the fractionation and then conditions you maintain such a way that most of the IPA or isopropyl alcohol goes as the top product and then you can condense it, partially condense it and then some of it you can reflux back if the concentration is not up to 87 to 88%. When the concentration of IPA in the top column becomes approximately 87 to 88% that you can completely condense and then take it as a product. Whereas the bottom of IPA column would be having water and then heavy ends as impurities that you can collect separately. If you are happy with this 87 to 88% IPA as a product that is okay. Otherwise, if you want like you know 99% absolute grade isopropanol what you have to do? You have to take it to the azeotropic distillation column and do the azeotropic distillation so that to get most of the isopropanol as a bottom which is having 99% IPA, right? So, bottom product would be 99% isopropyl alcohol whereas the top one would be the isopropyl ether that would be recycled back to the azeotropic column as a azeotropic agent, right? So, this is the flowchart for the production of both 87% isopropanol as well as the 99% isopropanol as well as the isopropyl ether byproduct or co-product.

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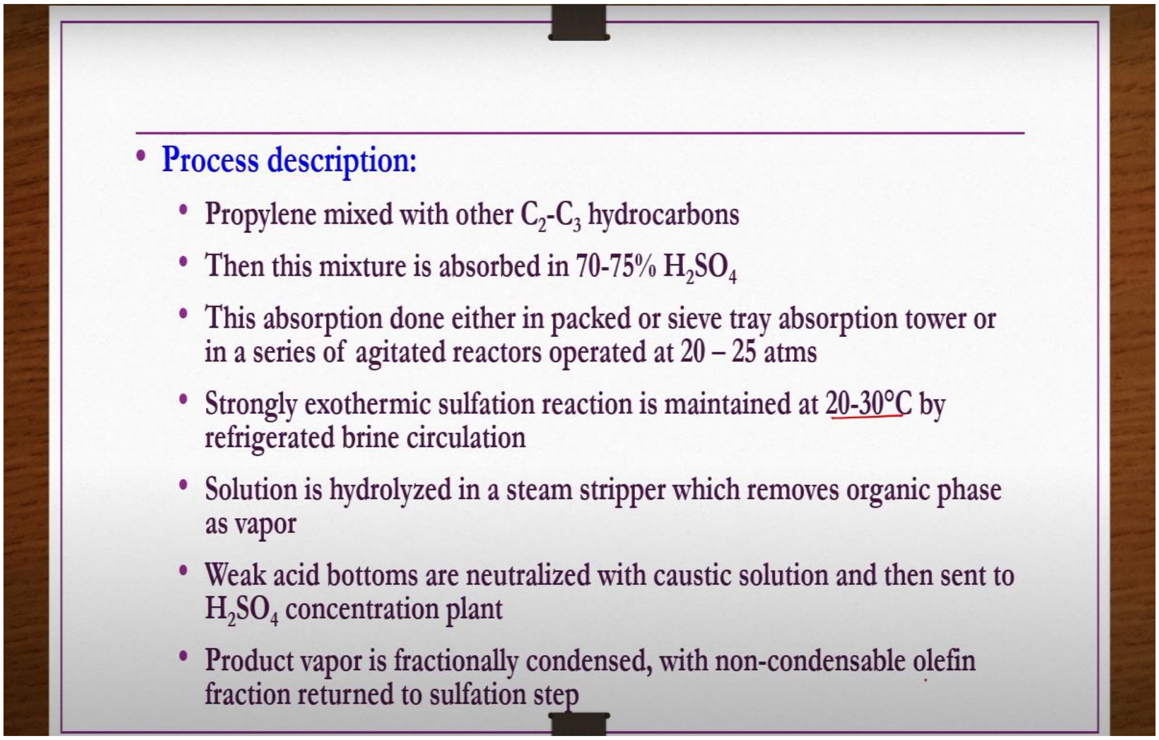

- **Process description:**
  - Propylene mixed with other C_2-C_3 hydrocarbons
  - Then this mixture is absorbed in 70-75% H_2SO_4
  - This absorption done either in packed or sieve tray absorption tower or in a series of agitated reactors operated at 20 – 25 atms
  - Strongly exothermic sulfation reaction is maintained at 20-30°C by refrigerated brine circulation
  - Solution is hydrolyzed in a steam stripper which removes organic phase as vapor
  - Weak acid bottoms are neutralized with caustic solution and then sent to H_2SO_4 concentration plant
  - Product vapor is fractionally condensed, with non-condensable olefin fraction returned to sulfation step

This description propylene mixed with other C2, C3 hydrocarbons then this mixture is absorbed in 70 to 75% H2SO4. This absorption done either in packed or sieve tray absorption tower or in a series of agitated reactors operated at 20 to 25 atmospheres. Strongly exothermic sulphation reaction is maintained at 20 to 30 degree centigrade by refrigerated brine circulation. Solution is hydrolyzed in a steam stripper which removes organic phase as vapor. Weak acid bottoms are neutralized with caustic solution and then sent to H2SO4 concentration plant. Product vapor is fractionally condensed with non-condensable olefin fraction returned to the sulphation step.

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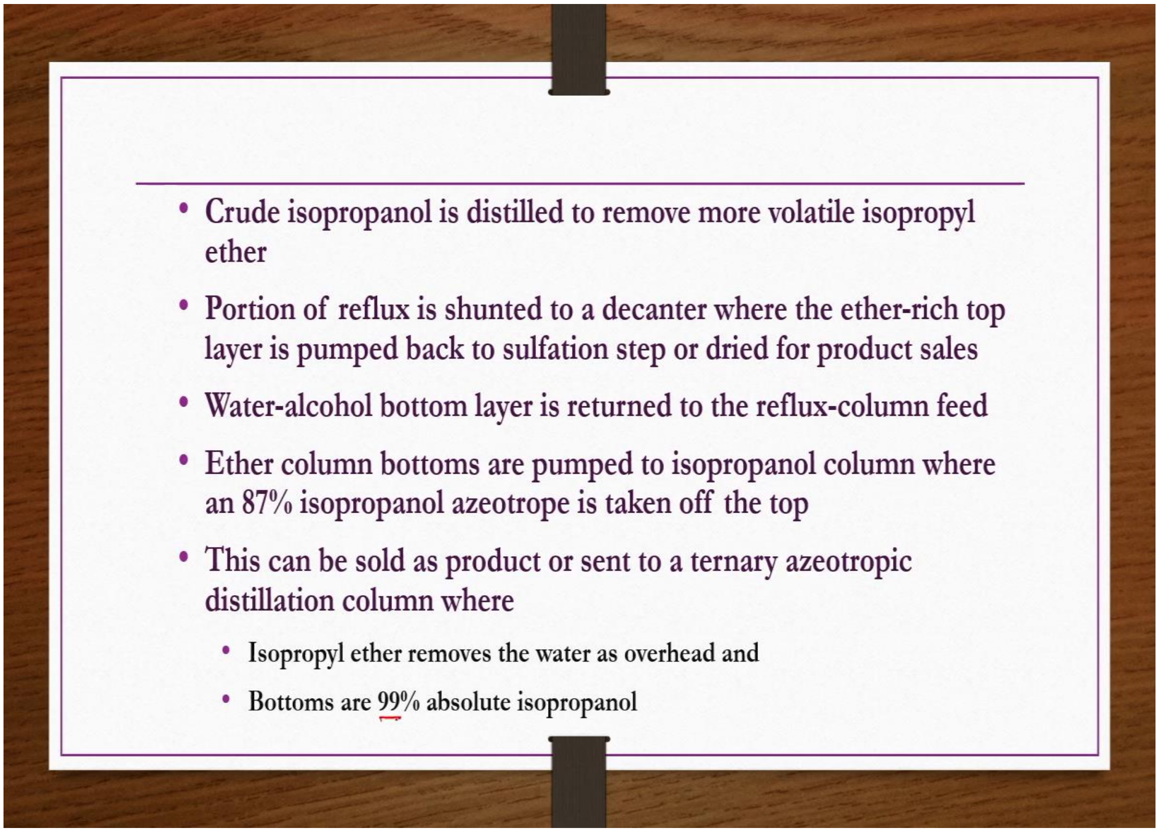

- Crude isopropanol is distilled to remove more volatile isopropyl ether
- Portion of reflux is shunted to a decanter where the ether-rich top layer is pumped back to sulfation step or dried for product sales
- Water-alcohol bottom layer is returned to the reflux-column feed
- Ether column bottoms are pumped to isopropanol column where an 87% isopropanol azeotrope is taken off the top
- This can be sold as product or sent to a ternary azeotropic distillation column where
    - Isopropyl ether removes the water as overhead and
    - Bottoms are 99% absolute isopropanol

Crude isopropanol is distilled to remove more volatile isopropyl ether. Portion of reflux is shunted to a decanter where the ether rich top layer is pumped back to sulphation step or dried for product sales purpose. Water alcohol bottom layer of decanter is returned to the reflux column feed. Ether column bottoms are pumped to isopropanol column where an 87% isopropanol isotope is taken off the top. This can be sold as product or sent to a ternary azeotropic distillation column where isopropyl ether removes the water as overhead and then bottoms are 99% absolute isopropanol.

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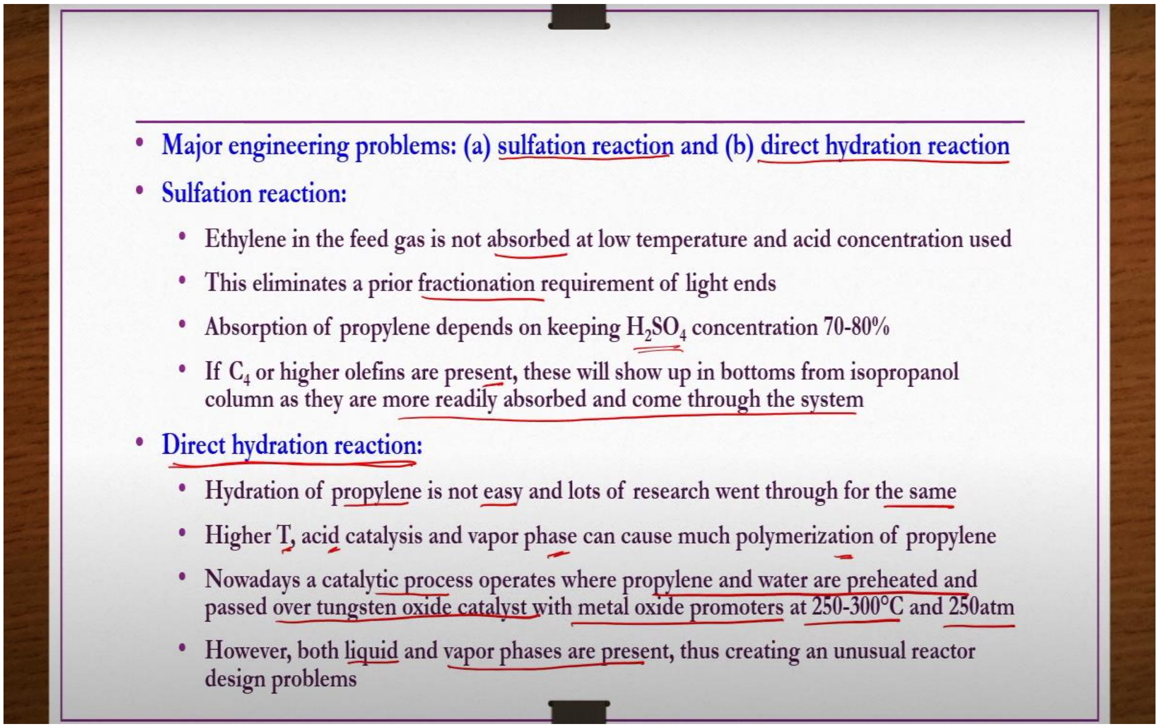

- Major engineering problems: (a) sulfation reaction and (b) direct hydration reaction
- Sulfation reaction:
  - Ethylene in the feed gas is not absorbed at low temperature and acid concentration used
  - This eliminates a prior fractionation requirement of light ends
  - Absorption of propylene depends on keeping H_2SO_4 concentration 70-80%
  - If C_4 or higher olefins are present, these will show up in bottoms from isopropanol column as they are more readily absorbed and come through the system
- Direct hydration reaction:
  - Hydration of propylene is not easy and lots of research went through for the same
  - Higher T, acid catalysis and vapor phase can cause much polymerization of propylene
  - Nowadays a catalytic process operates where propylene and water are preheated and passed over tungsten oxide catalyst with metal oxide promoters at 250-300°C and 250atm
  - However, both liquid and vapor phases are present, thus creating an unusual reactor design problems

Coming to the major engineering problems of the process, obviously 2 steps are important that is sulfation reaction and then direct hydration reaction, okay? Sulfation reaction, ethylene in the feed gas is not absorbed at low temperature and acid concentration that are being used in this process. This eliminates a prior fractionation requirement of light ends since it is not being absorbed, you do not need to worry about fractionation of this one and then you can let it be in the mixture as well. Absorption of propylene depends on keeping H2SO4 concentration between 70 to 80%. If C4 or higher olefins are present in the feed, these will show up in the bottoms from isopropanol column as they are more readily absorbed and come through the system. Coming to the direct hydration reaction, hydration of propylene is not easy and lots of research went through for this.

Actually this is the other process. If you wanted to get the isopropanol, you can do 2 steps. First you do the sulfation reaction and whatever the sulphates formed, you do the hydrolysis of such sulphates to get the isopropanol, right? Other option is that you do the direct hydration of propylene to get the isopropanol, but this process is not easy and lots of research has been carried out. Higher temperature and then higher acid catalyst and vapor phase can cause much polymerization of a propylene which is not desirable in production of isopropanol. However nowadays a catalytic process operates where propylene and water are preheated and passed over tungsten oxide catalyst with metal oxide promoters at 250 to 300 degrees centigrade and 250 atmospheres to get the required hydration of a propylene to take place. However in this process both liquid and vapor phases are present, so design of reactor would be unusual, a bit difficult. If it is pure liquid phase reaction or pure vapor phase reaction, design of corresponding reactors would be easy and comfortable, but if it is both liquid and vapor phase reaction both are there, so then design of reactor is a slightly difficult task. So this is all about isopropanol or isopropyl alcohol manufacturing industrially.

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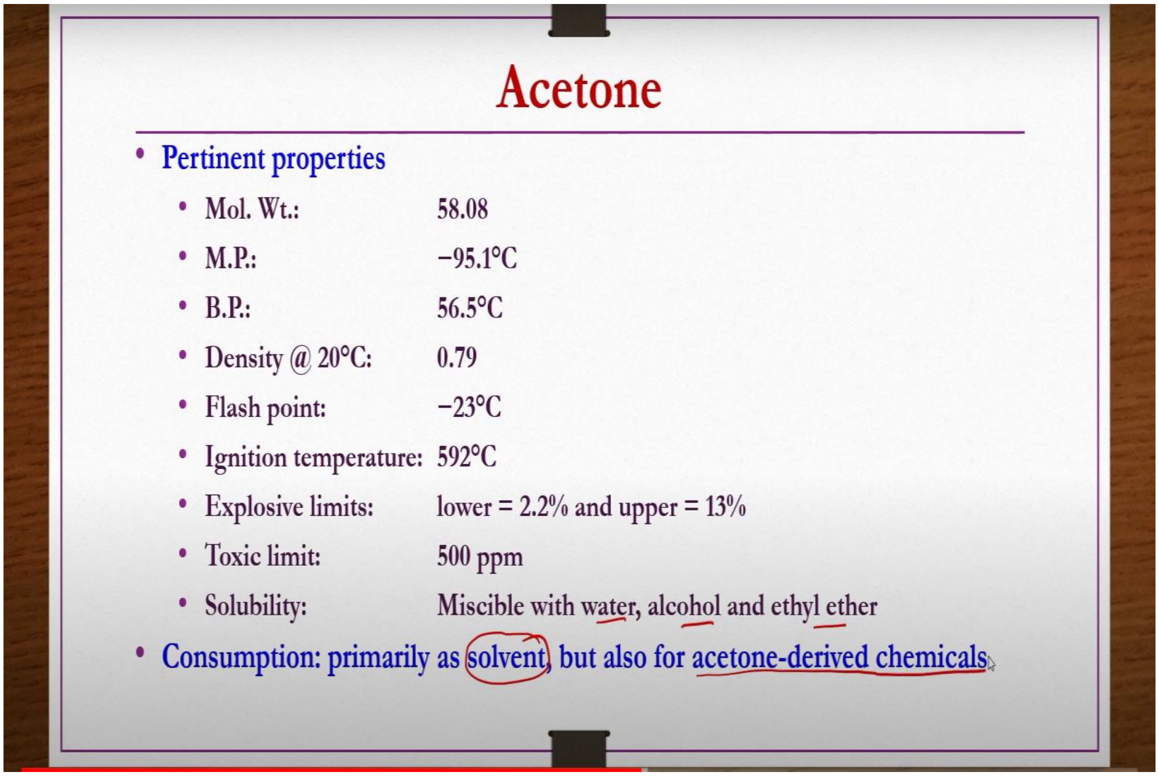

Acetone

- Pertinent properties
  - Mol. Wt.: 58.08
  - M.P.: −95.1°C
  - B.P.: 56.5°C
  - Density @ 20°C: 0.79
  - Flash point: −23°C
  - Ignition temperature: 592°C
  - Explosive limits: lower = 2.2% and upper = 13%
  - Toxic limit: 500 ppm
  - Solubility: Miscible with water, alcohol and ethyl ether
- Consumption: primarily as solvent, but also for acetone-derived chemicals

Now we discuss production of acetone from this isopropyl alcohol or isopropanol. So acetone before going into the production of acetone from the isopropanol, we see the pertinent properties of acetone. Molecular weight 58.08, melting point minus 95.1 degree centigrades, boiling point 56.5 degree centigrades, density at 20 degree centigrades is 0.

79, flash point minus 23 degree centigrades, ignition temperature 592 degree centigrades, explosive limits lower and upper limits are 2.2 and 13% respectively, toxic limit is 500 ppm, solubility it is soluble in water, alcohol and ethyl ethers. Consumption pattern if you see primarily acetone is used as a solvent, but however nowadays it is also being used for acetone derived chemicals production as well.

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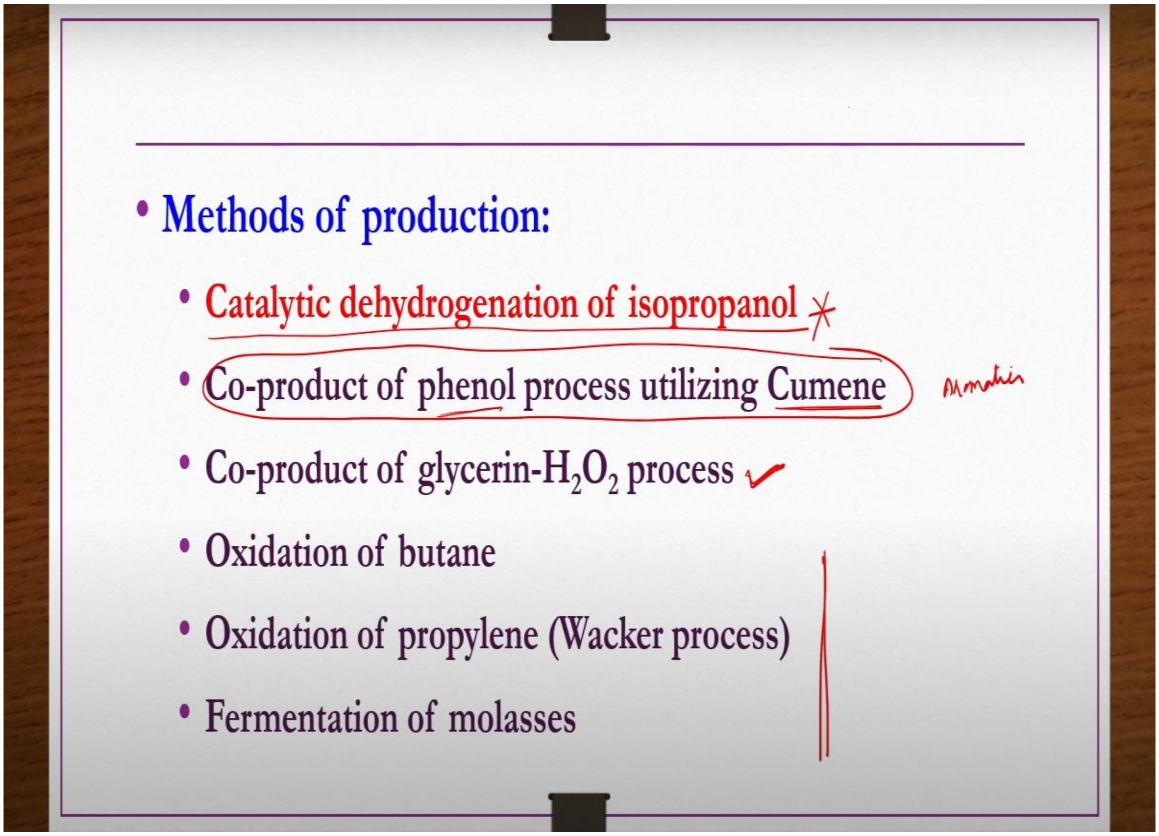

- Methods of production:
  - Catalytic dehydrogenation of isopropanol *
  - Co-product of phenol process utilizing Cumene
  - Co-product of glycerin-H_2O_2 process ✓
  - Oxidation of butane
  - Oxidation of propylene (Wacker process)
  - Fermentation of molasses

Methods of production, catalytic dehydrogenation of isopropanol, whatever isopropanol production that we have seen just now that isopropanol if you do dehydrogenation, then simply you can get the acetone, but it requires catalyst. Other process as I already mentioned the cumene is nowadays used for the production of phenol. So, when you do the production of phenol from cumene, then acetone is obtained as co-product, then co-product of glycerin hydrogen peroxide process. This is nothing but whatever the synthetic glycerol production process just now we have seen from propylene via allyl alcohol via acrolein reactions or acrolein process. In that process also we have seen that acetone is being formed as one of the co-product. Then oxidation of butane is one other option, oxidation of propylene, wacker process is also one option and then fermentation of molasses is also one option to get acetone. However, we discuss catalytic dehydrogenation of isopropanol process rather looking at the co-product processes. So, in this process anyway we are going to subsequently discuss when we discuss about the aromatics chapter. In the aromatics chapter, we will be using cumene to produce phenol. In that process, we can see how acetone is also being produced. This we have already seen. Remaining processes we cannot control all of them, so we are not discussing them.

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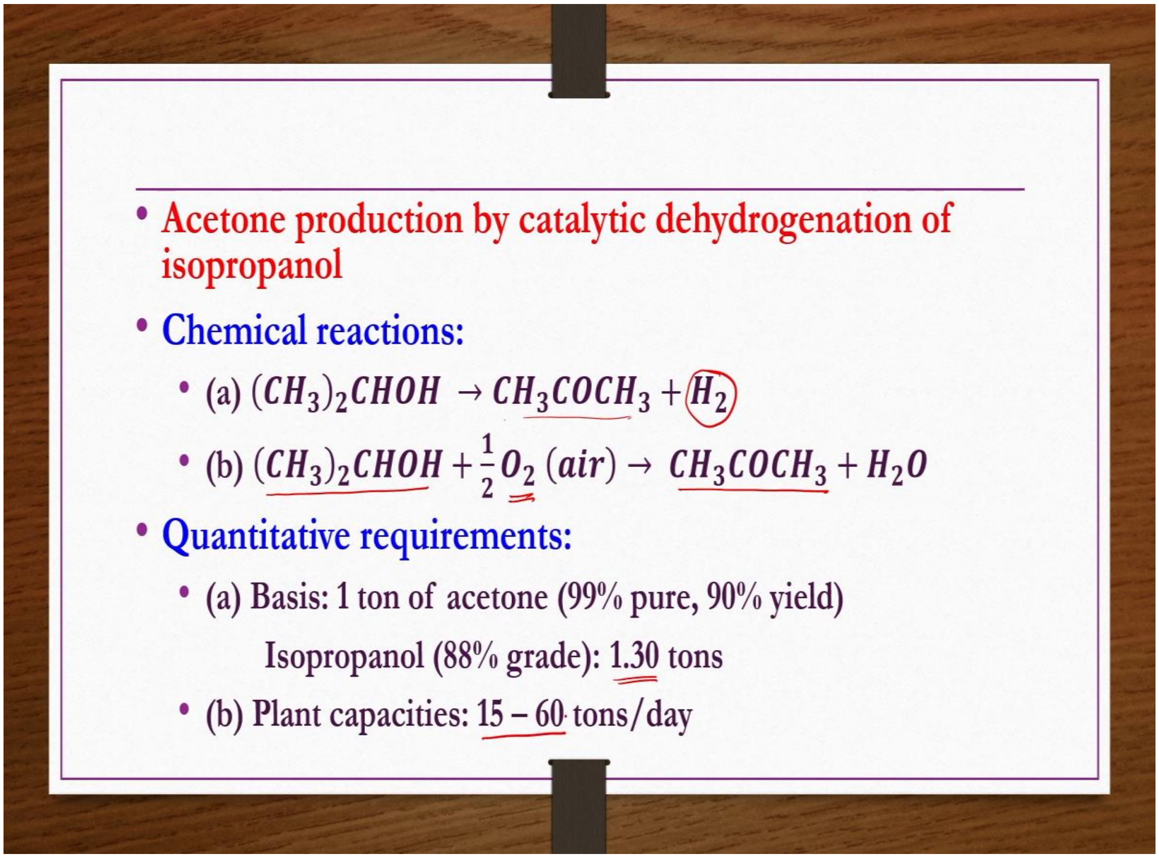

- Acetone production by catalytic dehydrogenation of isopropanol
- Chemical reactions:
  - (a) $(CH_3)_2CHOH \rightarrow \underline{CH_3COCH_3} + \boxed{H_2}$
  - (b) $\underline{(CH_3)_2CHOH} + \frac{1}{2}\underline{O_2}\ (air) \rightarrow \underline{CH_3COCH_3} + H_2O$
- Quantitative requirements:
  - (a) Basis: 1 ton of acetone (99% pure, 90% yield)

    Isopropanol (88% grade): $\underline{1.30}$ tons
  - (b) Plant capacities: $\underline{15 - 60}$ tons/day

So acetone production by catalytic dehydrogenation of isopropanol, chemical reaction simply you take isopropanol or isopropyl alcohol and do the dehydrogenation using the catalyst, then you can get acetone, right? Since you are doing dehydrogenation, hydrogen would be there. Other option is that you take isopropyl alcohol or isopropanol and do the oxidation using the air or oxygen, then also you get the acetone as a product, okay? So both the options one can have in the reactor or same setup can be used for production of acetone by either of the options as I will be discussing in flowchart. Quantitative requirements, basis 1 ton of acetone 99% pure with 90% yield, isopropanol 88% grade you required 1.3 tons and it is the only raw material required. Plant capacity is 15 to 60 tons per day.

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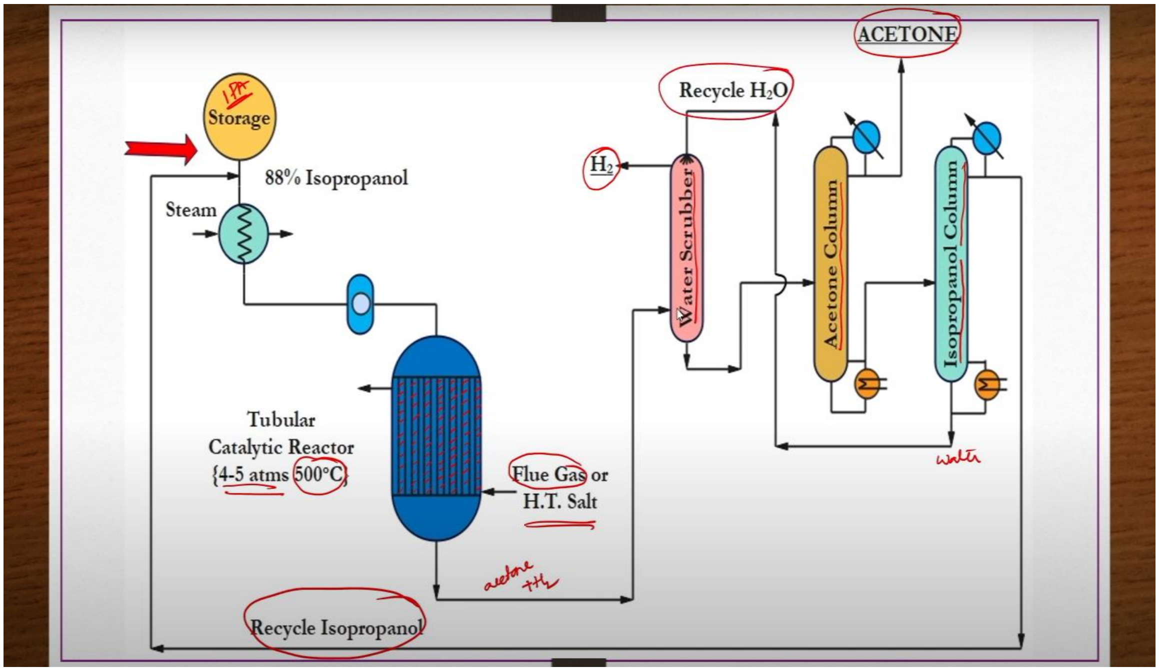

If you see the flowchart, whatever isopropyl alcohol storage is there from that you take 88% isopropanol, then pass it through heat exchanger to which the steam is supplied so that this IPA or isopropanol whatever is there that would be converted into the vapor phase and then compress it and then pass it through a tubular catalytic reactor. This tubular catalytic reactor is having number of tubes in a bundle form like this. These tubes are filled with catalyst like copper or brass so that to required reaction takes place, right? n number of tubes may be there, they may be bundled, okay? So there would be interstitial spaces between the tubes as well so that to control the temperature of the reactor. For that purpose, heat transfer salts are being supplied, right? So the reaction takes place at 500 degrees centigrade and at 4 to 5 atmosphere. In order to get such high temperature, you may also use flue gases and then combust them to get the required energy.

So once the temperature of the heated catalyst that is there inside the tubes is reached to 500 degrees centigrade, then you can allow the vapors of isopropanol to pass through these tubes so that the dehydrogenation of isopropanol will take place and then you get acetone plus H2 mixture, right? So this mixture you pass through water scrubber where whatever the hydrogen is there which cannot be scrubbed out with water is collected as one of the product and then from the bottom, the solution is taken to the acetone column because of scrubbing with water, the acetone is now diluted. So that is taken to the acetone column which is nothing but distillation column again. The temperature, pressure conditions are maintained such a way that most of the acetone get evaporated and then you can get it as a top product as acetone, 99%. Pure acetone you can get as a top product. Bottoms would be mostly water with unreacted isopropanol if at all present.

So they will be taken to the isopropanol column, right? Here the temperature, pressure conditions again are maintained such a way that most of the isopropanol which is present in the water solution that would be collected as top product and then recycled back to the reactor as a recycled isopropanol, okay? Whereas from the bottom you get the water, that water you can use as a recycled water for the water scrubber purpose. So this is the process if you are doing the direct dehydrogenation of isopropanol. Let us say if you wanted to do oxidation of isopropanol to get the acetone because if you do the oxidation of isopropanol also, then you get acetone. Now for this process what you have to do? The rest of the process is same. What you have to do here is that along with the IPA you also supply air or oxygen. If you are supplying the air, let us say oxidation of IPA takes place and then you get acetone plus in place of H2 you get the N2 because in the air whatever oxygen is there that is consumed for the oxidation and then N2 would be there. So that you can separate out by water scrubbing and then you can get the N2 in place of H2. Whereas the remaining of the process is entirely same, okay?

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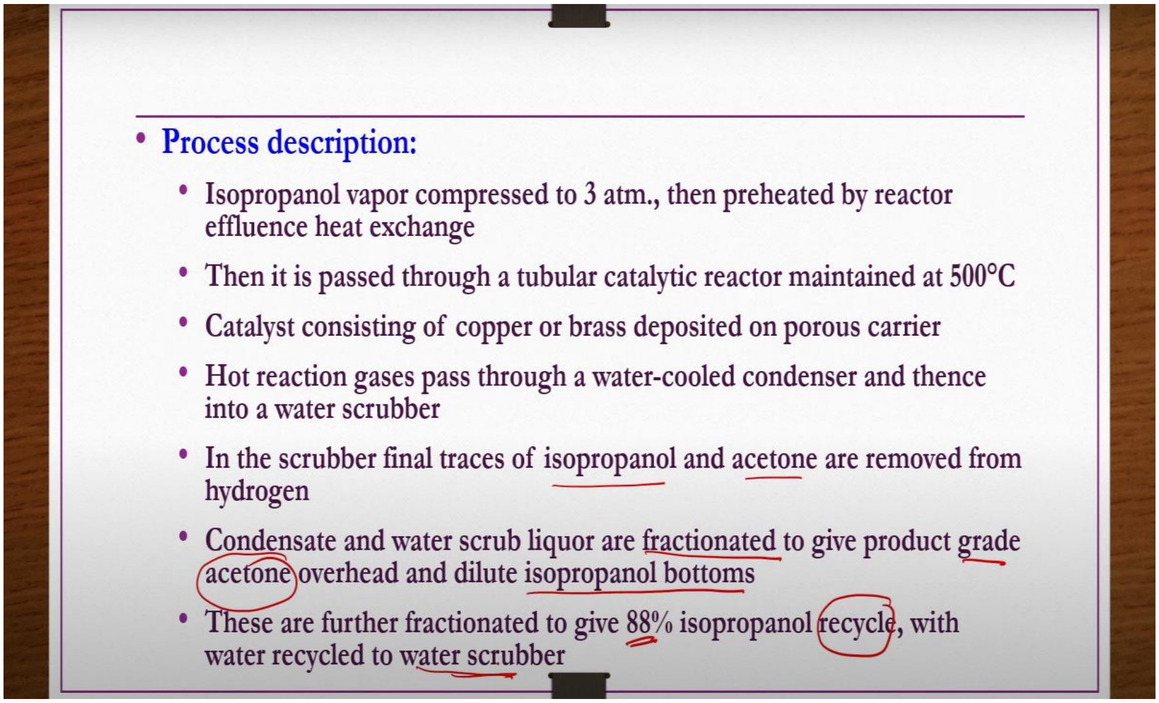

- **Process description:**
  - Isopropanol vapor compressed to 3 atm., then preheated by reactor effluence heat exchange
  - Then it is passed through a tubular catalytic reactor maintained at 500°C
  - Catalyst consisting of copper or brass deposited on porous carrier
  - Hot reaction gases pass through a water-cooled condenser and thence into a water scrubber
  - In the scrubber final traces of isopropanol and acetone are removed from hydrogen
  - Condensate and water scrub liquor are fractionated to give product grade acetone overhead and dilute isopropanol bottoms
  - These are further fractionated to give 88% isopropanol recycle, with water recycled to water scrubber

Process description, isopropanol vapor compressed to 3 atmosphere then preheated by reactor effluents heat exchange. Then it is passed through a tubular catalytic reactor maintained at 500 degree centigrades. Catalyst consisting of copper or brass deposited on porous carrier are used in the tubular catalytic reactor. Hot reaction gases pass through a water cooled condenser and thence into a water scrubber. In the scrubber, final traces of isopropanol and acetone are removed from hydrogen. Then condensate and water scrub liquor are fractioned to give product grade acetone as a overhead product and then dilute isopropanol you can get as bottoms. This isopropanol may be further fractionated to get 88 percent isopropanol which you can recycle whereas the bottoms you get the water that can be recycled to water scrubber as explained in the flowchart.

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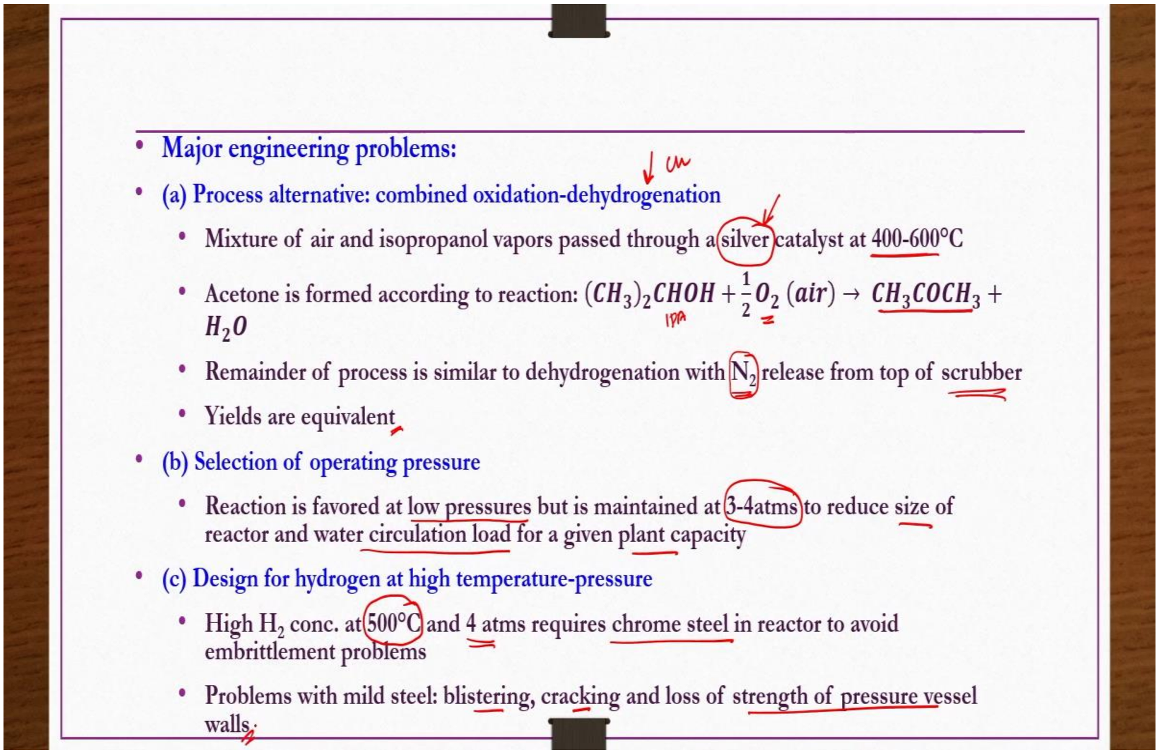

- Major engineering problems:

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- (a) Process alternative: combined oxidation-dehydrogenation
  - Mixture of air and isopropanol vapors passed through a silver catalyst at 400-600°C
  - Acetone is formed according to reaction: $\underset{\text{IPA}}{(CH_3)_2CHOH} + \frac{1}{2}O_2\,(air) \rightarrow CH_3COCH_3 + H_2O$
  - Remainder of process is similar to dehydrogenation with N_2 release from top of scrubber
  - Yields are equivalent
- (b) Selection of operating pressure
  - Reaction is favored at low pressures but is maintained at 3-4atms to reduce size of reactor and water circulation load for a given plant capacity
- (c) Design for hydrogen at high temperature-pressure
  - High H_2 conc. at 500°C and 4 atms requires chrome steel in reactor to avoid embrittlement problems
  - Problems with mild steel: blistering, cracking and loss of strength of pressure vessel walls.

Coming to the major engineering problems, process alternatives, combined oxidation dehydrogenation process. We have seen in the flowchart primarily drawing is done for the direct dehydrogenation of isopropyl alcohol, but I have also explained if the oxidation process to do what are the difference. So, we can do the combined oxidation and dehydrogenation process because either of the process acetone is being produced. Other option or major engineering problem is the selection of operating pressure and then last one is the design for hydrogen at high temperature pressure. Under the process alternatives, mixture of air and isopropanol vapors passed through a silver catalyst. If you are doing the oxidation process, then what you have to do? You have to use a different catalyst, silver catalyst you have to use.

If you are using dehydrogenation, then you have to use copper or brass catalyst you have to use. So, for the oxidation required temperature is 400 to 600 degrees centigrade. Then acetone is formed according to reaction CH3CHOH that is isopropyl alcohol or isopropanol plus of O2 giving rise to acetone plus water. After this reaction occurring in the reactor, remainder of the process is similar to dehydrogenation with N2 released from top of the scrubber rather H2 is being released from the top of the scrubber in the dehydrogenation process. In the oxidation process you get N2 from the scrubber, in the dehydrogenation process you get hydrogen from the top of the scrubber.

Either of the process produce acetone of equivalent yields. Reaction operating pressures if you see reaction is favored at low pressures, but 3 to 4 atmospheres or even 5 atmospheres are maintained to reduce the size of reactor and water circulation load for a given plant capacity. Coming to the design for hydrogen at high temperature pressure, whenever hydrogen is there it is always dangerous because it is explosive and then that hydrogen at such high temperature like 500 degrees centigrade and then high pressures like 4 atmosphere etc. You need to have a separate reactor so that you can handle this hydrogen properly. For that purpose it requires chrome steel in reactor to avoid embrittlement problems. What happens if you use mild steel? Some kind of blistering, cracking and loss of strength of pressure vessel walls may takes place. So, that is all about acetone production.

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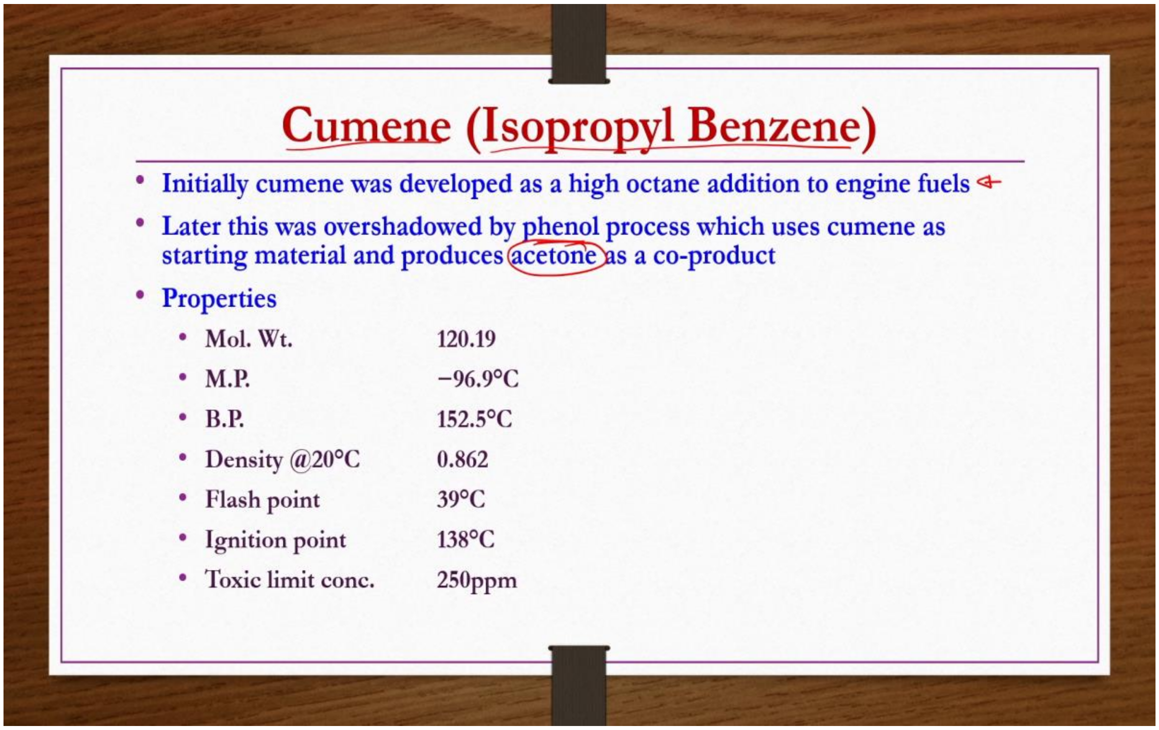

Cumene (Isopropyl Benzene)

- Initially cumene was developed as a high octane addition to engine fuels
- Later this was overshadowed by phenol process which uses cumene as starting material and produces acetone as a co-product
- Properties

Mol. Wt.	120.19
M.P.	−96.9°C
B.P.	152.5°C
Density @20°C	0.862
Flash point	39°C
Ignition point	138°C
Toxic limit conc.	250ppm

Now we discuss production of cumene by reaction between benzene and propylene. This cumene is also known as isopropyl benzene. In fact, chemical name is isopropyl benzene, commercial name is cumene. Initially cumene was developed as a high octane addition to engine fuels as I already mentioned, but however nowadays it is primarily used for the production of phenol. So when you produce phenol using the cumene, then you also get acetone as a co-product. First we see the properties of a cumene, then we go to the manufacturing processes. Molecular weight of cumene is 120.19, melting point minus 96.9 degrees centigrades, boiling point 152.5 degrees centigrades, density at 20 degrees centigrades is 0.862, flash point is 39 degrees centigrades, ignition point is 138 degrees centigrades. Toxic limit concentration is 250 ppm.

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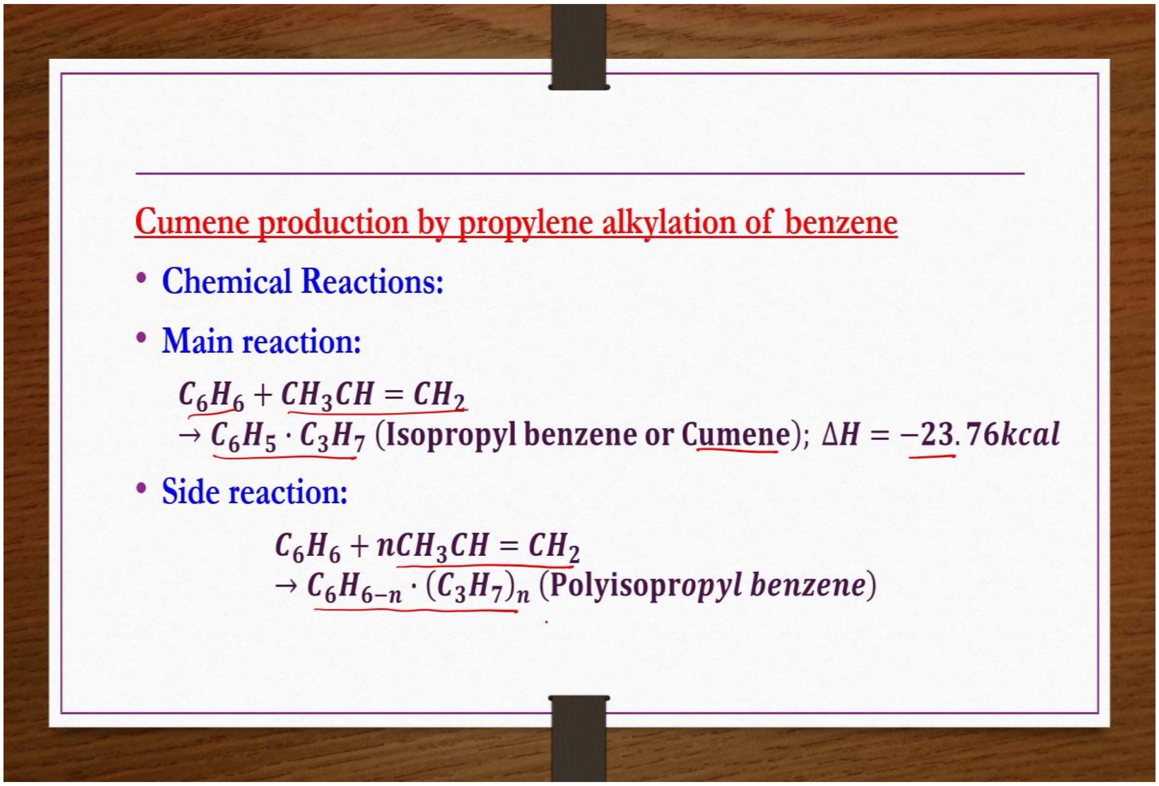

Cumene production by propylene alkylation of benzene

- Chemical Reactions:
- Main reaction:

$$C_6H_6 + CH_3CH = CH_2 \rightarrow C_6H_5 \cdot C_3H_7 \text{ (Isopropyl benzene or Cumene)};\ \Delta H = -23.76kcal$$

- Side reaction:

$$C_6H_6 + nCH_3CH = CH_2 \rightarrow C_6H_{6-n} \cdot (C_3H_7)_n \text{ (Polyisopropyl benzene)}$$

Now cumene production we discuss by one method that is alkylation of benzene using propylene or propylene alkylation of benzene to produce cumene. Chemical reaction, simple straightforward reaction between benzene and propylene will give you so called cumene C6H5C3H7 which is exothermic reaction. Side reaction may also takes place where polycumenes may form if you have n number of moles of you know propylene reacting with the benzene. So this is what you have polyisopropyl benzene or polycumene.

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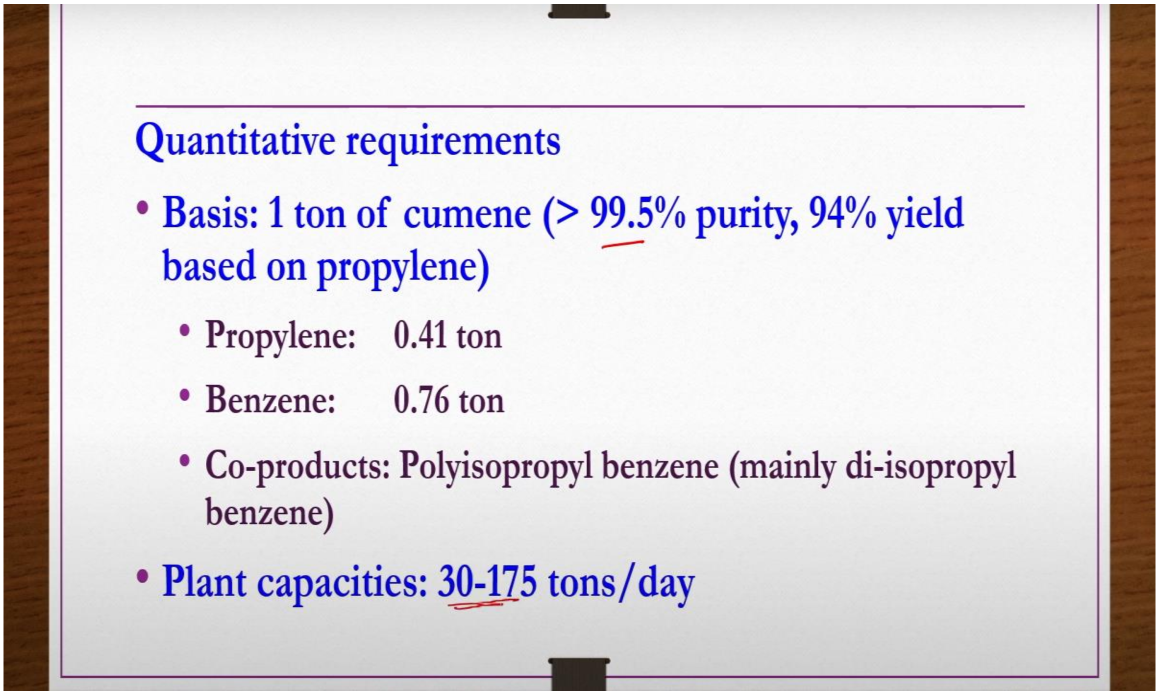

Quantitative requirements

- Basis: 1 ton of cumene (> 99.5% purity, 94% yield based on propylene)
    - Propylene: 0.41 ton
    - Benzene: 0.76 ton
    - Co-products: Polyisopropyl benzene (mainly di-isopropyl benzene)
- Plant capacities: 30-175 tons/day

Quantitative requirements, basis 1 ton of cumene if you want to produce more than 99.5% purity with 94% yield based on propylene. Propylene requirement is 0.41 tons, benzene requirement is 0.76 tons. Co-products, Polycumenes mainly dicumene or diisopropyl benzene is produced as co-product. Plant capacities usually vary between 30 to 175 tons per day.

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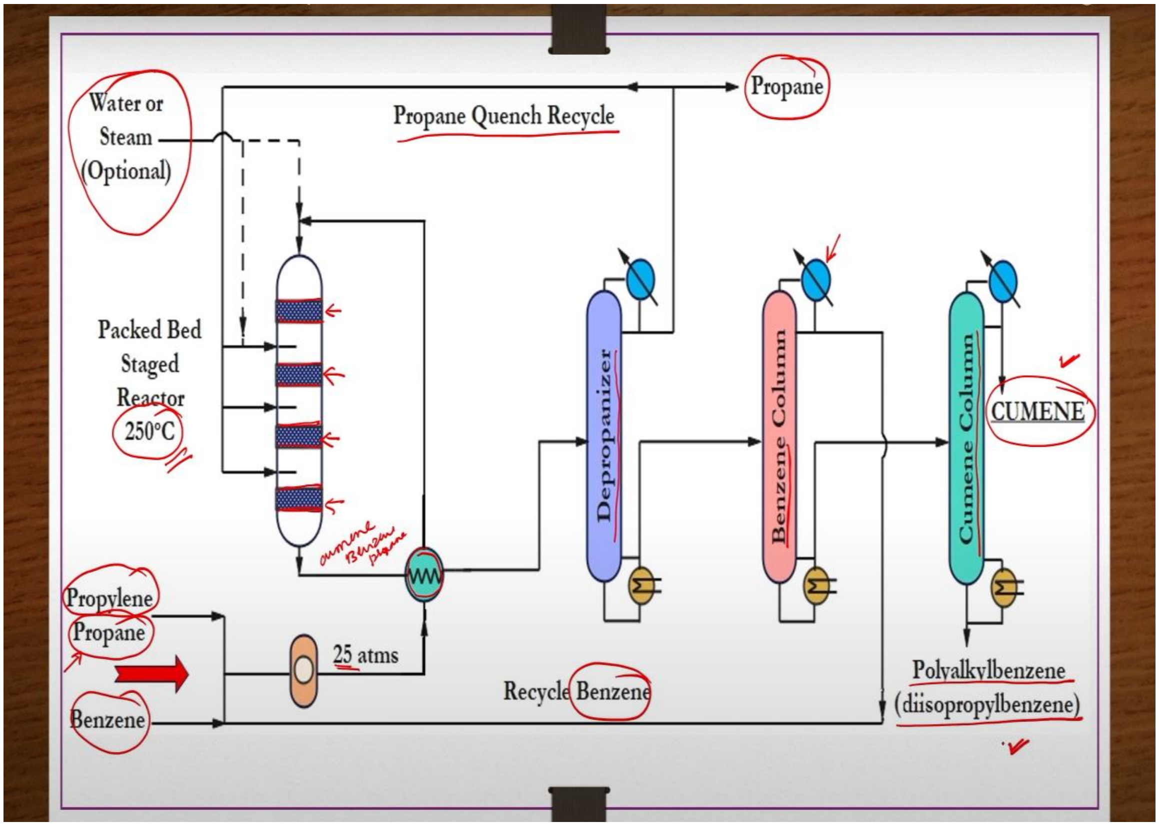

This is the flow chart that we have for the production of a cumene, right? So here whatever the raw materials benzene and propylene are there, they are mixed along with the propane. Propane is a diluent as well as quenching purpose also it is used. Why it is diluent? If you wanted to reduce production of polycumenes, propane is going to be useful. It will not allow more of the polycumenes forming. So for that purpose, propane is used as a diluent along with the reactants. So this mixture of propylene, propane and benzene is mixed and then compressed to 25 atmosphere, then preheated by passing through a heat exchanger, then it is sent to the packed bed reactor which is staged reactor. So what do you mean by packed bed staged reactors? So packing is done in stages, not like entire column is packed with the packing material. So you have the stages like some portion of the bed is confined between 2 perforated plates and then between these plates only you are having the packing material. So like that different stages of packings are possible. So that is the reason this packed bed reactor is known as staged packed bed reactor, okay? This reactor is maintained at 250 degree centigrade, so that is the reaction takes place. To this reactor whatever the reactant is there that is being supplied or the mixture of reactants is there that is being supplied so that the required reaction takes place and then you get the cumene, unreacted benzene, unreacted propane, etc. because propane is anyway here inert. So all that mixture you get from the bottom that you can preheat or you can heat it and then send it to the de-propanizer to recover the propane from the top.

This propane you can take it as a product or you can send it as a quench to the reactor. So to the reactor in order to control the temperature rather using water we will be using propane quench because it is also required as a inert within the reactant mixture so that to suppress the production of polycumenes. So that propane can also be used for the quenching purpose, okay? So water or steam options are also possible for this reactor to control the temperature, but that is optional anyway. So better is to use the propane quench, right? After removing the propane from the product mixture, the mixture is primarily having cumene and an unreacted benzene.

So that mixture is taken to the benzene column. So here this is also distillation column. The temperature, pressure, etc. are maintained in such a way that more volatile benzene. Benzene is more volatile compared to the cumene. So the more volatile benzene would be collected as the top product. Once the benzene concentration in the top trays is of high concentration or almost pure, then you can condense it and then take it back to the reactant mixtures as a recycled benzene. Whereas the bottom of the benzene would be primarily having the cumene and then polycumene if at all some polycumene are forming, that you can take to the cumene column and then this is also a distillation column. So temperature, pressure are maintained in such a way that more volatile cumene. Out of the cumene and polycumenes, cumene is more volatile. So that would be collected as a top product from the top trays. Once the concentration of the cumene is sufficiently pure, 99.5% or something like that, that can be condensed and then taken it as a product. Whereas from the bottom you get the diisopropyl benzene or dicumene or polycumenes you can get as a bottom products, okay?

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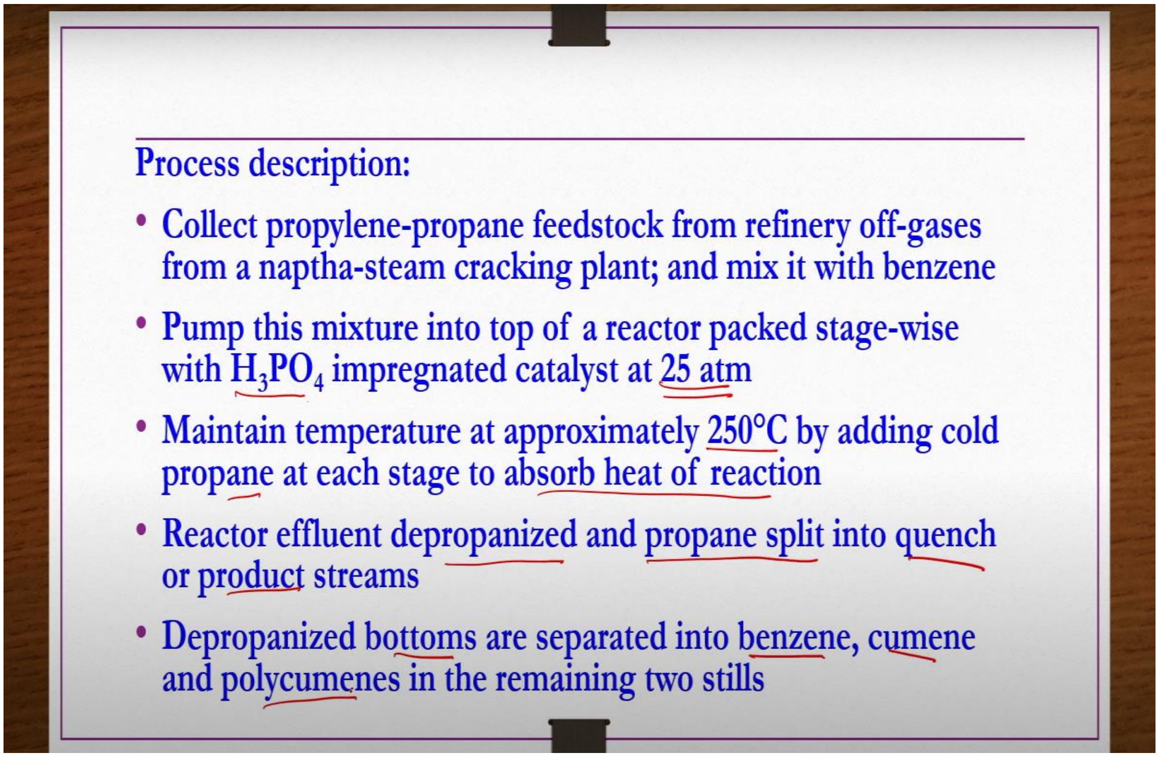

Process description:

- Collect propylene-propane feedstock from refinery off-gases from a naptha-steam cracking plant; and mix it with benzene
- Pump this mixture into top of a reactor packed stage-wise with H_3PO_4 impregnated catalyst at 25 atm
- Maintain temperature at approximately 250°C by adding cold propane at each stage to absorb heat of reaction
- Reactor effluent depropanized and propane split into quench or product streams
- Depropanized bottoms are separated into benzene, cumene and polycumenes in the remaining two stills

Process description, collect propylene propane feedstock from refinery of gases from a naphtha steam cracking plant and mix it with benzene. Pump this mixture into the top of a reactor, packed stage wise with phosphoric acid impregnated catalyst at 25 atmosphere. Maintain temperature at approximately 250 degrees centigrade by adding cold propane at each stage to absorb heat of reaction. Reactor effluent depropanized and propane split into quench or product streams as per the requirement. Depropanized bottoms are separated into benzene, cumene and polycumenes in the remaining 2 steels as shown in the flow chart and discussed accordingly.

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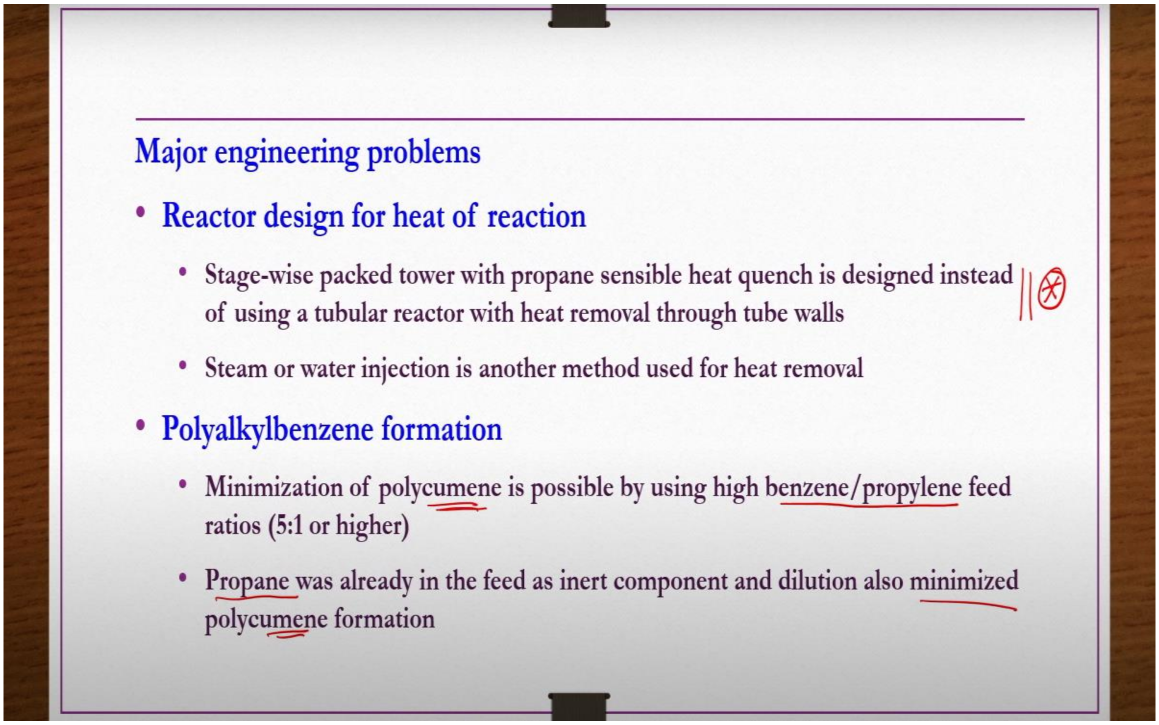

Major engineering problems

- Reactor design for heat of reaction
  - Stage-wise packed tower with propane sensible heat quench is designed instead of using a tubular reactor with heat removal through tube walls
  - Steam or water injection is another method used for heat removal
- Polyalkylbenzene formation
  - Minimization of polycumene is possible by using high benzene/propylene feed ratios (5:1 or higher)
  - Propane was already in the feed as inert component and dilution also minimized polycumene formation

Coming to the major engineering problems, reactor design for a heat of reaction is one important factor, other one is the separation of polycumene formation. Under the reactor design for heat of reaction, stage wise packed tower with propane sensible heat quench is designed instead of using a tubular reactor with heat removal through tube walls. So, this is one important reason that we have a stage wise packed bed reactor so that you know propane can be used to recover or take the sensible heat of the reaction and then control the temperature of the reaction. Steam or water injection is another method for heat removal as well. Coming to the other problem of polycumene formation, minimization of polycumene is possible by using high benzene to propylene feed ratio more than 5 to 1 ratio, right? If you have one part of propylene, at least 5 parts of benzene are required, then only you can minimize polycumene. Other option is that propane is acting as an inert compound and dilution within the reaction mixture that also minimizes the polycumene formation, okay? So, that is all about the cumene production.

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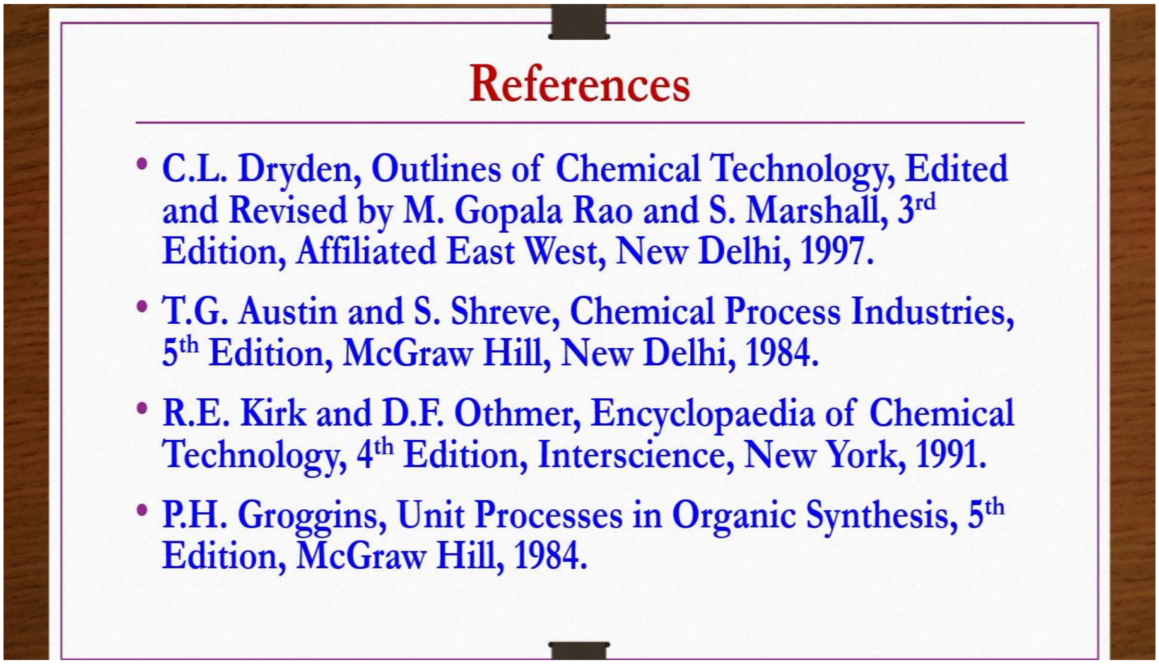

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