Lec 25: Chemicals from C_2 Compounds – 2.

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is chemicals from C_2 compounds part 2.

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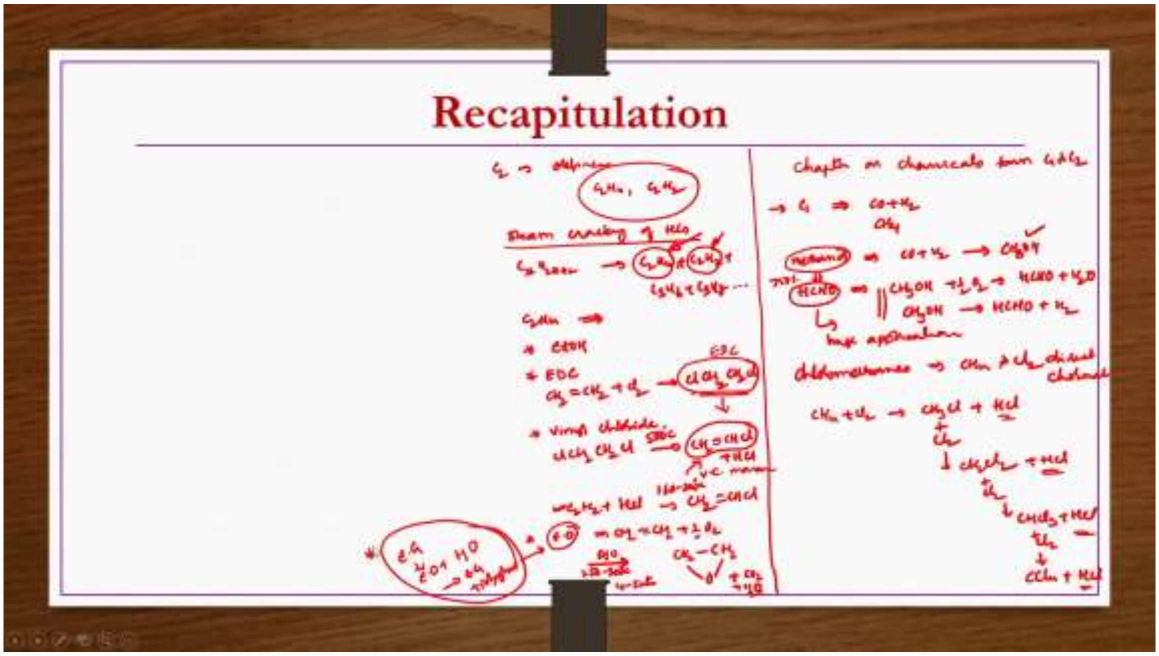

Recapitulation

Before going into the details of today's lecture, we will have a recapitulation of what we have discussed in the previous few lectures in this particular chapter. We started the chapter on chemicals from C_1 and C_2 compounds. What do you mean by C_1 and C_2 compounds? That means, you know in the compound that you have taken as a raw material only one carbon atom is there. Let us say CO plus H_2 synthesis gas if you take as raw material then you can regard it as a C_1 compound because only one carbon atom is there.

Likewise, methane you can take so, which is also having only one carbon atom. So, what we have done under the chemicals to be produced from C_1 compounds we started with production of methanol for which what we have done, we have done catalytic hydrogenation of carbon monoxide or CO plus H_2 mixture when you do the catalytic reaction, then you get methanol, this is one compound we produce one chemical we produced. Then other one is that formaldehyde that we produce where what we have done, we have done 2 types of methods like methanol you take and then you do oxidation to get formaldehyde and water vapors. This is one method, other method that we have done is pyrolysis or catalytic pyrolysis of a methanol to give formaldehyde plus hydrogen.

These 2 methods we have seen for the formaldehyde preparation. So, the major purpose of methanol application is that production of a formaldehyde because this formaldehyde is having huge applications in resins, etc. So, whatever methanol is produced more than 50% is used for production of formaldehyde by either of this process because formaldehyde is having much more applications. Then chloromethanes also we have seen how to produce chloromethanes. So, here we have taken methane and then C_{l2} we have done direct chlorination reactions.

So, this reaction we found it as a series reaction where 1 H atom of methane is being replaced by the 1 chlorine atom to get chloromethanes plus HCl. So, let us say here whatever form that again reacts with the Cl_2 to give CH_2Cl_2 which is nothing but methylene chloride plus HCl. This methylene chloride again reacts with chlorine to give chloroform plus HCl. This chloroform again reacts with Cl_2 to give carbon tetrachloride plus HCl. So, HCl is a byproduct and then it produced in huge quantities.

So, that is about production of chemicals from C_1 compounds.

Likewise, production of C_2 compounds also we have seen and then from those C_2 compounds producing different types of chemicals also we have seen. Let us say under the C_2 compounds we have taken olefins only because from the petrochemicals industries point of view olefins are present in less quantities and then those olefins you take and then do some kind of reaction. So, wide spectrum of products you can get. Let us say this steam cracking of hydrocarbons when we have done not only ethylene, acetylene, but also several n number of compounds are being produced in the steam cracking of hydrocarbons, okay? So, that is the reason under the C_2 compounds though ethane also comes into the picture we started taking only C_2H_4 ethylene and then C_2H_2 acetylene, right? So before producing chemicals from them production of these themselves we have discussed like you know steam cracking of hydrocarbons if you do let us say C_xH_{2x+2} you take and then do cracking reaction then you get C_2H_4 plus C_2H_2 plus C_3H_6 plus C_3H_8 like that so many compounds you get that is what we have done and then but primarily the reaction conditions are mainly such a way that more of the ethylene and acetylene you get because ethylene is one of the most in fact the most important olefin is ethylene after that acetylene is the second most C_2 compound, okay? That is based on the application this we decide because ethylene is having huge number of applications compared to the other olefins that are being produced by steam cracking of hydrocarbons, right? So, then once we have this one from the ethylene and then acetylene what kind of products we can produce that we started.

So, first we started with ethanol production, right? Synthetic ethanol production by just hydration of ethylene if you do you get the ethanol but fermentation process is mostly used because of you know economics, right? Then we started discussion on EDC ethylene dichloride which is produced by you know direct chlorination between ethylene and then chlorine or thermal reaction between ethylene and chlorine if you do directly you get $ClCH_2CH_2Cl$ which is nothing but ethylene dichloride, okay? So, this is having you know applications mostly like you know production of vinyl acetate these kind of chemicals for the production or vinyl chloride monomer production this ethylene dichloride is in general use and that was the third component that we discussed that can be produced from the C_2 chemicals vinyl chloride. So, here that is EDC that is ethylene dichloride pyrolysis if you do at high temperature like 500 degrees centigrade then you get CH_2CHCl plus HCl which is the CH_2CHCl is nothing but vinyl chloride monomer whereas the $ClCH_2CH_2Cl$ is nothing but ethylene dichloride EDC. This is vinyl chloride monomer. This vinyl chloride can also be produced by acetylene and then HCl reaction, right? So, that also we have discussed, okay? This reaction occurs at 160 to 200 degrees centigrade whatever the second reaction is there between acetylene and HCl to give vinyl chloride monomer that is what we have discussed and then after that we discussed ethylene oxide production which is we got by oxidation of ethylene in the presence of a silver oxide catalyst at about 250 to 300 degrees centigrades and then 4 to 5 atmospheric pressures then we got CH_2CH_2 and then ethylene oxide but impurities CO_2 and then water vapors also you get in this reaction, right? So up to this part we have discussed on chemicals production from C_1 and C_2 chemicals. Now some more chemicals we are going to produce from C_2 compounds.

Now what are those C_2 compounds? Like now we take ethylene oxide as a raw material because we have seen ethylene oxide is primarily used for production of ethyl glycol by hydration reaction, okay? So that is what we are going to discuss now. So now in this lecture we start with the production of ethylene glycol which you can get by doing the hydration of ethylene oxide, okay? Ethylene oxide hydration if you do then you can get ethylene glycol plus polyglycol as well you may get. So, this is the starting topic of today's lecture.

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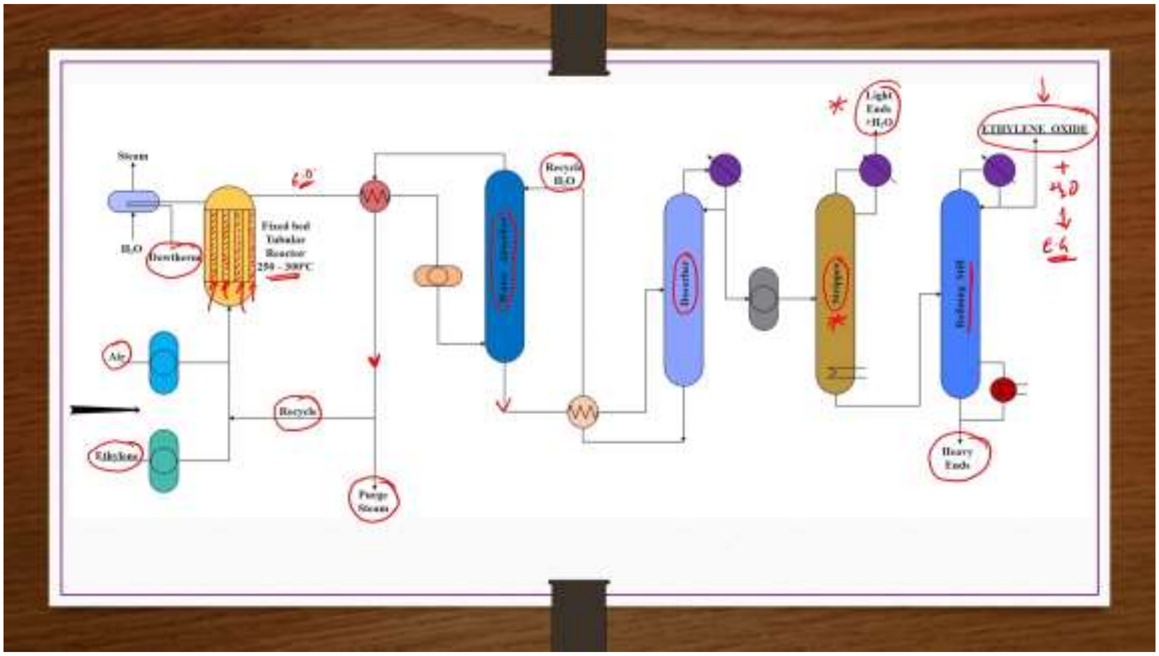

Since this ethylene glycol is produced by the hydration of ethylene oxide we have a recapitulation of a flowchart on production of ethylene oxide, okay? Which we have discussed in previous lecture anyway, okay? So, this reaction now here what we have whatever the ethylene that you have that you can compress and then you can take air, you can take oxygen also if you take oxygen the reaction is better and then less severe conditions are required as we have discussed previously. So, this ethylene and then air you can mix and then send it to a tubular reactor.

This tubular reactor is nothing but a bundle of tubes. In these tubes what you have silver oxide catalyst packed with some kind of promoters if required, okay? So, this whatever the ethylene and air mixture goes through this tubes then what happens required reaction takes place and then you get the products, okay? But these tubes are clustered in a shell kind of thing. There is an interstitial space because of this bundling of tubes. So, in the interstitial space what you do? You allow some kind of dowtherm, etc. to control the reaction temperature.

You do not want the reaction temperature to go beyond 250 to 300 degrees centigrade. For that dowtherm heat transfer fluids are in general used, okay? Now whatever the product mixture is there, that product mixture is primarily ethylene oxide and then some kind of impurities or unreacted ethylene, air, etc. So, what you do? This product mixture you pass through steam heat boiler, you know, then so that you know you reduce the temperature or recover some of the energy from it, right? Then whatever the unreacted ethylene, air, etc. are there, so those things you can separate out here, right? And then you can recycle back to the reactor along with the reactant or you can take them as a purge stream also because you do not want so much of gases to be accumulated within the tubes, otherwise required reaction may not take place. Then after this step, this product mixture whatever is there that you compress and then pass through a water wash absorber, right? Here what happens? Here also if at all some amount of unreacted, you know, reactant they will be collected and then sent back to the waste steam boiler to recover as the energy, okay? Then from the bottom of this one you get ethylene oxide absorbed in water, so then that you preheat, when you preheat whatever the water is there in the solution that would be evaporated and then pass through, will be passed through water absorber as a recycle, right? Then after that what you do? You send it to the packed bed desorber where you try to strip out the H_2O and then you purify whatever the ethylene oxide is there that much as much as possible that you take to a stripper because even after the desorption what happens? Lot of light ends and then H_2O may be present in this may be present in large quantities, not in small quantity.

So, this stripper is very much essential. In the stripper you remove such water vapors and light ends from the ethylene oxide mixture and then after that you take the ethylene oxide crude to the refining still where you do the refining of the ethylene oxide and then get it as a top product and then from the bottoms if at all any heavy ends are there, they will be separated out. So, this process we have seen. Now, this ethylene oxide we take as a raw material and then you react with water to get ethylene glycol that is we are discussing now.

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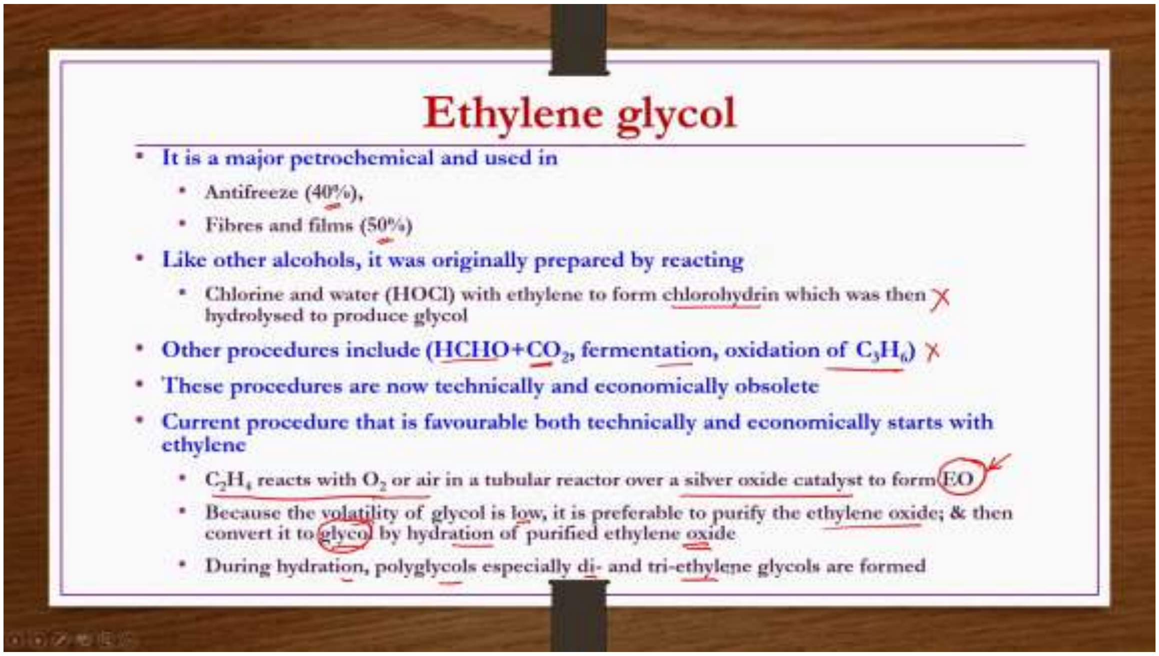

Ethylene glycol

- It is a major petrochemical and used in
  - Antifreeze (40%),
  - Fibres and films (50%)
- Like other alcohols, it was originally prepared by reacting
  - Chlorine and water (HOCl) with ethylene to form chlorohydrin which was then hydrolysed to produce glycol
- Other procedures include (HCHO+CO_2, fermentation, oxidation of C_3H_6)
- These procedures are now technically and economically obsolete
- Current procedure that is favourable both technically and economically starts with ethylene
  - C_2H_4 reacts with O_2 or air in a tubular reactor over a silver oxide catalyst to form EO
  - Because the volatility of glycol is low, it is preferable to purify the ethylene oxide; & then convert it to glycol by hydration of purified ethylene oxide
  - During hydration, polyglycols especially di- and tri-ethylene glycols are formed

So, now we discuss ethylene glycol. It is a major petrochemical and used in antifreeze and then fibers and films production up to 40 and then 50% respectively that much it is used. So, most of the ethylene in glycol is going for these 2 products. Like other alcohols, it was originally prepared by reacting chlorine and water with ethylene to form chlorohydrin which was then hydrolyzed to produce glycol. Other procedures include formaldehyde reacting with CO_2 to give ethylene glycol and then fermentation and oxidation of propene, these kind of reactions are there to produce so called ethylene glycol, okay? These procedures are now technically and economically obsolete because current procedure whatever is there that is hydration of ethylene oxide is both technically and economically more favorable because of that method whatever these methods are there, they are not even being used nowadays, okay? In the present method, ethylene reacts with oxygen or air as just discussed in a tubular reactor over silver oxide catalyst to form ethylene oxide first. Then because of the volatility of glycol is low, it is preferable to purify the ethylene oxide and then convert it to glycol by hydration of purified ethylene oxide.

So, whatever this ethylene oxide you get you purify it and then do the hydration reaction to get ethylene glycol. During the hydration polyglycols especially di and triethylene glycols are also formed.

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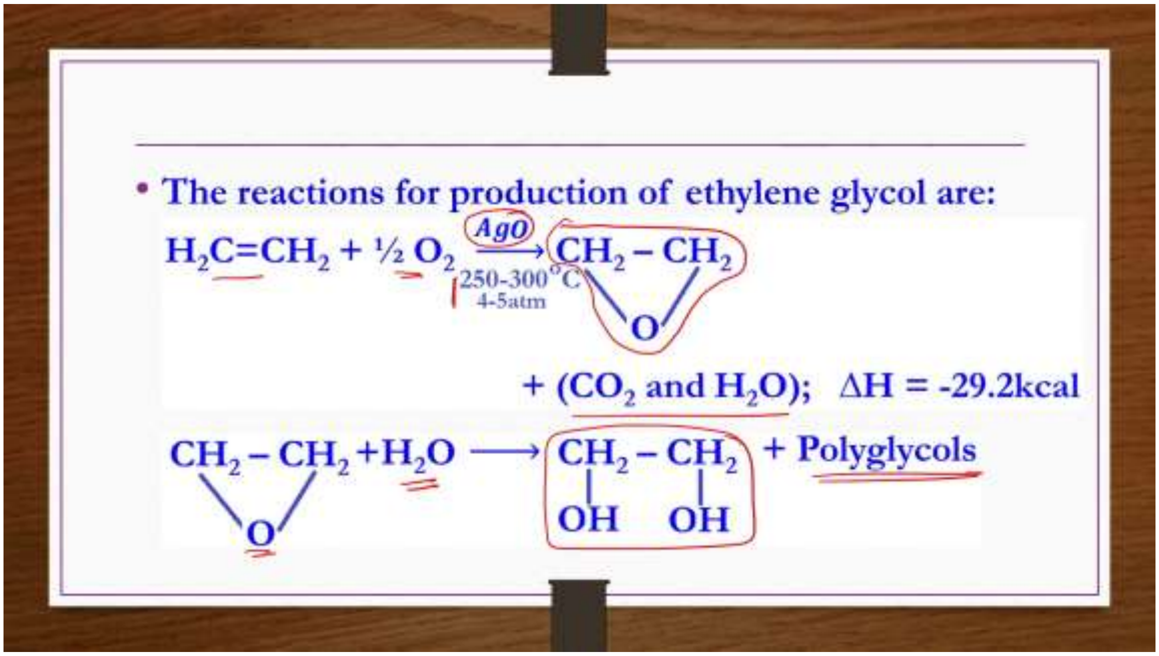

- The reactions for production of ethylene glycol are:

$$H_2C{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow[\substack{250\text{-}300^{\circ}C\\ 4\text{-}5\,atm}]{AgO} \underset{O}{CH_2-CH_2} + (CO_2 \text{ and } H_2O);\quad \Delta H = -29.2\,kcal$$

$$\underset{O}{CH_2-CH_2} + H_2O \longrightarrow \underset{OH\qquad OH}{CH_2-CH_2} + \text{Polyglycols}$$

So, the reaction for production of ethylene glycol are the first one is nothing but the reaction for production of ethylene oxide where ethylene reacts with oxygen or oxidation of ethylene takes place in the presence of silver oxide catalyst at 250 to 300 degrees centigrade and 4 to 5 atmosphere to get ethylene oxide along with CO_2 and then H_2O vapors. This ethylene oxide after purifying if you do the hydration then you can get ethyl glycol along with it some kind of polyglycols byproducts also forms.

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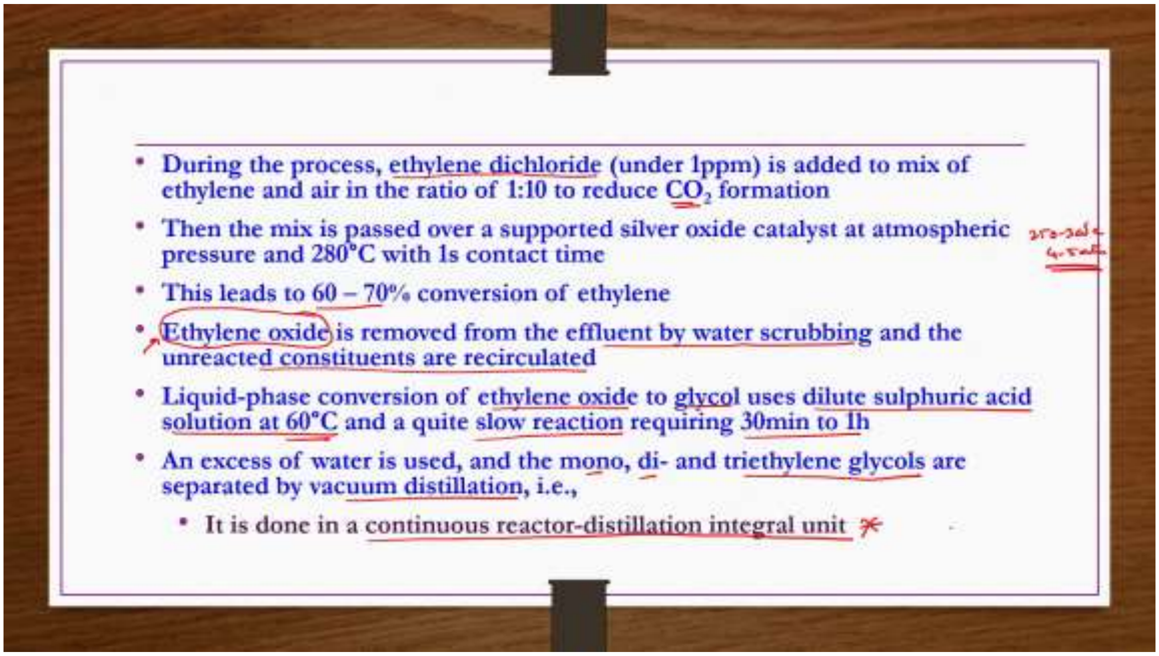

- During the process, ethylene dichloride (under 1ppm) is added to mix of ethylene and air in the ratio of 1:10 to reduce CO_2 formation
- Then the mix is passed over a supported silver oxide catalyst at atmospheric pressure and 280°C with 1s contact time

250-300°C
4-5 atm

- This leads to 60 – 70% conversion of ethylene
- Ethylene oxide is removed from the effluent by water scrubbing and the unreacted constituents are recirculated
- Liquid-phase conversion of ethylene oxide to glycol uses dilute sulphuric acid solution at 60°C and a quite slow reaction requiring 30min to 1h
- An excess of water is used, and the mono, di- and triethylene glycols are separated by vacuum distillation, i.e.,
  - It is done in a continuous reactor-distillation integral unit

During the process ethylene dichloride is added to mixture of ethylene and air in the ratio of 1 is to 10 to reduce CO_2 formation.

That is one of the engineering problem that we have already discussed. What happens if CO_2 formation is more? It acts as inert and then occupies most of the reactor space or interstitial space between the particles within the tube which is packed with the AGO catalyst. So, then there will not be enough space for the reactants to pass through and then react to produce the required ethylene oxide. So, this CO_2 formation has to be reduced for that purpose traces of EDC in general used. Traces of EDC in general used that we know in the previous lecture where we discussed engineering problems of ethylene oxide manufacture. Then the mixture is passed over a supported silver oxide catalyst at atmospheric pressure and 280 degrees centigrade with 1 second of contact time.

It can be varying like you know 250 to 300 degrees centigrade even 4 to 5 atmospheres are also possible. But mostly reaction is carried out at atmospheric pressure. This leads to 60 to 70 percent conversion of ethylene giving rise to ethylene oxide. Ethylene oxide is removed from the effluent by water scrubbing as discussed in the flowchart and then unreacted constituents are separated and re-circulated to the reactor. So, once you have this ethylene oxide which is purified after removing water vapors, unreacted ethylene, oxygen and then light ends, water vapor, etc., everything is been removed and then you get purified ethylene oxide. Once you get the purified ethylene oxide, then liquid phase conversion of ethylene oxide to glycol takes place by using water, but for this reaction, you need dilute sulfuric acid solution as catalyst at 60 degrees centigrade, but though you are using sulfuric acid, the reaction rate is slow and then it requires 30 minutes to 1 hour and then usually it is done in the batch reactor or continuous straight tank reactors. An excess of water is used and the mono, di and tri ethylene glycols are separated by vacuum distillation, okay? How it is done? It is done in a continuous reactor distillation integral part, okay? The reaction is very simple. So, that is the reason we are not having the flowchart for this one, okay?

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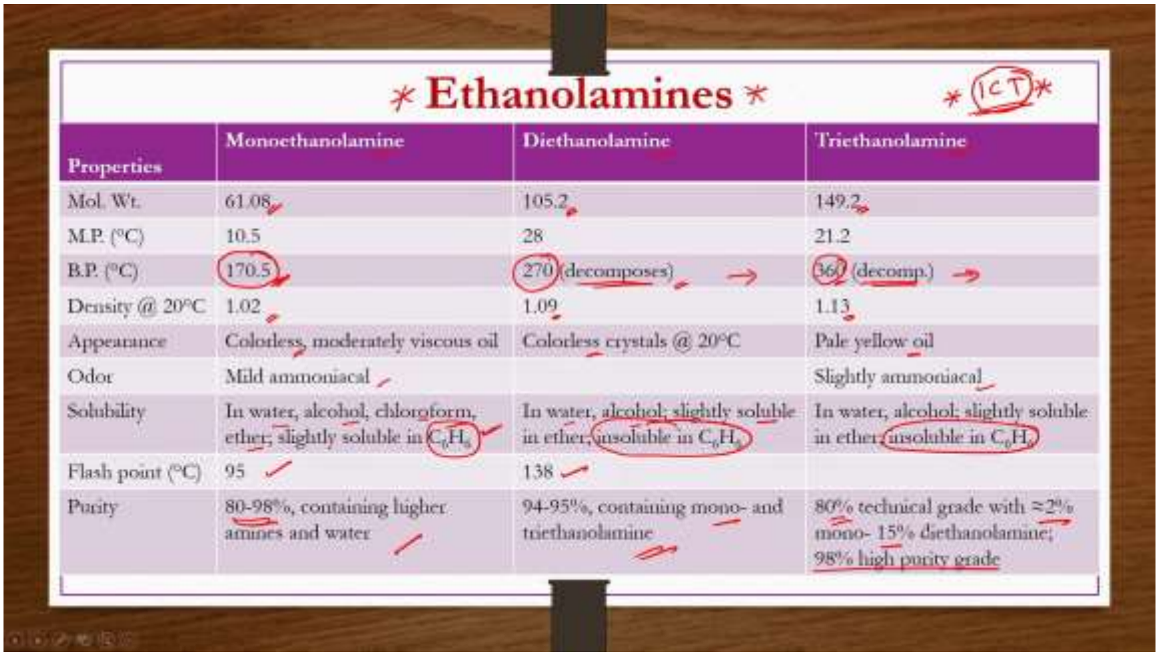

* Ethanolamines *

* ICT *

Properties	Monoethanolamine	Diethanolamine	Triethanolamine
Mol. Wt.	61.08	105.2	149.2
M.P. (°C)	10.5	28	21.2
B.P. (°C)	170.5	270 (decomposes) →	360 (decomp.) →
Density @ 20°C	1.02	1.09	1.13
Appearance	Colorless, moderately viscous oil	Colorless crystals @ 20°C	Pale yellow oil
Odor	Mild ammoniacal		Slightly ammoniacal
Solubility	In water, alcohol, chloroform, ether; slightly soluble in C_6H_6	In water, alcohol; slightly soluble in ether; insoluble in C_6H_6	In water, alcohol; slightly soluble in ether; insoluble in C_6H_6
Flash point (°C)	95	138	
Purity	80-98%, containing higher amines and water	94-95%, containing mono- and triethanolamine	80% technical grade with ≈2% mono- 15% diethanolamine; 98% high purity grade

So, now we discuss about ethanol amines. If you remember a few lectures before ethanol amines were used as a kind of solvent to absorb some kind of impurity gases especially acidic gases, right? For that purpose, ethanol amines were used as a solvent, right? So, this we have already seen in this course for some of the gases absorption but mostly it was seen several times in the inorganic chemical technology course which is also available on NPTEL MOOCs portal, right? So, there we have seen several times it has been used, this ethanol amine has been used to absorb some kind of impurity gases like H_2S, etc., okay? Then after that stripping has been done to purify the ethanol amines to remove the absorbed H_2S and then purified ethanol amines are recirculated back for the absorption purpose, okay? But that is one of the application. Other application also if you remember it is used in the soaps and detergents manufacturing in general where fats are in general reacts with ethanol amines to give the fatty acid salts, etc. So, from which you can prepare the detergents or soaps, etc. that is what also we have discussed. So, these are the 2 important applications of ethanol amines, okay? So, but how to produce them that is what we are going to discuss now.

It is obviously by the name ethanol amine so that amine is there so whenever amine functional group is there, amine analysis reaction is in general taken place or you know applied. This is also series reaction, okay? Like you know chloromethanes in a series reaction here also it is similar kind of series reaction is there, okay? So, but however before going to the production details we will have a comparison of the properties so that we can understand their importance, okay? So monoethanol amine, diethanol amine, triethanol amine as you move from the mono to di, di to triethanol amines obviously their molecular weight would increase, boiling points of these compounds also increases and then density also increases, right? So, you can see boiling point for the diethanol amine and triethanol amine beyond 270 it decomposes, triethanol amine beyond 360 it decomposes, okay? Only monoethanol is having 170.5 degrees centigrade of a boiling point. What does it mean by so if you wanted to separate this because this is a series reaction, so then all these three products would be forming. Of course, your catalyst reaction condition should be selected such a way that as per your product requirement whether you need more monoethanol amine or more diethanol amine or more triethanol amine accordingly you have to fix the conditions.

That is a different thing but all of them would definitely be present whatever the conditions you take. So, separation is required, okay? The appearance mostly colorless, monoethanol amine, moderately viscous oil whereas diethanol amine colorless crystals at 20 degrees centigrade, triethanol amine, pale yellow oil is the appearance. Order mild ammoniacal order or slightly ammoniacal order is possible. Solubility, monoethanol amine soluble in water, alcohol, chloroform, ethers but slightly soluble in benzene whereas diethanol amine is soluble in water and alcohol but slightly soluble in ether and then insoluble in benzene. These two are insoluble in benzene.

Even the third one also triethanol amine also insoluble in benzene whereas the monoethanol amine is soluble in benzene, right? Flash point 95, 138 degrees centigrade. Purity different grades, purities are there 80 to 98 percent containing higher amines and water here, right? And then 94 to 95 percent containing mono and triethanol amines as impurities and then here triethanol amine 80 percent technical grade is available with approximately 2 percent monoethanol amine and 15 percent diethanol amine as impurities that is one grade and then high purity 98 percent triethanol amine is also available, okay?

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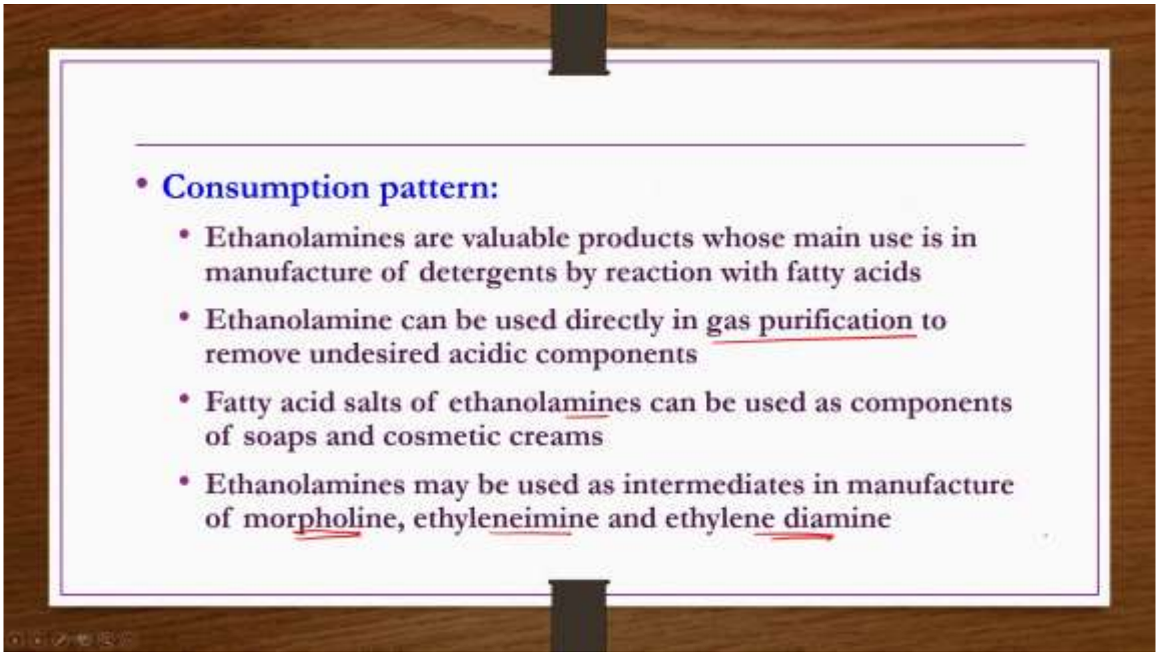

- **Consumption pattern:**
  - Ethanolamines are valuable products whose main use is in manufacture of detergents by reaction with fatty acids
  - Ethanolamine can be used directly in gas purification to remove undesired acidic components
  - Fatty acid salts of ethanolamines can be used as components of soaps and cosmetic creams
  - Ethanolamines may be used as intermediates in manufacture of morpholine, ethyleneimine and ethylene diamine

Consumption pattern if you see, ethanol amines are valuable products whose main use is in manufacture of detergents by reaction with fatty acids. Ethanol amine can be used directly in gas purification to remove undesired acidic components. Fatty acid salts of ethanol amines can be used as components of soaps and cosmetic creams. Ethanol amines may be used as internal intermediates in manufacture of morpholine and then ethylene amine and ethylene diamine also.

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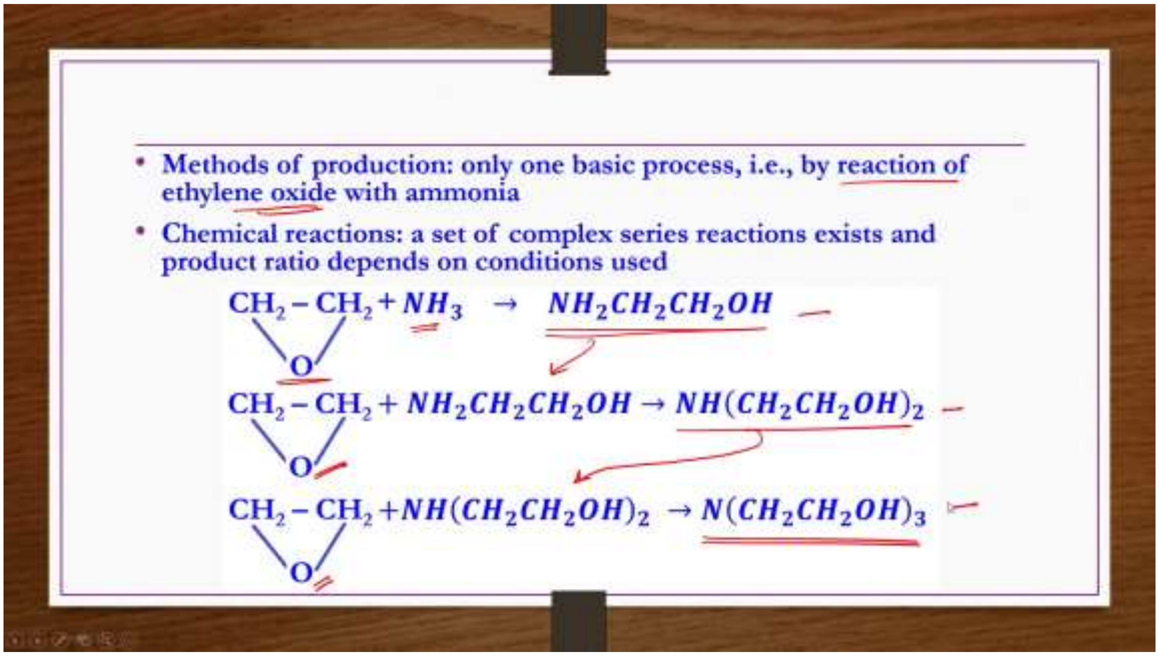

- Methods of production: only one basic process, i.e., by reaction of ethylene oxide with ammonia
- Chemical reactions: a set of complex series reactions exists and product ratio depends on conditions used

$$\underset{O}{CH_2-CH_2} + NH_3 \rightarrow NH_2CH_2CH_2OH$$

$$\underset{O}{CH_2-CH_2} + NH_2CH_2CH_2OH \rightarrow NH(CH_2CH_2OH)_2$$

$$\underset{O}{CH_2-CH_2} + NH(CH_2CH_2OH)_2 \rightarrow N(CH_2CH_2OH)_3$$

Methods of production, only one basic process is there that is the reaction of ethylene oxide and ammonia, okay? Chemical reactions, a set of complex series of reactions exist and product ratio depends on the conditions used. Let us say you have 1 mole of ethylene oxide reacting with ammonia to give monoethanol amine. This monoethanol amine is reacting with 1 mole of ethylene oxide to give diethanol amine. This diethanol amine is reacting with 1 mole of ethylene oxide to give triethanol amine.

So, it is a series reaction. So, when you take a ethylene oxide and then ammonia mixture and do the reaction, so all these mono, di and triethanol amines are going to form because it is a series reaction, okay?

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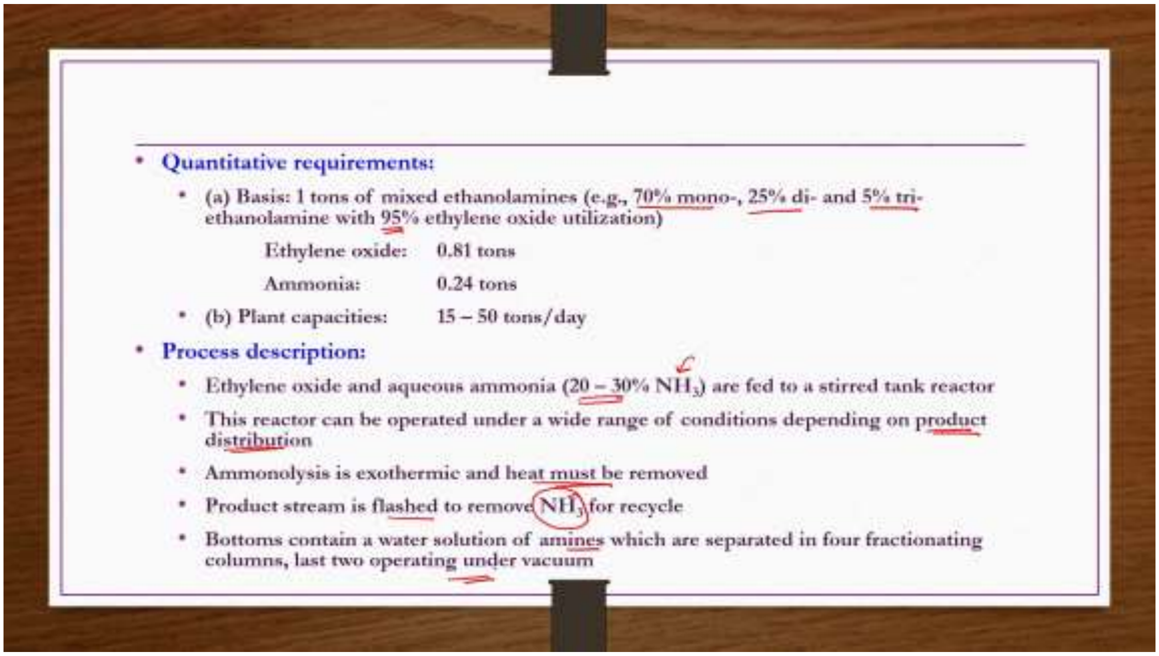

- **Quantitative requirements:**
  - (a) Basis: 1 tons of mixed ethanolamines (e.g., 70% mono-, 25% di- and 5% tri-ethanolamine with 95% ethylene oxide utilization)

    Ethylene oxide: 0.81 tons

    Ammonia: 0.24 tons
  - (b) Plant capacities: 15 – 50 tons/day
- **Process description:**
  - Ethylene oxide and aqueous ammonia (20 – 30% NH_3) are fed to a stirred tank reactor
  - This reactor can be operated under a wide range of conditions depending on product distribution
  - Ammonolysis is exothermic and heat must be removed
  - Product stream is flashed to remove NH_3 for recycle
  - Bottoms contain a water solution of amines which are separated in four fractionating columns, last two operating under vacuum

Quantitative requirements, basis 1 tons of mixed ethanol amines if you want to produce. Let us say for example, 70% monoethanol amine, 25% diethanol amine and 5% triethanol amine with 95% ethylene oxide utilization. Then ethylene oxide you required 0.81 tons, ammonia 0.24 tons, plant capacity usually 15 to 50 tons per day.

Process description if you see ethylene oxide and aqueous ammonia solution having 20 to 30% ammonia are fed to a stirred tank reactor, simple reactor. So, wherever this ammonia involved in such kind of ammonia-less reactions are taking place, so then lot of heat would be evaluated. So that heat has to be controlled by providing the reactor with a jacketed system through which you can circulate cold water to control the temperature of the reactor as per the requirement. This reactor can be operated under a wide range of conditions depending on the product distribution. As per your product distribution, your required of a mono, di or triethanol amine accordingly you have to make the process conditions.

Ammonolysis is exothermic and heat must be removed and recovered. Product stream is flash to remove ammonia for recycle because ammonia wherever is there, the conversion is not so easy. It takes high temperature, high pressure and then catalyst in general and then despite of that one the complete conversion may not take place in most of the cases wherever there is such kind of ammonolysis reactions are occurring. Same may be true here also, so that ammonia has to be removed from the product mixture by the flash operation and then that ammonia can be recycled. Bottoms contain a water solution of amines which are separated in 4 fractionating columns, last 2 operating under vacuum.

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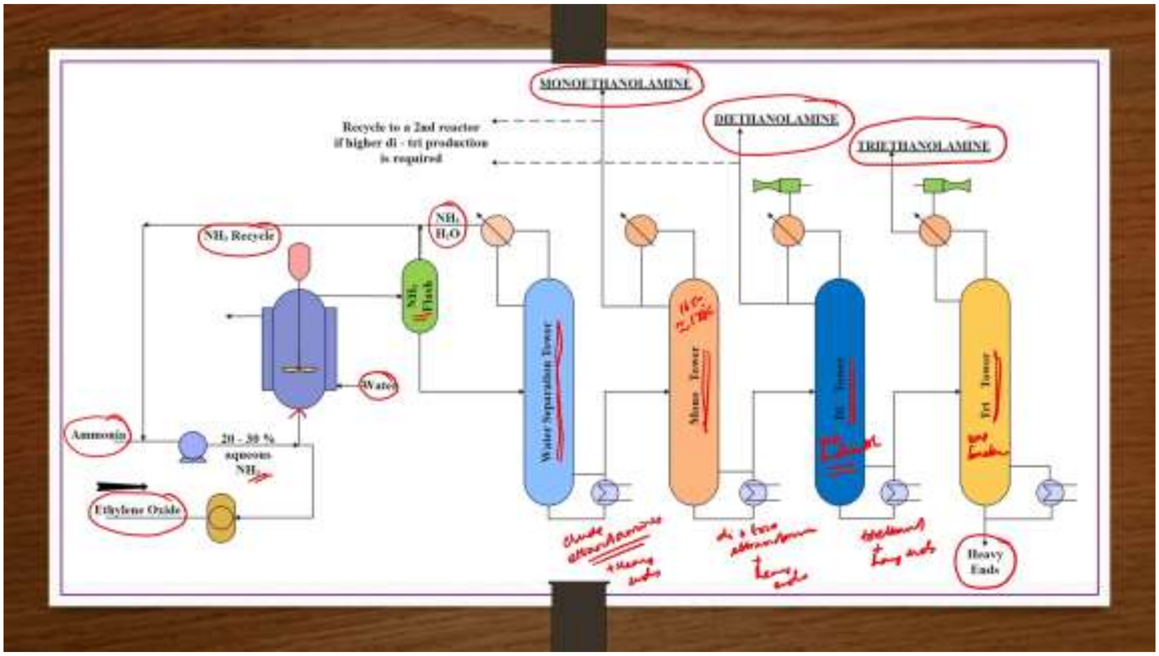

So, this is the flowchart here. Now, whatever the ethylene oxide is there that you can compress and then ammonia solution whatever is there you make 20 to 30% ammonia solution. Both of them you take to stirred tank reactor. Here the required reaction takes place, but the reaction evolved lot of heat also for that purpose in order to keep the reaction temperature conditions as per the requirement, water is being circulated outside of the reactor through jackets. So, whatever the product mixture is there that would be having unreacted ammonia obviously because ammonia conversion is not easy. So that mixture is passed through ammonia flash to recover the ammonia and then that ammonia can be taken as a recycle.

After that what you do in the reaction lot of water formation also takes place. So, water separation tower, the reaction mixture after ammonia flash is assigned to water separation tower where lot of the water is separated out. In this process some of the ammonia is also separated out. In other words, when you do the partial condensation, you get ammonia solution that can also be recycled back to the reactor whereas the bottom of the water separation tower whatever is there that would be crude ethanol amines. It will be having mixture of a mono di and tri ethanol amines along with the heavy ends also would be there.

So, this you pass through sequence of a mono tower, di tower and tri tower. These towers are nothing but the fractionators. The first one is the distillation column. Here your operating conditions would be roughly 170, 165, 170 degrees centigrade. So that whatever the mono ethanol amine is there, so its boiling point is 171.

So most of the mono ethanol amine would be going as a vapor in the top product and then that can be condensed and collected as a mono ethanol amine. Whereas the now bottoms would be di and tri ethanol amines plus heavy ends would be there. They will be taken to the di and tri tower. So, these are nothing but the vacuum fractionators. Because here they decompose beyond 270 degrees centigrade, di ethanol amine decompose and then beyond 360 degrees centigrade tri ethanol amine decompose.

So, then they do not undergo boiling so you have to do the vacuum fractionation. So, in the first vacuum fractionator, the conditions are maintained such a way that di ethanol amine is collected as a top product and then from the bottom you will be having tri ethanol amine and then heavy ends mixture. So that you can take to another vacuum fractionator where the conditions are maintained such a way that tri ethanol amine you can get it as a top product whereas the heavy ends are collected from the bottom. So, the process is simple, simple reaction removing or recovering the unreacted ammonia solution etc. recycling back to the reactor and then after that doing the separation of the products. That is the process, very simple process.

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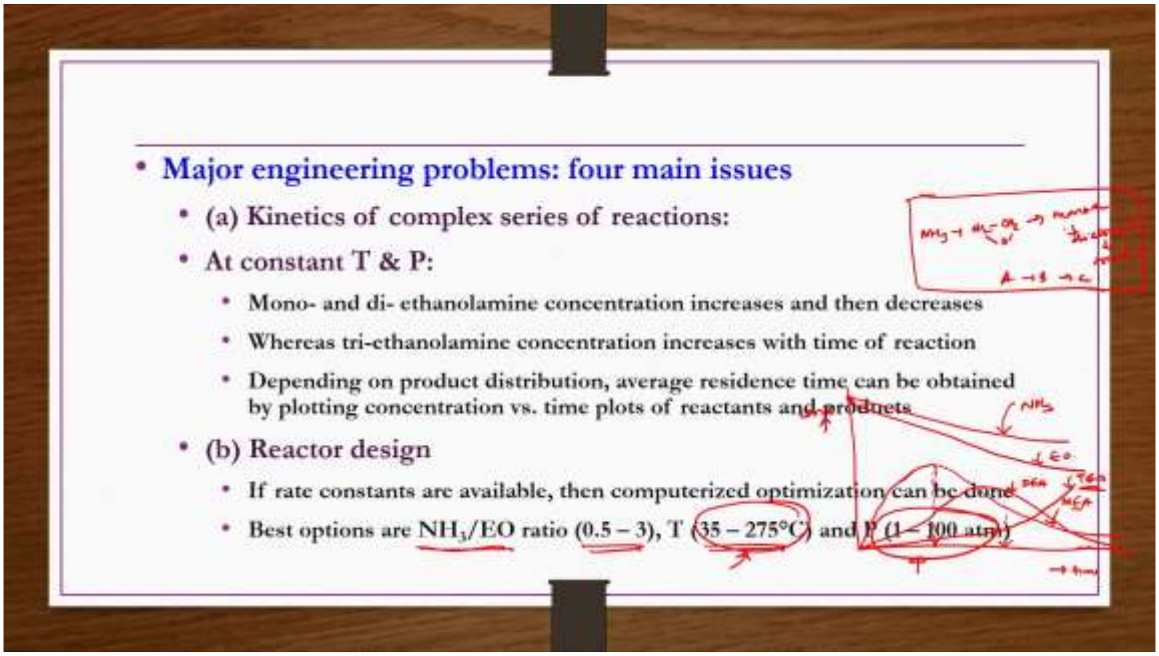

- Major engineering problems: four main issues
  - (a) Kinetics of complex series of reactions:
  - At constant T & P:
    - Mono- and di- ethanolamine concentration increases and then decreases
    - Whereas tri-ethanolamine concentration increases with time of reaction
    - Depending on product distribution, average residence time can be obtained by plotting concentration vs. time plots of reactants and products
  - (b) Reactor design
    - If rate constants are available, then computerized optimization can be done
    - Best options are NH_3/EO ratio (0.5 – 3), T (35 – 275°C) and P (1 – 100 atm)

Major engineering problems, 4 main issues are there. One is the kinetics of complex series reactions. Let us say whenever we have series reaction if you remember A goes to B, B goes to C kind of series reaction. So now here this is what you are having. You are having ammonia plus ethylene oxide you are having.

Now you are getting mono ethanol amine that reacts with ethylene oxide again and to give di ethanol amine. This di ethanol amine reacts with ethylene oxide again to give tri ethanol amine. This kind of series reaction is taking place. So, for such kind of series reaction if you plot concentration of reactants and products versus time what you have? Let us say the concentration of ammonia and then ethylene gradually decreases. Ethylene oxide concentration and ammonia concentration gradually decreases, but which one decreases more and then which one decreases less that again depends on the conversion.

As we already know that ammonia conversion is very difficult. So, concentration of ammonia reduction would be less or less ammonia would be participating in the reaction compared to the other component. In this case other component is nothing but ethylene oxide. So, this is ammonia. So qualitatively also when you present you have to present systematically you cannot say the top curve is for ethylene oxide and then second curve is the ammonia like that you cannot say that.

So, about the products first mono ethanol amine so that concentration is very less small initially and then gradually its concentration increases as the reaction progresses. But as the reaction progresses that mono ethanol amine reacts with the 1 mole of ethylene oxide to produce diethanol amine. So, after certain time its concentration gradually decreases like this. So, there would be a maxima kind of thing. So, because of that one mono ethanol amine is having like this kind of concentration profile.

But initially diethanol amine concentration is also very low and then it gradually increases and gradually increases and then that depends on how much mono ethanol amine is reacting with the ethylene oxide to give diethanol amine. So, its concentration also increases gradually but as its concentration increases this diethanol amine also reacts with the ethylene oxide to give triethanol amine. So, after certain point its concentration also decreases something like this. So, this is you know diethanol amine whereas the triethanol amine its concentration is very small negligible for initial period of time and then but it gradually its concentration increases. Its concentration gradually increases with time but it does not decrease because after triethanol amine it is not being consumed by any of the reactants or any of the other products.

So, such kind of reaction kinetics are possible in the series reactions like this and then of course this can be taken as one of the example of a series reaction. Same is true in the chloromethanes preparation also. They also you know undergo series reaction methane and then chlorine undergo series reaction to give different types of chloromethanes. At constant temperature and pressure mono and diethanol amine concentration increases and then decreases as explained here whereas triethanol amine concentration increases with time of reaction as shown here as explained. So, depending on product distribution average residence time can be obtained by plotting concentration versus time plots of reaction and products.

Let us say you need to have more of monoethanol amine. So, then you try to fix the maximum residence time up to this one only. So that there would not be sufficient time for the monoethanol amine to react with ethylene oxide to form a more of the diethanol amine. So, this kind of if you want let us say more of the diethanol amine so then you have to make sure that residence time according like this. Then reactor design is also one of the important thing. If rate constants are available then computerized optimization can be done.

Best options for ammonia to ethylene oxide ratio is 0.5 to 3 temperature 35 to 275 degree centigrade very broad that is the reason computerized optimization is required whereas the pressure is also very high 1 to 100 atmosphere. So, these wide range of conditions are provided they can be best option but you know you have to do more optimization as per your requirement.

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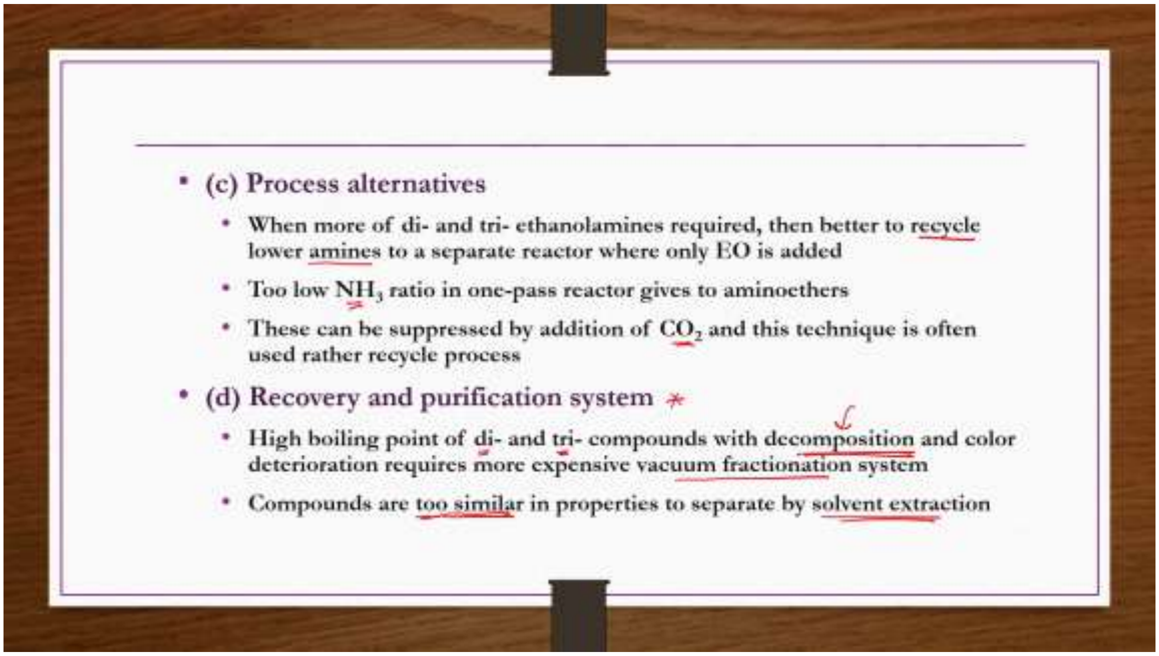

- (c) Process alternatives
  - When more of di- and tri- ethanolamines required, then better to recycle lower amines to a separate reactor where only EO is added
  - Too low NH_3 ratio in one-pass reactor gives to aminoethers
  - These can be suppressed by addition of CO_2 and this technique is often used rather recycle process
- (d) Recovery and purification system *
  - High boiling point of di- and tri- compounds with decomposition and color deterioration requires more expensive vacuum fractionation system
  - Compounds are too similar in properties to separate by solvent extraction

Third one is process alternatives when more of di and tri ethanol amines are required then better to recycle lower amines to a separate reactor where only ethylene oxide is used. Too low ammonia ratio in one pass reactor gives amino ethers. These can be suppressed by addition of CO_2 and this technique is often used to rather recycle process.

Fourth one is the recovery and purification of the system. So that is another important engineering problem. High boiling point of di and tri compounds with decomposition that is the problem. Not only high boiling point temperatures for these two components but also they undergo decomposition and also color deterioration takes place with the temperature. The separation of di and tri components require more expensive vacuum fractionation system rather simple distillation column. Compounds are too similar in properties also so it is difficult to do separation by solvent extraction also.

If the distillation is not possible by certain reason like you know decomposition with the temperature or you know close boiling point of the components that are present in the mixture then solvent extraction may be thought of but that is also not possible in this case because the properties of dye and dry ethanol amines are you know very similar to each other, okay? So that is what about the production of ethanol amines.

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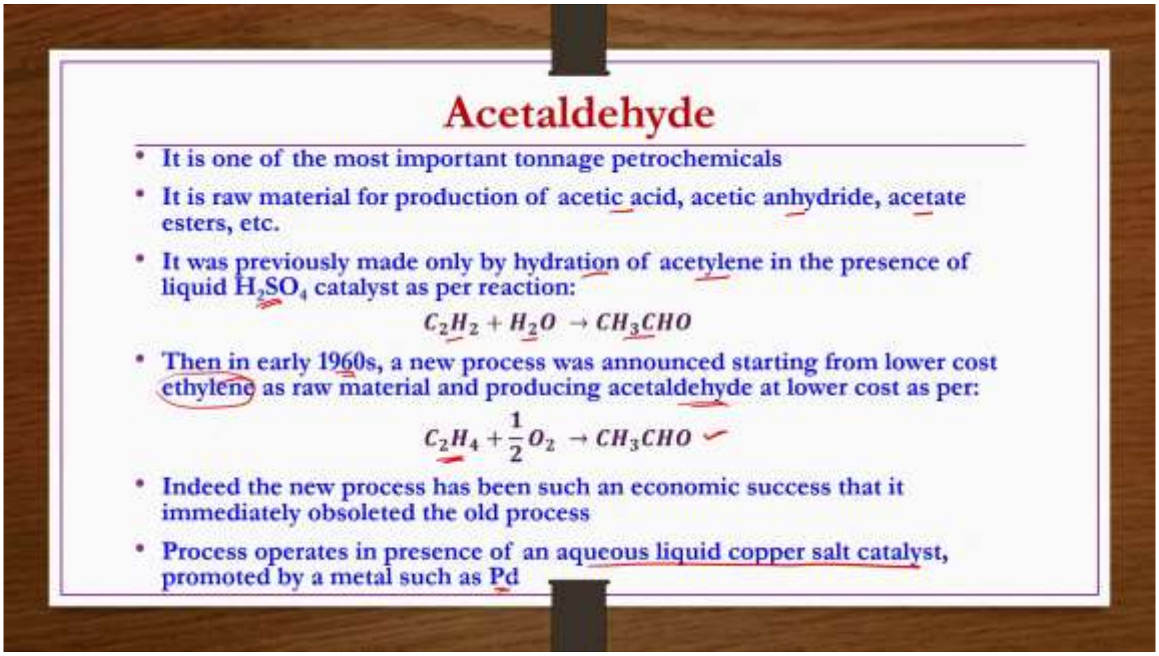

Acetaldehyde

- It is one of the most important tonnage petrochemicals
- It is raw material for production of acetic acid, acetic anhydride, acetate esters, etc.
- It was previously made only by hydration of acetylene in the presence of liquid H_2SO_4 catalyst as per reaction:

$$C_2H_2 + H_2O \rightarrow CH_3CHO$$

- Then in early 1960s, a new process was announced starting from lower cost ethylene as raw material and producing acetaldehyde at lower cost as per:

$$C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_3CHO$$

- Indeed the new process has been such an economic success that it immediately obsoleted the old process
- Process operates in presence of an aqueous liquid copper salt catalyst, promoted by a metal such as Pd

Now we discuss about production of acetaldehyde. It is one of the most important tonnage petrochemical. It is raw material for production of several compounds like acetic acid, acetic anhydride, acetate esters, etc. The conventional process was hydration of acetylene that is acetylene and water reaction in the presence of liquid sulfuric acid catalyst.

As per the reaction, the acetylene reacts with water in the presence of H_2SO_4 to give acetaldehyde. This is the conventional process. The new process was announced where lower cost ethylene was used as raw material and produce acetaldehyde at much lower cost compared to the previous one and then reaction was also simple. Just you take ethylene and do the oxidation, you get acetaldehyde. So, this process was so better economically that immediately other process were obsoleted, okay? Process operates in the presence of an aqueous liquid copper salt catalyst promoted by metal such as palladium.

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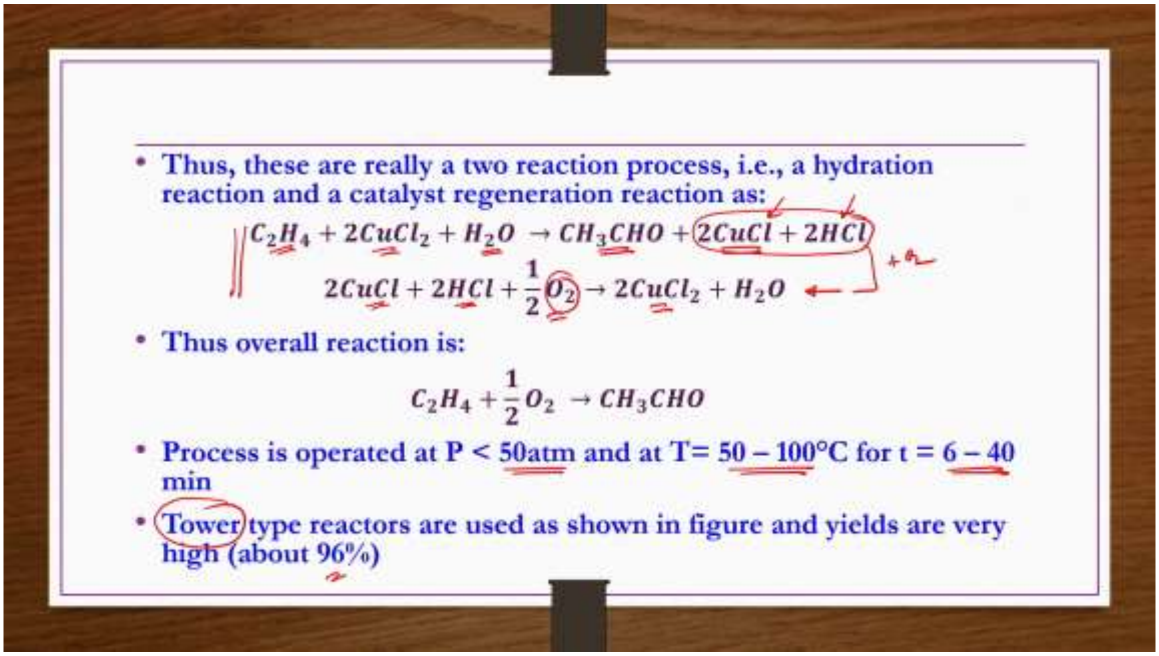

- Thus, these are really a two reaction process, i.e., a hydration reaction and a catalyst regeneration reaction as:

$$C_2H_4 + 2CuCl_2 + H_2O \rightarrow CH_3CHO + \boxed{2CuCl + 2HCl}$$

$$2CuCl + 2HCl + \frac{1}{2}O_2 \rightarrow 2CuCl_2 + H_2O$$

- Thus overall reaction is:

$$C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_3CHO$$

- Process is operated at P < 50atm and at T= 50 – 100°C for t = 6 – 40 min
- Tower type reactors are used as shown in figure and yields are very high (about 96%)

So thus, there are generally 2 reaction process that is hydration reaction and catalyst regeneration reaction. In the hydration reaction, the first ethylene reacts with water in the presence of catalyst to give acetaldehyde and then second reaction is that whatever the $2CuCl_2$ is there that is converted into 2CuCl. That 2CuCl reacts with the 2HCl in the presence of oxygen, then you regenerate the catalyst. Actually, this is nothing but catalyst regeneration by oxidation reaction, right? From the product mixture whatever the acetaldehyde you separate and then remaining ones whatever are there that you react with oxygen, do the oxidation, then you can regenerate your catalyst, okay? So overall reaction is that C_2H_4 plus half O_2 is CH_3OH, but it is actually 2-step reactions are there like this. Otherwise, every batch you have to give the fresh catalyst and then wasting disposing CuClHCl is another problem.

So, catalyst regeneration is always essential and then beneficial both from technical as well as economical point of view and that is being satisfied here. This process is operated at pressures less than 50 atmosphere and then at temperatures 50 to 100 degrees centigrade, but the time is slightly higher 60 to 40 minutes. Towertype reactors are used as shown in the picture we are discussing in the next slide, but however, the yields are very high up to 96%.

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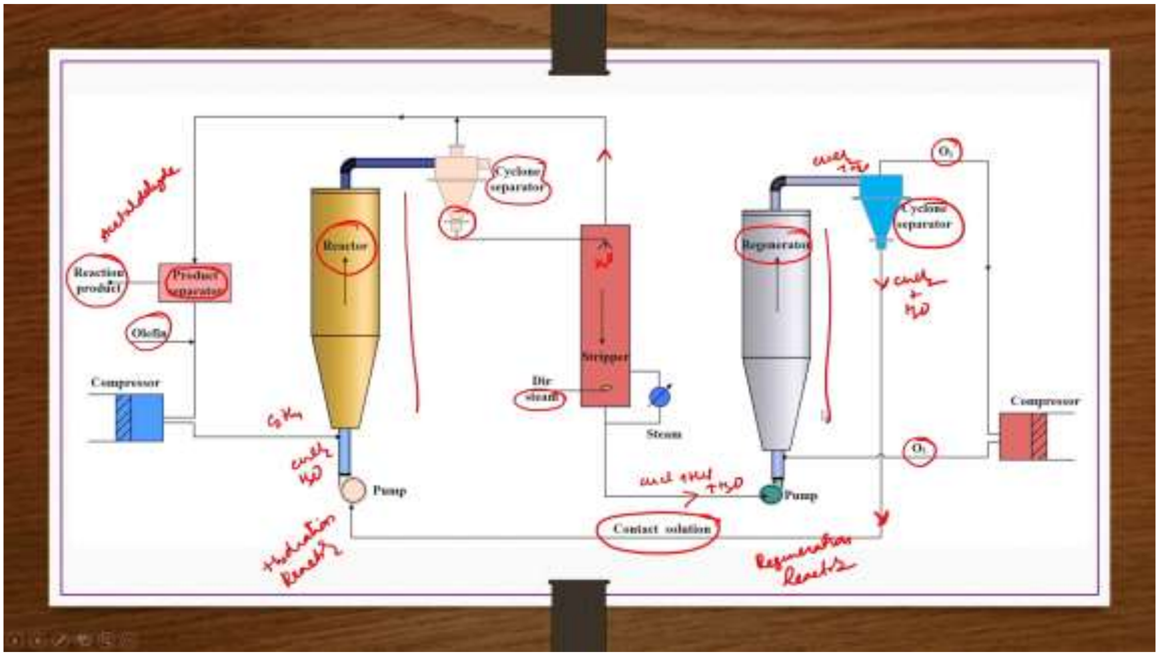

So, this is the setup for the production of acetaldehyde from the ethylene. So, here what you do ethylene you take through compressor and then whatever the $CuCl_2$ and then H_2O is required that you pass through a pump from the bottom of the reactor.

In the reactor required reaction takes place and then reactor mixture whatever is there that is taken to a cyclone separator. So, the products whatever are there which are lighter ones they are taken to the product separator and then required separation is done to get the whatever the final product that you are expecting to have here acetaldehyde. Whereas the bottoms of cyclone separator would be the heaviest one, they would be taken to a stripper where the steam is applied directly to the mixture so that if at all any water vapor, etc. and then still acetaldehyde, etc. are there they will be evaporated and collected from the top and then sent to the product separator to recover more of the acetaldehyde.

Then from the bottom of the stripper whatever you get that is primarily nothing but CuCl plus HCl plus H_2O mixture that you take to the regenerator which is also a towertype reactor to which you supply oxygen and then do the oxidation. So, here what you get you get the most of the products like $CuCl_2$ plus H_2O, etc. So, that you take to the cyclone separator here from here whatever the unreacted oxygen or the gases, etc. are there they will be collected from the top and then fed back to the compressor and then recirculated back to the regenerator. Whereas from the bottom primarily you get $CuCl_2$ and then water mixture that is nothing but the contact solution that you can take it back to the reactor as a recycle through pump.

So, that more reaction takes place. So, here this here you can call it as hydration reactor. This you call it as catalyst regeneration reactor. Both of them are towertype reactors as shown here.

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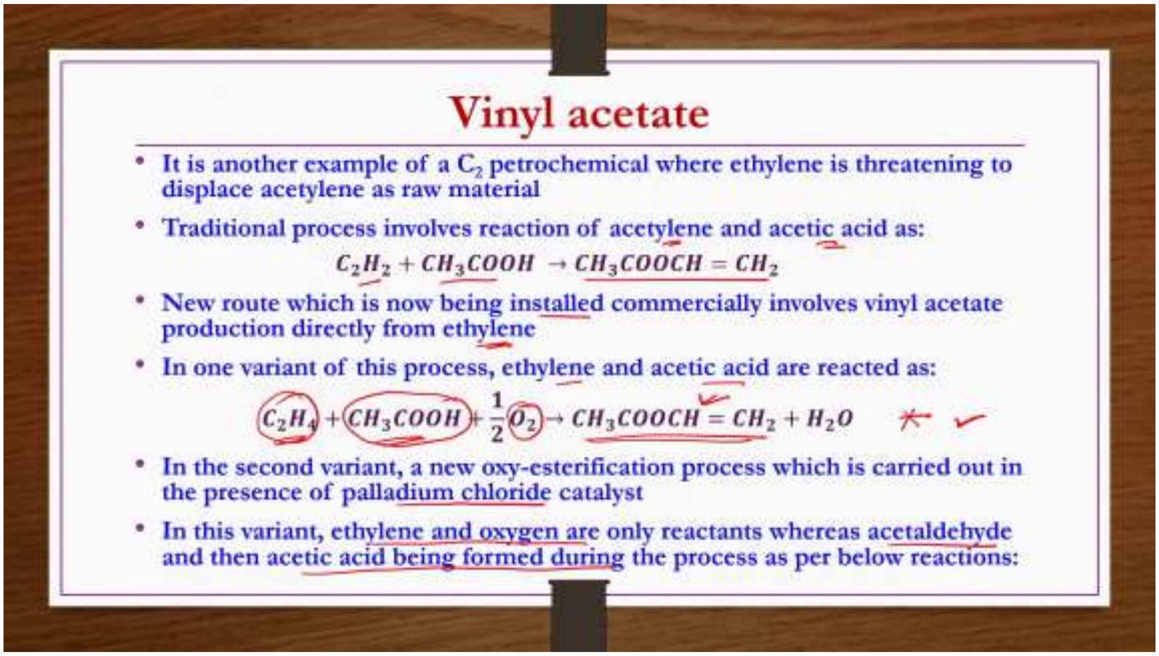

Vinyl acetate

- It is another example of a C_2 petrochemical where ethylene is threatening to displace acetylene as raw material
- Traditional process involves reaction of acetylene and acetic acid as:

$$C_2H_2 + CH_3COOH \rightarrow CH_3COOCH = CH_2$$

- New route which is now being installed commercially involves vinyl acetate production directly from ethylene
- In one variant of this process, ethylene and acetic acid are reacted as:

$$C_2H_4 + CH_3COOH + \frac{1}{2}O_2 \rightarrow CH_3COOCH = CH_2 + H_2O$$

- In the second variant, a new oxy-esterification process which is carried out in the presence of palladium chloride catalyst
- In this variant, ethylene and oxygen are only reactants whereas acetaldehyde and then acetic acid being formed during the process as per below reactions:

Last chemical that we are producing from a C_2 compound is vinyl acetate actually n number of are there we have selected a few in the selected ones vinyl acetate is the last one. It is another example of a C_2 petrochemical where ethylene is threatening to displace acetylene as raw material.

Actually, earlier acetylene was used as raw material to produce vinyl acetate but nowadays ethylene is being used and then vinyl acetate is produced at much cheaper cost. Traditional process involves reaction of acetylene and then acetic acid as per the reaction like acetylene reacting with the acetic acid to give vinyl acetate. Now, new route which is being installed commercially involves vinyl acetate production directly from ethylene. So, here in this process different variants are there one of the variants is ethylene and then acetic acids are reacting together to give vinyl acetate. But however, in addition to ethylene and then acetic acid you also required oxygen for this reaction.

So, this process is being found more technically more feasible techno economically. So, people are following these kinds of trends. There is another variant in which oxy esterification process is carried out in the presence of palladium chloride catalyst where different reactions takes place. In this variant ethylene and oxygen are only reacts where acetaldehyde and then acetic acid being formed during the process as per the below reaction. Actually, ethylene here is reacting with the acetic acid along with the oxygen to give vinyl acetate. So, now, but this acetic acid from where are we getting we are getting from the acetaldehyde first you know acetaldehyde being produced and then that acetaldehyde is being converted into the acetic acid and that acetic acid is reacting with the ethylene that is the second variant that reactions are given here.

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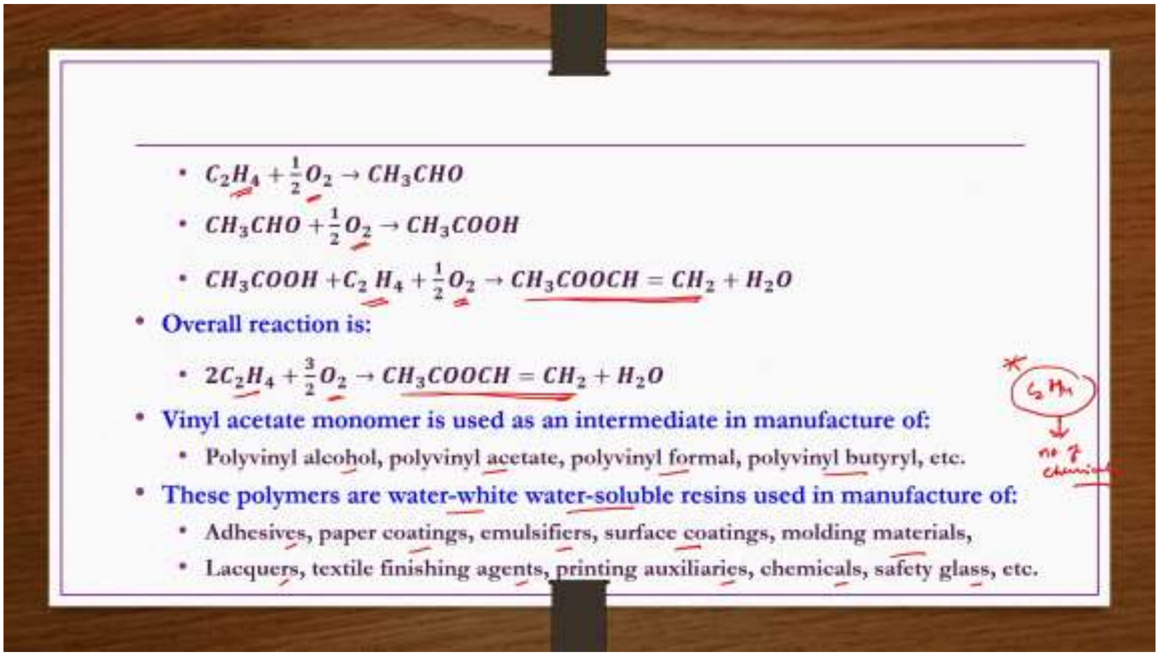

- $C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_3CHO$
- $CH_3CHO + \frac{1}{2}O_2 \rightarrow CH_3COOH$
- $CH_3COOH + C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_3COOCH = CH_2 + H_2O$

- **Overall reaction is:**
  - $2C_2H_4 + \frac{3}{2}O_2 \rightarrow CH_3COOCH = CH_2 + H_2O$
- **Vinyl acetate monomer is used as an intermediate in manufacture of:**
  - Polyvinyl alcohol, polyvinyl acetate, polyvinyl formal, polyvinyl butyryl, etc.
- **These polymers are water-white water-soluble resins used in manufacture of:**
  - Adhesives, paper coatings, emulsifiers, surface coatings, molding materials,
  - Lacquers, textile finishing agents, printing auxiliaries, chemicals, safety glass, etc.

So, ethylene oxidation if you do acetaldehyde you get this acetaldehyde will be further oxidized to acetic acid. This acetic acid will react with the ethylene and then oxygen to give vinyl acetate. So, overall reaction is that 2 moles of ethylene reacts with 1.5 moles of oxygen to give vinyl acetate. Vinyl acetate monomer is used as intermediate in manufacture of several products like polyvinyl alcohol, polyvinyl acetate, polyvinyl formyl, polyvinyl butyryl, etc.

These polymers are water-white water-soluble resins used in manufacture of issues adhesives, paper coatings, emulsifiers, surface coatings, molding materials. These polymers are also used for the lacquers, textile finishing agents, printing auxiliaries, chemicals, safety glasses, etc. It is having so many applications. So, now we can see ethylene is having you know option like you know you can produce number of chemicals compared to the acetylene and then propylene other kind of olefins that is the reason ethylene is the most important olefin from the synthetic chemical industries point of view.

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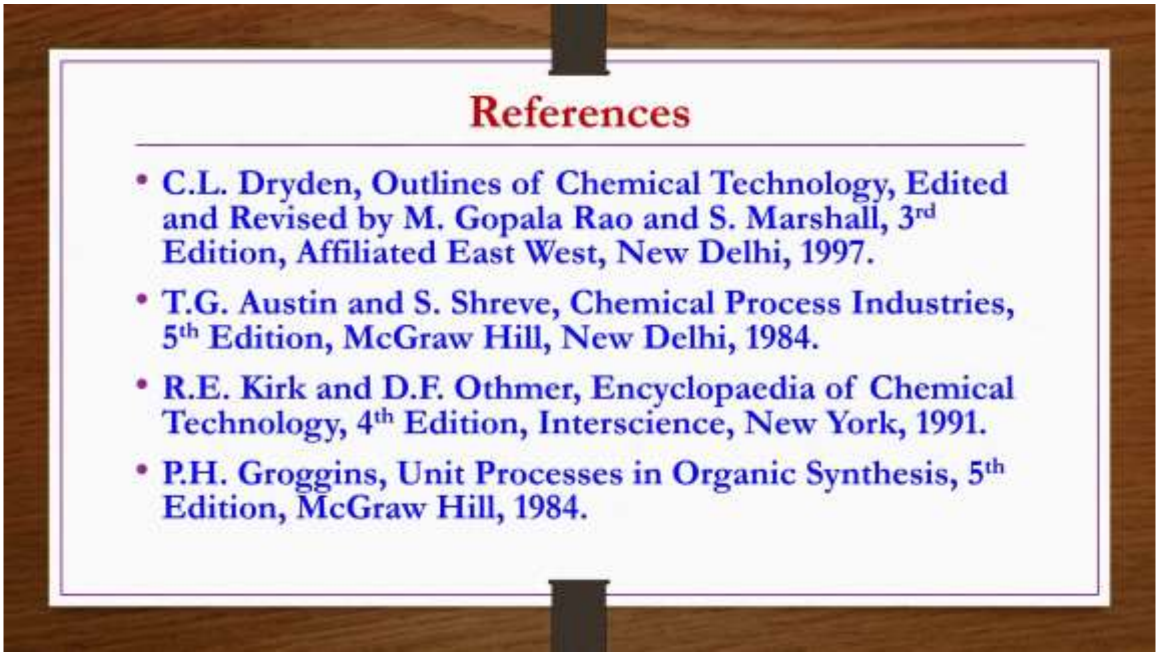

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