Organic Chemical Technology
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Lecture - 24
Chemicals from C2 Compounds

Welcome to the MOOCs course organic chemical technology, the title of today's lecture is chemicals from C2 compounds. Before going into the details of today's lecture, we have a recapitulation of what we have discussed in the previous couple of lectures. We started discussing production of different types of chemicals from C1 and C2 compounds. In the context of petrochemical industry, C1 compound means the compound which is having only one carbon atom. Let us say CO plus H2 synthesis gas if you have, so you have only one carbon atom and let us say if you have methane, then also you have only one carbon atom. Such kind of compounds are referred to as C1 compounds. So, using such C1 compounds, we started producing different types of chemicals. In fact, we have seen using these C1 compounds, methane, methanol, etc., then you can produce n number of products, right? So, let us say we started with production of methanol from the CO plus H2 mixture, this is what we have seen and then this methanol whatever is there that if you do oxidation or pyrolysis, it is possible that you get formaldehyde.

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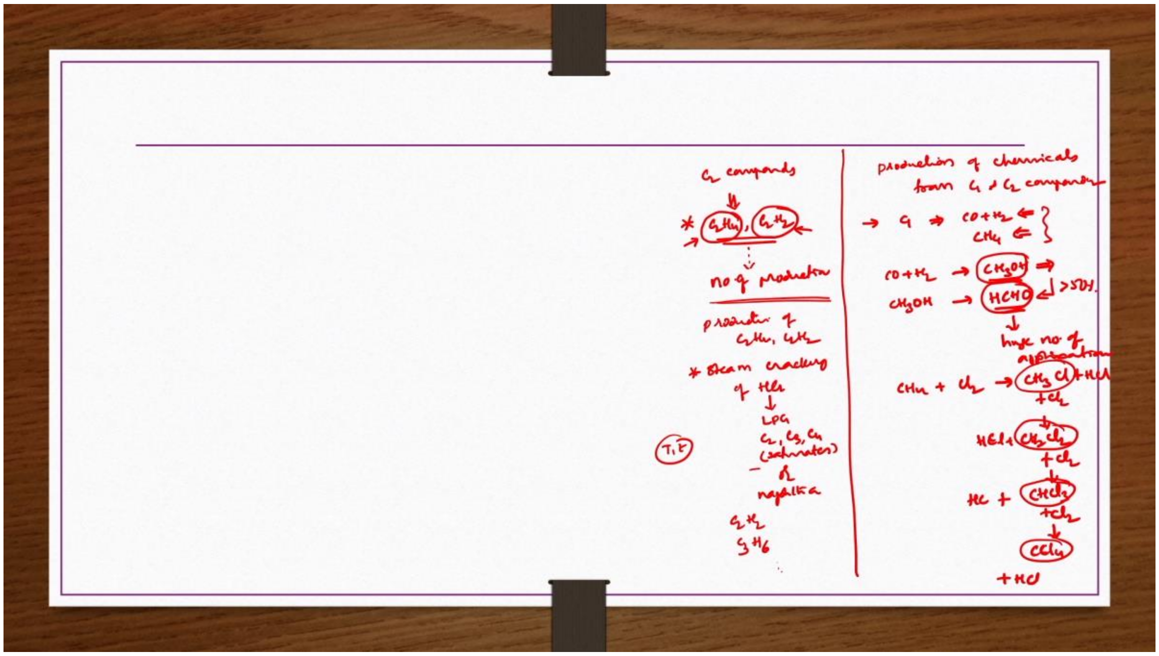

The methanol that whatever is available in industry, more than 50% is utilized for the production of formaldehyde because it has huge number of applications, especially in the synthetic chemicals or like polymer industries etc., it is having huge number of applications, okay? So, that is the reason we selected production of certain kind of chemicals which are having much applications because we have seen like you know pictorially n number of intermediates or n chemicals are produced from C1 and C2 compounds. We cannot discuss all of them, selectively we have considered a few. Then we have taken methane and then we reacted with chlorine to get methyl chloride which further react with the Cl_2 to give methylene chloride which further reacted with Cl_2 to give chloroform which further reacted with the chlorine to give carbon tetrachloride etc. And then plus HCl was forming in all of these reactions, right? So, this chloro-methane production also we have seen. So, from C1 compounds, we discussed production of methanol, formaldehyde and then different types of chloro-methane, all 4 types of chloro-methane we have discussed that properties, chemical reactions associated with the selected process, process flowchart, description, engineering problems, all of them we have discussed. Then in the previous lecture, we started discussions on C2 compounds where primarily we have taken olefins, we did not take ethane, but we have taken C_2H_4 ethylene and then C_2H_2 acetylene, right? So, these are the 2 C2 compounds we have selected and then we have listed what are the types of different products you can get. Here also number of products can be produced. So, ethylene is the one out of all olefins is having huge number of applications. So, one has to see how to improve the production of this one because we have seen in the process both ethylene and acetylene are being produced simultaneously. So, next to the ethylene, acetylene is the one which is having large number of applications. Since the ethylene is having more applications as primary chemical as well as the intermediate chemical to produce different types of end chemicals as well as other intermediate chemicals, the process should be made such a way that more ethylene should be formed compared to the acetylene. Next to the ethylene, acetylene is the one which is having more applications, right? Then, however, before going into the production of such kind of chemicals from C2 compounds, we discussed the production of the C2 compounds, especially ethylene, acetylene we have seen, right? So, here steam cracking or pyrolysis of hydrocarbons is one of the important process where hydrocarbons you can use LPG or C2, C3, C4 chemicals, especially saturated ones that is alkanes, right? Or you can use naphtha as well, right? Within the same process you can choose any of the feed or both feeds you can choose to produce these chemicals, ethylene, acetylene, etc., right? So, but the problem is that both of them are having different reaction temperature and time. So, you cannot use both of them in the same reactor, same furnace you cannot use, same pyrolysis reactor you cannot use, different reactors you have to use and then after the pyrolysis or steam cracking whatever the products are there, those processing you may do simultaneously that is what we have seen. In this process of production of ethylene, we also get acetylene, propylene, propane, butane, butylene, etc., so many other products also we were getting and then separation of those products we had done such a way that you know more ethylene and then acetylene we get. If you do not want acetylene then the reaction mixture containing primarily this ethylene and acetylene has to undergo mild hydrogenation so that that acetylene will also be converted into the ethylene such all those details we have seen. We have also seen engineering problems associated with such process of steam cracking of hydrocarbons to get ethylene and acetylene, right? So, now in today's lecture we are going to produce different types of chemicals using such C2 compounds, right?

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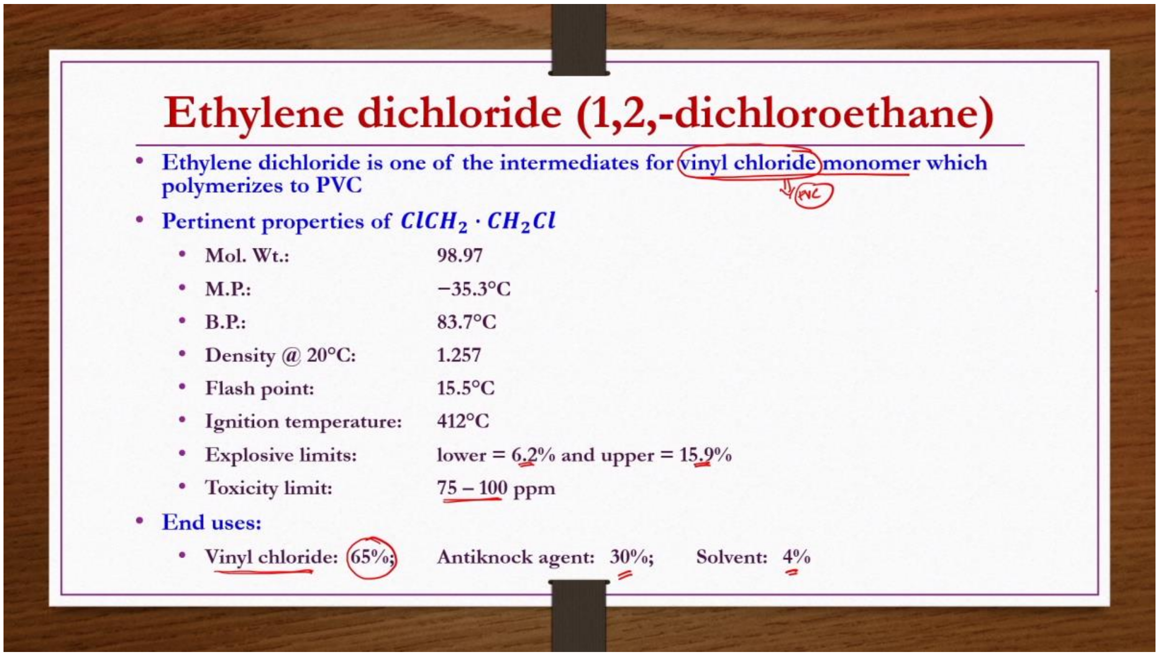

Ethylene dichloride (1,2,-dichloroethane)

- Ethylene dichloride is one of the intermediates for vinyl chloride monomer which polymerizes to PVC

PVC

- Pertinent properties of $ClCH_2 \cdot CH_2Cl$
  - Mol. Wt.: 98.97
  - M.P.: −35.3°C
  - B.P.: 83.7°C
  - Density @ 20°C: 1.257
  - Flash point: 15.5°C
  - Ignition temperature: 412°C
  - Explosive limits: lower = 6.2% and upper = 15.9%
  - Toxicity limit: 75 – 100 ppm
- End uses:
  - Vinyl chloride: 65%; Antiknock agent: 30%; Solvent: 4%

First we start with ethylene dichloride which is also known as 1,2-dichloroethane, okay? Now we are going to discuss about its properties, processes that are available to produce this chemical from C2 compounds and then out of the available process we select one of the particular process which is more economically feasible and then we discuss in detail flowchart engineering problems of such processes, okay? So, ethylene dichloride is one of the intermediates for vinyl chloride monomer which polymerizes to PVC. Actually, the very next topic we are going to discuss the production of vinyl chloride, right? So, ethylene dichloride can be used as a raw material to produce vinyl chloride monomer. This vinyl chloride monomer we use to get PVC. Otherwise, vinyl chloride is not having any other application other than getting the polyvinyl chloride. So, it is in the captive products list, okay? So, that we discuss after completion of ethylene dichloride production, then we go to vinyl chloride production. Pertinent properties of ethylene dichloride, molecular weight 98.97, melting point minus 35.3 degrees centigrade, boiling point 83.7 degrees centigrade, density at 20 degrees centigrade is 1.257 gram per cc, flash point is 15.5 degrees centigrade, ignition temperature is 412 degrees centigrade, explosive limits lower and upper limits are 6.2 percent and 15.9 percent respectively, toxicity it is toxic and then limit is 75 to 100 ppm only, it should not be present more than that one otherwise it will become dangerous. End uses as mentioned primarily it is used for the production of vinyl chloride. This ethylene dichloride is used as a raw material to produce vinyl chloride and then that vinyl chloride is usually polymerized to get PVC or polyvinyl chloride. This ethylene dichloride is also used for the production of some anti-knocking agents which are useful in the automobile industries and then it is also used as solvent.

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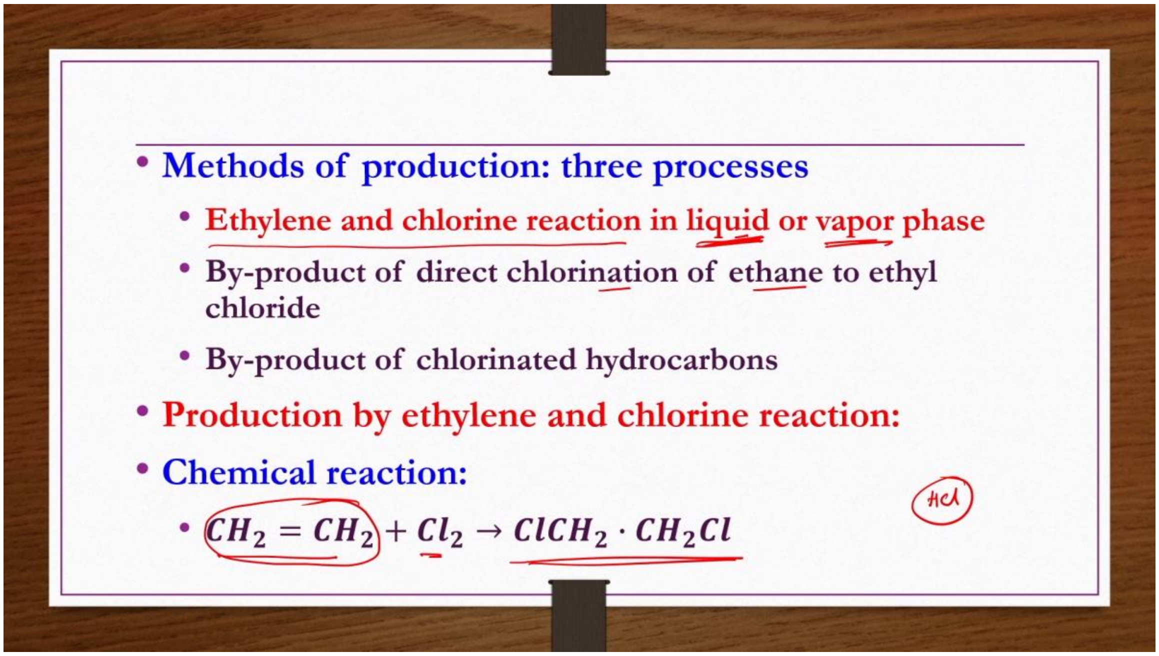

- Methods of production: three processes
  - Ethylene and chlorine reaction in liquid or vapor phase
  - By-product of direct chlorination of ethane to ethyl chloride
  - By-product of chlorinated hydrocarbons
- Production by ethylene and chlorine reaction:
- Chemical reaction:
  - $\boxed{CH_2 = CH_2} + Cl_2 \rightarrow \underline{ClCH_2 \cdot CH_2Cl}$

HCl

Methods of production, 3 methods are there. First one is direct reaction between ethylene and then chlorine that can be done in liquid phase or vapor phase and then byproduct of direct chlorination of ethane to ethyl chloride. When you do chlorination of ethane that is ethane you take and then react with the chlorine to get the ethyl chloride like substitution reaction then in addition to ethyl chloride ethylene dichloride is also produced as a byproduct. Then sometimes you do chlorination of different types of hydrocarbons then also there is a possibility that this ethylene dichloride we get as a byproduct. However, looking about byproducts is not wise way of discussing the production of this product. So, then what we do we discuss the major process that is a reaction between ethylene and chlorine to get ethylene dichloride and then that reaction we can do in both liquid and vapor phase. So, production by ethylene and chlorine reaction if you take the reaction ethylene you react with the chlorine to get ethylene dichloride you also get byproducts like HCl etc. would also be there all those things we are going to see that depends on you know how pure is your feed material.

Quantitative requirements basis 1 ton of ethylene dichloride if you want to produce with 95 percent yield ethylene 0.3 tons required chlorine 0.75 tons required ethylene dibromide catalyst at few traces are required actually if you do without this catalyst then yield would be slightly less if you wanted to get 90 to 95 percent yield some traces of ethylene dibromide or ferric chloride may be added as a catalyst to the system. By adding this catalyst the yield increases substantially that is the point and then you can see this catalyst you required only in traces not in much quantity.

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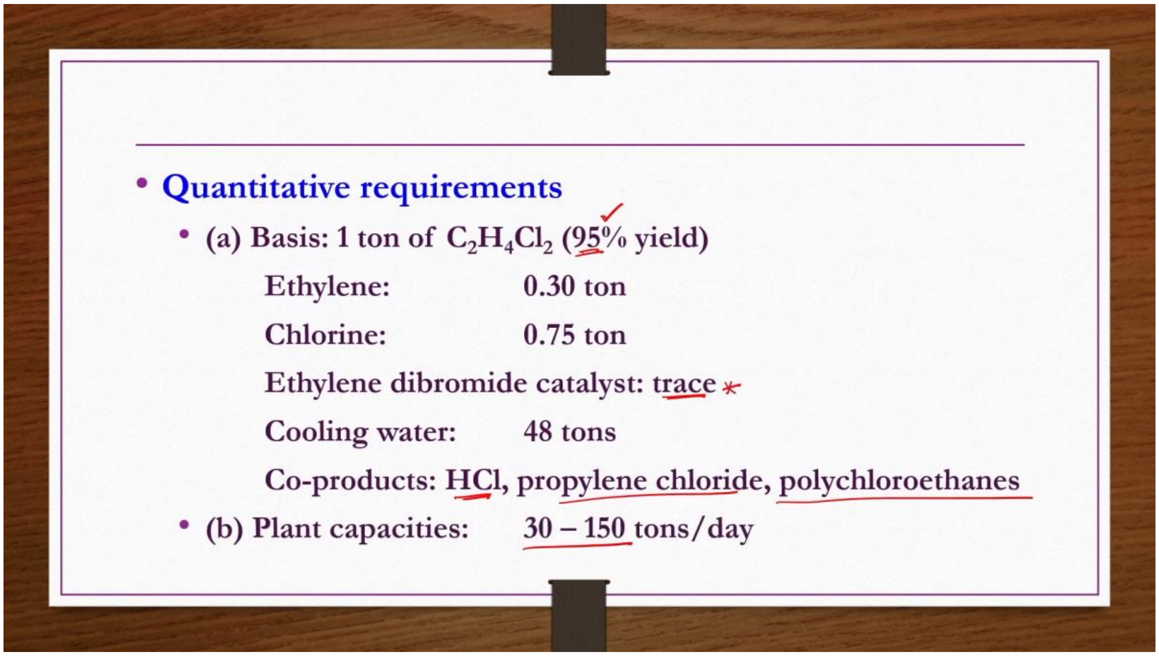

- **Quantitative requirements**
  - (a) Basis: 1 ton of $C_2H_4Cl_2$ (95% yield) ✓

    Ethylene: 0.30 ton

    Chlorine: 0.75 ton

    Ethylene dibromide catalyst: trace *

    Cooling water: 48 tons

    Co-products: HCl, propylene chloride, polychloroethanes
  - (b) Plant capacities: 30 – 150 tons/day

Cooling water 48 tons are required, co-products HCl is possible not only ethylene dichloride but propylene chloride, polychloroethanes, polychlorides may also be possible in this particular process. Plant capacity usually 30 to 150 tons per day.

Now, we discussed the flowchart first and then discuss the process with the major engineering problems. So, whatever the raw materials ethylene and then chlorine are there they are sent to a reactor by bubbling because this reaction whatever is there that we are discussing liquid phase reaction. So, they will be bubbled to the tubular reactor to which ferric chloride or ethylene bromide may also be added in some traces as catalyst. Now, the reaction takes place here the reaction is exothermic reaction as we have seen when this chlorine is involved whenever the reaction takes place between chlorine and some kind of hydrocarbons the reactions are mostly exothermic and then lot of heat is evolved in general but the reaction condition may not be required such high temperature. So, temperature may be required to maintain 45 to 50 degrees centigrade only in this reactor and then pressure should not be more than 2 atmosphere. In general, such conditions are maintained.

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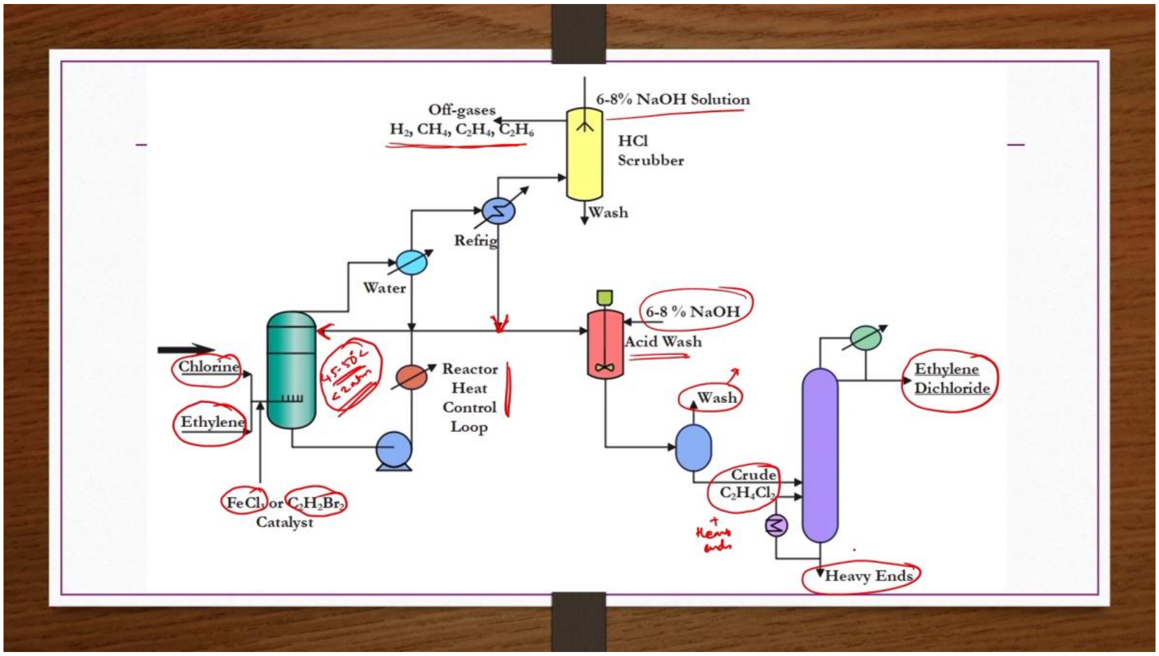

So, then only proper yield or sufficient yield of the main product will take place otherwise byproducts or unreacted reactants etc may be there these are the optimized conditions. So, the control of heat may be done using reactor heat control loop by heat exchangers or by coil or jacketed heat transfer fluids etc are used in order to maintain such temperature. So, some partial recycling is also done in order to maintain the temperature because after the reaction whatever the products are there they would be refrigerated and then some of them are taken as a recycle to the system to the reactor so that the temperature would be under control because these reaction product mixture whatever is there that are being refrigerated before sending to the recycle only purpose is to control the temperature within the reactor. So, then after this step what we do we whatever the reaction product mixture is there that is usually in the 2 phases one is the liquid phase another one is the gases phase. Whatever the gases are there they would be scrubbed with 6 to 8 percent NaOH solution so that to scrub out the HCl and then whatever the non-dissolving components like methane, hydrogen etc are there they will be collected as off gases. Whereas the liquid portion of the product whatever is there that is also acid washed so that to remove any traces of HCl that are present along with the product for that purpose also you are using 6 to 8 percent of NaOH. So, now here also after removing the acid what you do you do the some kind of compression to remove the acid wash completely as much as possible then primarily after that compression you will be having crude ethylene dichloride as a product crude in the sense it may be having some heavy ends also. So, what you do you take this crude ethylene dichloride to a fractionator where ethylene dichloride you can get as a top product whereas the heavy ends whatever are there they will be collected as a bottom products. So, this is the flow chart for ethylene dichloride production by using reaction between ethylene and chlorine.

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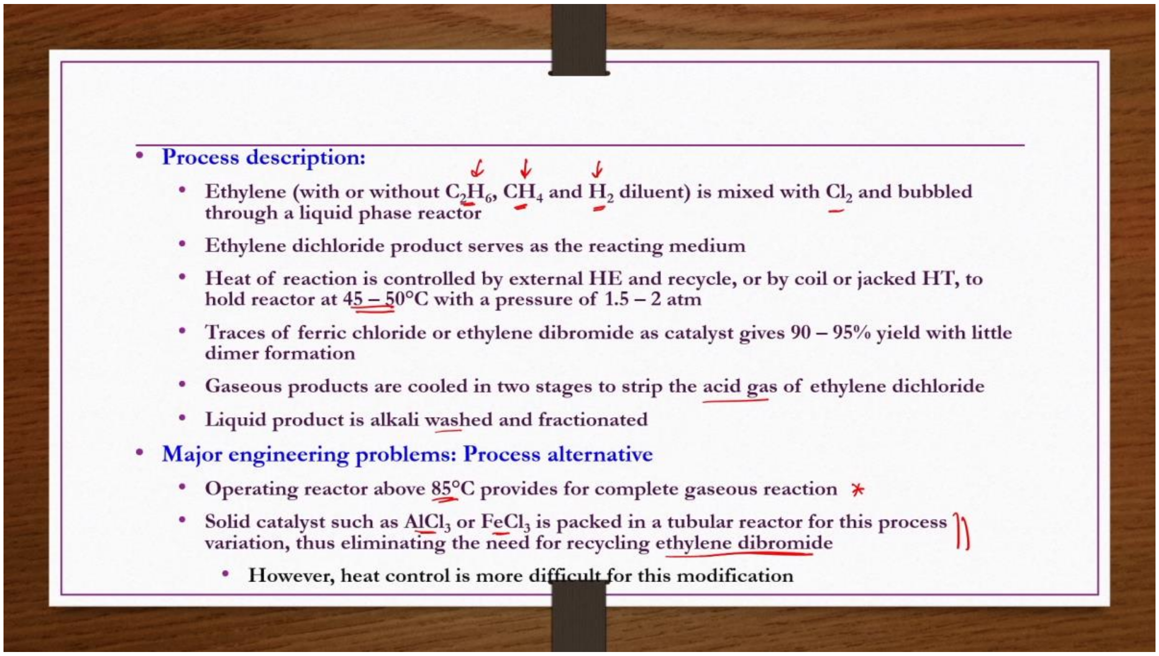

- **Process description:**
  - Ethylene (with or without C_2H_6, CH_4 and H_2 diluent) is mixed with Cl_2 and bubbled through a liquid phase reactor
  - Ethylene dichloride product serves as the reacting medium
  - Heat of reaction is controlled by external HE and recycle, or by coil or jacked HT, to hold reactor at 45 – 50°C with a pressure of 1.5 – 2 atm
  - Traces of ferric chloride or ethylene dibromide as catalyst gives 90 – 95% yield with little dimer formation
  - Gaseous products are cooled in two stages to strip the acid gas of ethylene dichloride
  - Liquid product is alkali washed and fractionated
- **Major engineering problems: Process alternative**
  - Operating reactor above 85°C provides for complete gaseous reaction
  - Solid catalyst such as $AlCl_3$ or $FeCl_3$ is packed in a tubular reactor for this process variation, thus eliminating the need for recycling ethylene dibromide
    - However, heat control is more difficult for this modification

Process description ethylene with or without ethane, methane and H2 diluent is mixed with Cl2 and bubbled through a liquid phase reactor. So, you can use them if required otherwise you may not need to use them especially the selection of these diluent should be done such a way that if they are suppressing the reaction temperature or it is not allowing the reaction temperature to go beyond 45, 50 degrees centigrade for that purpose if they are useful then only you have to use. But anyway if you use these kind of chemicals like methane and ethane then some other products may also form like chlorinated methane may also be forming ethyl chloride may also be forming then purification become difficult. So, one has to be very careful whether to take these additional diluents to control the temperature pressure conditions within the reactor or is it better to control the temperature pressure by proper heat exchangers and then heat transfer fluids etc. or by recirculating the refrigerated product mixture to the reactor. So, these are the option you have to think before making a decision. Ethylene dichloride product serves as the reacting medium. Heat of reaction is controlled by external heat exchangers and recycle or by coil or jacketed heat transfer to hold reactor at 45 to 50 degrees centigrade with a pressure of 1.222 atmosphere. So, this is because we are doing the whatever the process we discussed is for the liquid phase reaction. If you are doing for the gaseous phase reaction then condition may be different. Traces of ferric chloride or ethylene dibromide as catalyst gives 90 to 95 percent yield with little dimer formation. Gases products are cooled in 2 stages to strip the acid gas of ethylene dichloride. Liquid product is alkali washed and fractionated to get the product. Major engineering problems are primarily process alternatives only. Operating reactor above 85 degrees centigrade provides for complete gaseous phase reaction if you wanted to do in the gaseous phase then you do the reaction above 85 degrees centigrade. That is one option or alternative available. Other thing is that solid catalyst such as aluminum chloride or ferric chloride is packed in a tubular reactor for this process variation thus eliminating the need for recycling ethylene dibromide. However, but if you do this process then what is the problem is that heat control is more difficult for this modification. So, better is to go for the liquid phase reaction because there separation etcetera is also easy and then temperature you can control by applying the refrigerator and then cooling the product mixture and then sending some of the product mixture to the reactor. So, that to control the temperature of the reactor.

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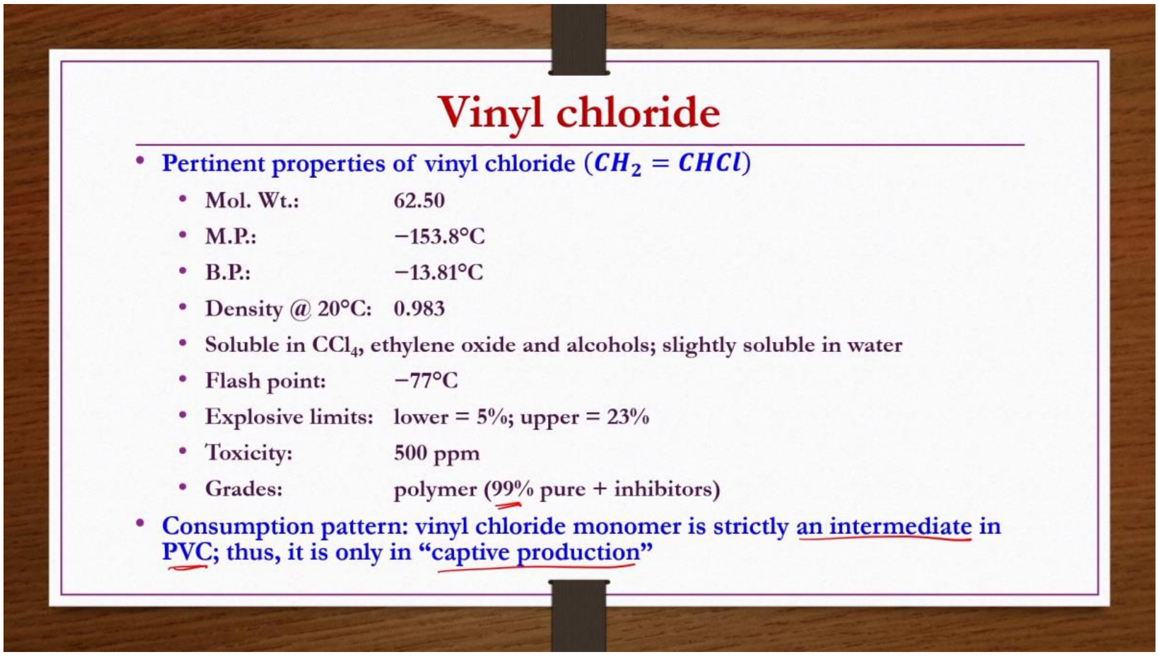

Vinyl chloride

- Pertinent properties of vinyl chloride ($CH_2 = CHCl$)
  - Mol. Wt.: 62.50
  - M.P.: −153.8°C
  - B.P.: −13.81°C
  - Density @ 20°C: 0.983
  - Soluble in CCl_4, ethylene oxide and alcohols; slightly soluble in water
  - Flash point: −77°C
  - Explosive limits: lower = 5%; upper = 23%
  - Toxicity: 500 ppm
  - Grades: polymer (99% pure + inhibitors)
- Consumption pattern: vinyl chloride monomer is strictly an intermediate in PVC; thus, it is only in "captive production"

Now, we talk about vinyl chloride as already mentioned just now ethylene dichloride is a raw material to produce vinyl chloride that is one of the major process. Other process is that you know you take acetylene and then react with hydrochloric acid to get the vinyl chloride. Both the processes we are going to discuss now. However, first we see the pertinent properties of vinyl chloride and then what are the processes available, what are the reactions of respective processes, then we talk about the flowchart and then major engineering problems associated with such processes. Pertinent properties of vinyl chloride, vinyl chloride is nothing but CH2 double bond CHCl. Molecular weight is 62.5, melting point is minus 153.8 degrees centigrade, boiling point is minus 13.81 degree centigrade, density at 20 degree centigrade is 0.983 gram per cc. It is soluble in carbon tetrachloride, ethylene oxide and alcohols but slightly soluble in water. Flash point is minus 77 degree centigrade, explosive limits lower and upper limits are 5 percent and 23 percent respectively. Toxicity limit is 500 ppm. Grade, primarily vinyl chloride is used for the production of PVC only. So, only grade available is that polymer grade which is having 99 percent pure with some inhibitors as per the strength and other properties of the final PVC product. Those inhibitors etc., we discuss in the chapter on polymerization. Consumption pattern vinyl chloride monomer is strictly an intermediate in PVC making, polyvinyl chloride making, thus it is only in captive production. Other than PVC making, vinyl chloride is not having any other applications.

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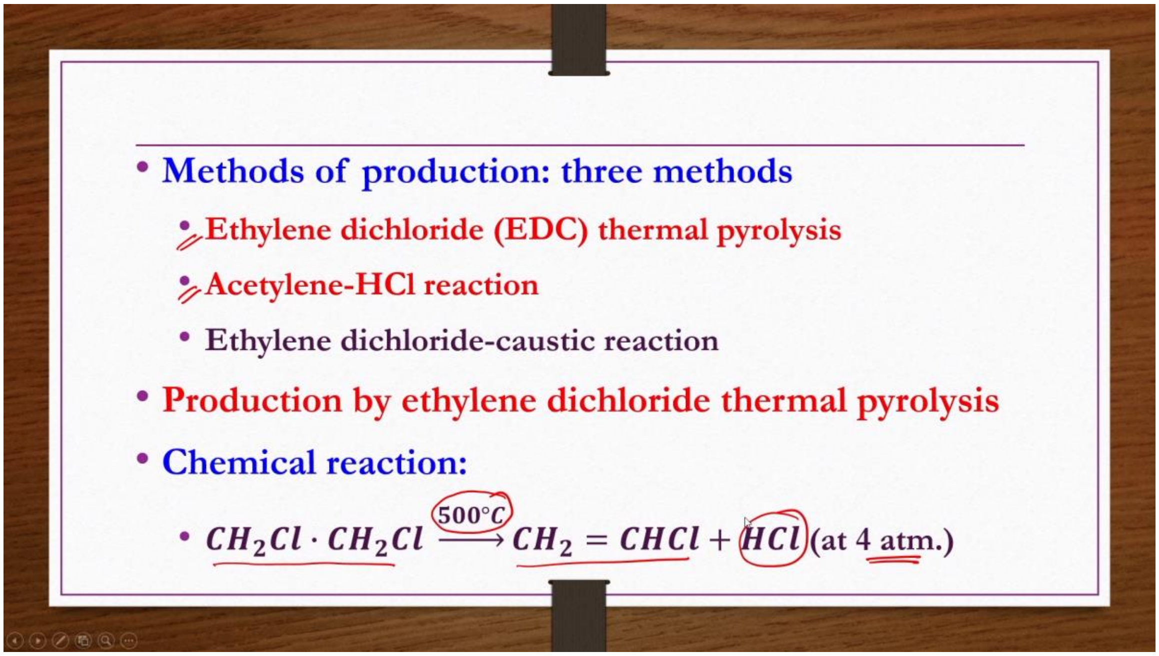

- **Methods of production: three methods**
  - **Ethylene dichloride (EDC) thermal pyrolysis**
  - **Acetylene-HCl reaction**
  - **Ethylene dichloride-caustic reaction**
- **Production by ethylene dichloride thermal pyrolysis**
- **Chemical reaction:**
  - $CH_2Cl \cdot CH_2Cl \xrightarrow{500°C} CH_2 = CHCl + HCl$ (at 4 atm.)

But PVC is very much useful for large number of applications, so vinyl chloride production is very much essential to understand. Coming to the methods of production, 3 methods are there. Ethylene dichloride thermal pyrolysis, you just take the EDC ethylene dichloride and then do the thermal pyrolysis in the presence of catalyst or in the absence of catalyst whatever possible based on the economics. You do the pyrolysis, you can get the vinyl chloride monomer. Other process is that acetylene HCl reaction, you take acetylene and then react with HCl, then also you can get the vinyl chloride monomer. Other options are ethylene dichloride caustic reaction etc., but however we discuss these 2 methods now. Let us start with production of vinyl chloride monomer by ethylene dichloride thermal pyrolysis. If you take the reaction, you have ethylene dichloride and then you do the thermal pyrolysis at 500 degrees centigrade and then 4 atmosphere, then you get the vinyl chloride as well as HCl co-product.

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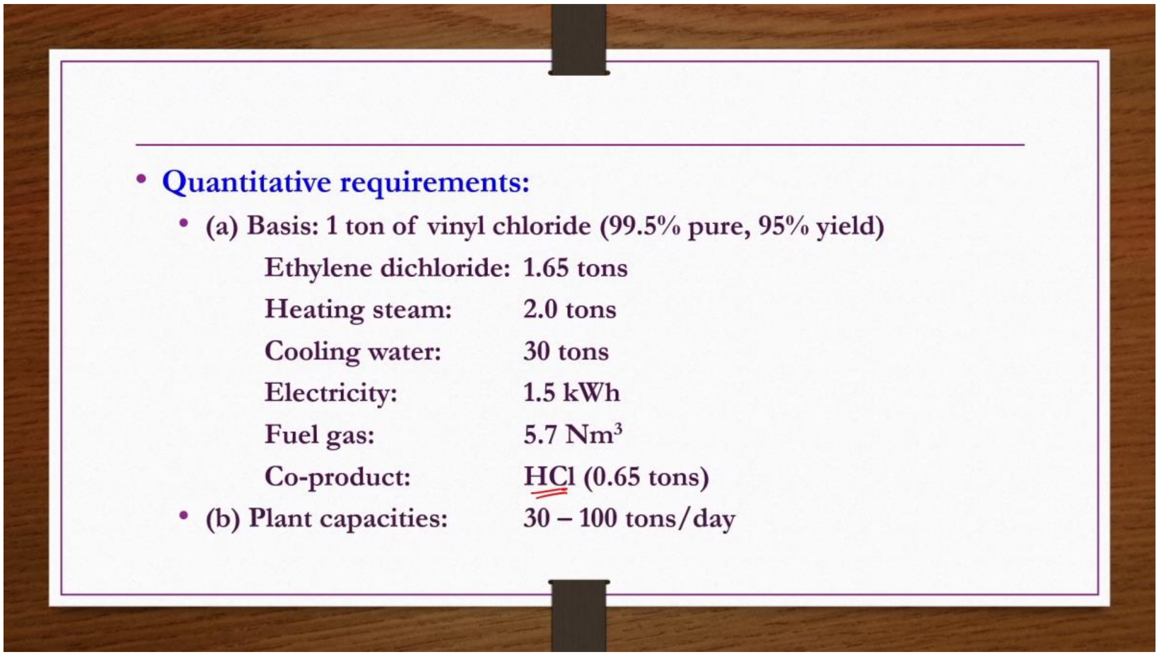

- **Quantitative requirements:**
  - (a) Basis: 1 ton of vinyl chloride (99.5% pure, 95% yield)
    Ethylene dichloride: 1.65 tons
    Heating steam: 2.0 tons
    Cooling water: 30 tons
    Electricity: 1.5 kWh
    Fuel gas: 5.7 Nm^3
    Co-product: HCl (0.65 tons)
  - (b) Plant capacities: 30 – 100 tons/day

Quantitative requirements, basis 1 ton of vinyl chloride 99.5% pure with 95% yield if you want to produce. Ethylene dichloride 1.65 tons is required because it is the major raw material. This one is only undergoing pyrolysis to give vinyl chloride monomer. Heating steam because only reactant is ethylene dichloride here in this case. In addition to that one, you need to supply the energy for the thermal pyrolysis to take place. So, heating requirement whatever is there that is supplied by the heating steam 2 tons required. Cooling water 30 tons required, electricity 1.5 kilowatt hours required. Fuel gas 5.7 normal cubic meters are required. Co-product HCl you get and then that also 0.65 tons you get if you are using 1.65 tons of ethylene dichloride as a reactant. Plant capacity usually 30 to 100 tons per day.

Now, first we see flowchart and then we go to the engineering problems associated with this process. Whatever ethylene dichloride that you have in the storage that you take pump it through a heat exchanger to which steam is supplied so that this ethylene dichloride would be vaporized. So, vapors of ethylene dichloride would be passed through a dryer where you have silica gel adsorbents. And the silica gel would be absorbing any of the moisture etc. that is present along with the ethylene dichloride vapors. Because in this process corrosion is one of the major engineering problem. So, that is the reason this drying by silica gel is required. This dried ethylene dichloride is passed through tubular pyrolysis furnace where the tubes are there. So, in the reactor 500 degrees centigrade and then 4 atmosphere pressure is maintained.

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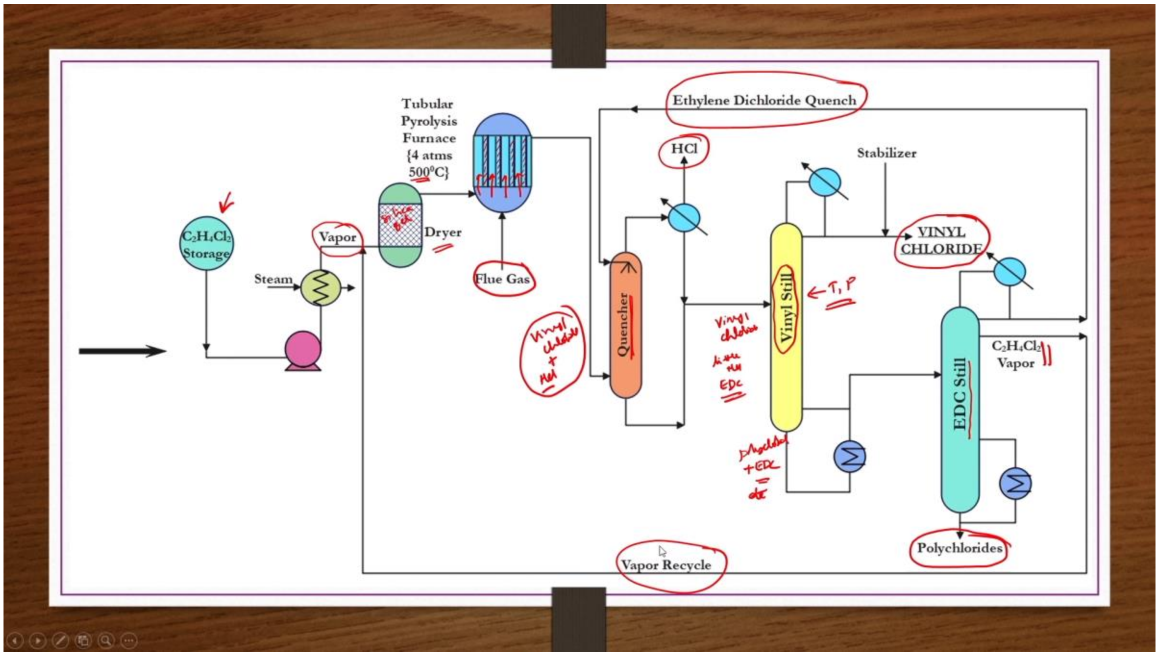

So, what happens here these are the tubes. The ethylene dichloride whatever is there that passes through these tubes only and these tubes are filled with charcoal or the suitable catalyst whatever is required. Primarily charcoal is taken as the catalyst. Now, the temperature has to be maintained higher because it is a thermal pyrolysis process. So, selected temperature is 500 degrees centigrade. In order to get such high temperature within the reactor flue gases are supplied to the shell but they would be passing between the spaces that are available with these tubes. These tubes are taken as bundles and they are inserted in a shell. Between the tubes whatever the free area is there through those free areas the flue gases are being supplied and then from these flue gases the required energy of 500 degrees centigrade is attained. So that whatever the vapors of ethylene dichloride passing through charcoal bed they will also be heated to high temperature of 500 degrees centigrade and then the thermal pyrolysis takes place. So, when this pyrolysis is taking place what are you getting? You are getting vinyl chloride and HCl primarily. So, what you do that you that mixture would be at high temperature because the reactor is at high temperature. So, the product mixture whatever is coming that would also be at high temperature. So, that product mixture is quenched using ethylene dichloride quench. So, why are we selecting ethylene dichloride for quenching the purpose because the mixture whatever is there or vinyl chloride monomer is there it is only slightly soluble in water. So, if you use the water it is not possible to do the required absorption of monomer into the water and so that you can subsequently do the desorption and then purification etcetera that is not possible here that is one reason. Other reason is that if you are using ethylene dichloride quench for the quenching of vinyl monomer the back reaction will not take place otherwise what happened vinyl chloride will be forming back ethylene dichloride in order to stop that back reaction this ethylene dichloride quench is being utilized. So, in the quencher the HCl vapors are condensed and collected as a HCl acid some of that would be taken to the vinyl steel. So, now here primarily you have the vinyl chloride only you are having here with a little you know HCl or you know EDC etcetera may be there. So, what you do you take it to the vinyl still, still in the sense fractionators like distillation column. So, when you take this mixture to the vinyl still and apply the conditions temperature pressure conditions in such a way that you know vinyl still would be more on the top side and then it will be collected as top product after condensation and stabilization. Whereas the possible polychlorides and then unreacted EDC etcetera whatever are there they will be collected as bottom product and then they will be sent to EDC still where this EDC that is ethylene dichloride would be collected as a top product whereas the polychlorides and then any heavy ends are there they will be collected as bottoms. The top product ethylene dichloride that can be taken as ethylene dichloride quench and sent to the quencher or otherwise it can be taken and then mixed with the reactant ethylene dichloride vapor dry it and then send back to the reactor as a recycle vapor recycle as either way it can be utilized.

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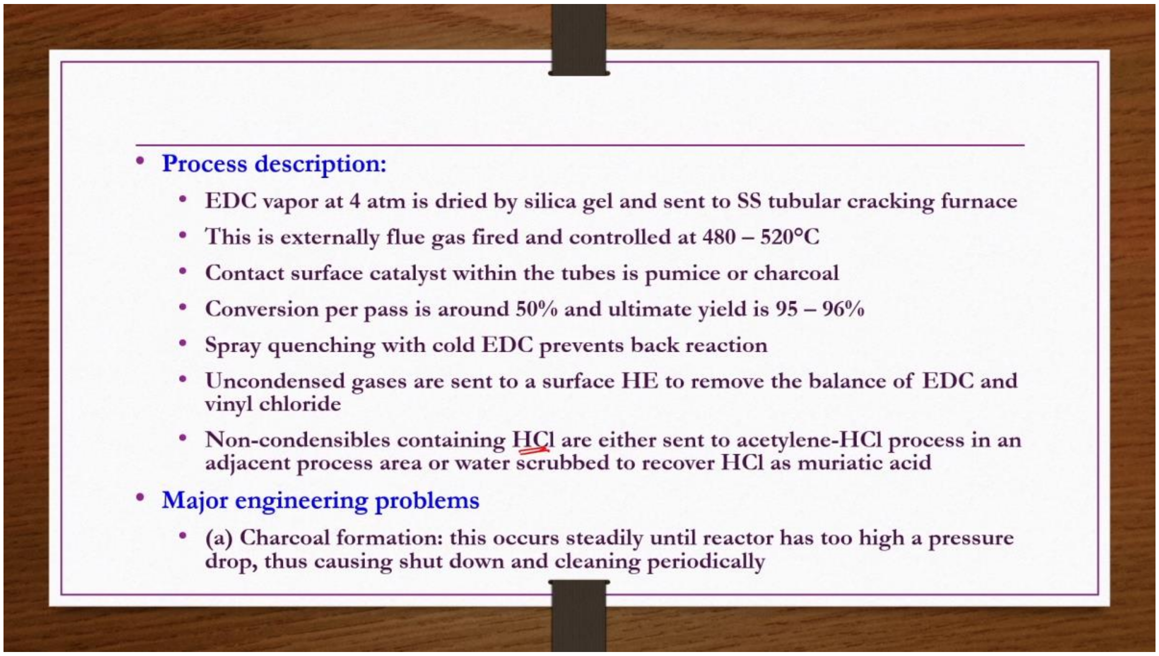

- **Process description:**
  - EDC vapor at 4 atm is dried by silica gel and sent to SS tubular cracking furnace
  - This is externally flue gas fired and controlled at 480 – 520°C
  - Contact surface catalyst within the tubes is pumice or charcoal
  - Conversion per pass is around 50% and ultimate yield is 95 – 96%
  - Spray quenching with cold EDC prevents back reaction
  - Uncondensed gases are sent to a surface HE to remove the balance of EDC and vinyl chloride
  - Non-condensibles containing HCl are either sent to acetylene-HCl process in an adjacent process area or water scrubbed to recover HCl as muriatic acid
- **Major engineering problems**
  - (a) Charcoal formation: this occurs steadily until reactor has too high a pressure drop, thus causing shut down and cleaning periodically

Process description EDC vapor at 4 atmosphere is dried by silica gel and sent to stainless tubular cracking furnace. This is externally flue gas fired and controlled at 480 to 520 degrees centigrade. Contact surface catalyst within the tubes is often charcoal in general. Power pass is around 50% and ultimate yield is 95 to 96%. Spray quenching with cold EDC prevents back reaction. Uncondensed gases are sent to the surface heat exchange to remove the balance of ethylene dichloride and vinyl chloride. Non-condensables containing hydrochloric acid are either sent to acetylene HCl process in an adjacent process area or water scrub to recover HCl as muriatic acid with 30 to 32% HCl purification. What does it mean by whatever this HCl that you get, you can take it to the plant where acetylene is available and then react with this acetylene then also you get vinyl chloride. This is the second process we are going to discuss. So, whatever the HCl is produced here that can be utilized such a way that if you react with acetylene you get vinyl chloride as well. Major engineering problems, charcoal formation, if you do the pyrolysis at higher temperatures more than 400, 500 degrees centigrade then hydrocarbons whatever are there they will definitely form some amount of the free carbon or charcoal. So, that occurs steadily until reactor has too high a pressure drop thus causing shutdown and cleaning periodically that is one problem one has to look in.

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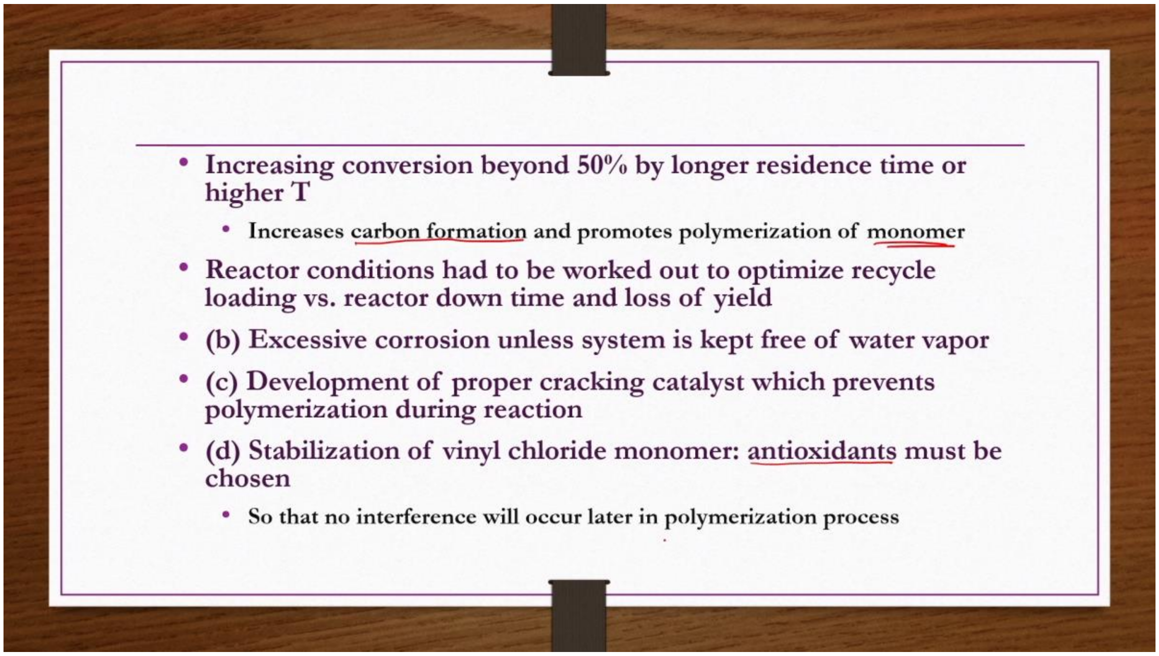

- Increasing conversion beyond 50% by longer residence time or higher T
  - Increases carbon formation and promotes polymerization of monomer
- Reactor conditions had to be worked out to optimize recycle loading vs. reactor down time and loss of yield
- (b) Excessive corrosion unless system is kept free of water vapor
- (c) Development of proper cracking catalyst which prevents polymerization during reaction
- (d) Stabilization of vinyl chloride monomer: antioxidants must be chosen
  - So that no interference will occur later in polymerization process

But however, increasing conversion beyond 50% by longer residence time or higher temperature increases the carbon formation as well and promotes polymerization of monomer which you do not want. Polymerization subsequently later on you can do in a separate plant. Even carbon formation you do not want in any of the processes that we are discussing. Same is true for this process also because once the carbon formation is done only you can produce CO or CO2 from it and nothing else. Of course, there may be some energy but this carbon quantity is very less that whatever the energy produced by combusting carbon is going to be very less and of no use at all. So, you have to make sure that the carbon formation is negligible. Reactor conditions has to be worked out to optimize recycle loading versus reactor downtime and loss of yield. Second engineering problem is excessive corrosion is one important thing. So, excessive corrosion unless system is kept free of water vapor that is the reason drying of the reactants etc. has been done and then water is not used for the quenching rather EDC has been used. Another advantage of using EDC as quench is that will stop the back reaction. Third engineering problem is development of proper cracking catalyst which prevents polymerization during the reaction. Now, we have taken charcoal but you know you can develop certain kind of catalyst which can provide a good yield but with negligible or no polymerization. Stabilization of vinyl chloride monomer is another important thing for that what you have to do antioxidants must be chosen appropriately. So, that no interference will occur later in polymerization process.

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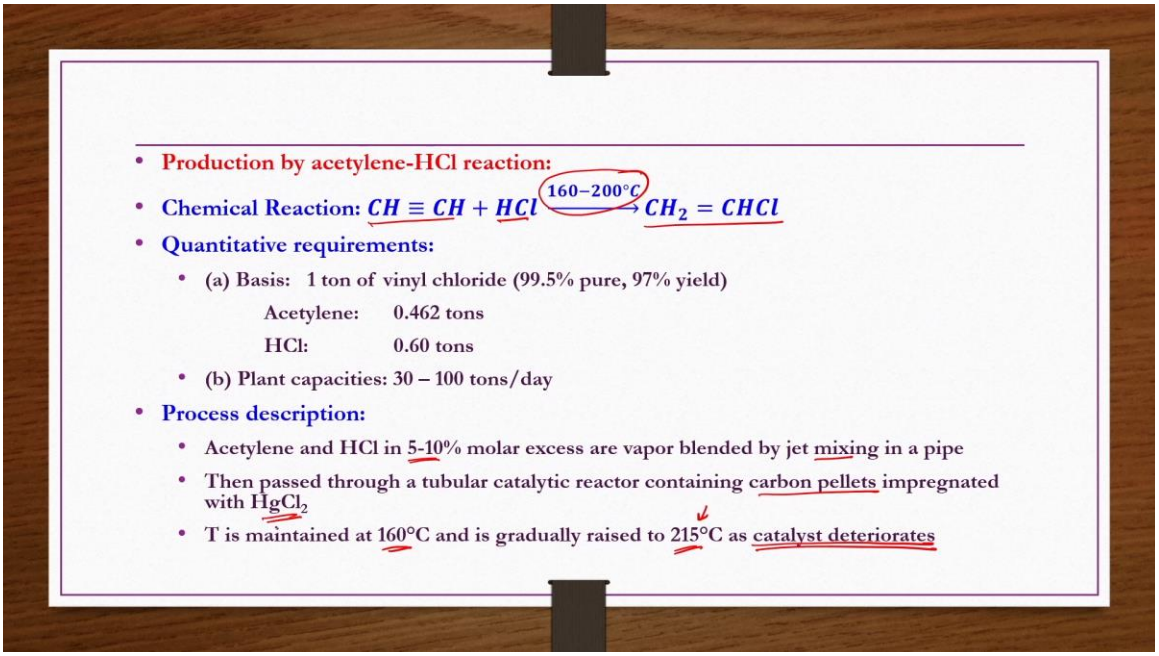

- **Production by acetylene-HCl reaction:**
- **Chemical Reaction:** $CH \equiv CH + HCl \xrightarrow{\boxed{160-200°C}} CH_2 = CHCl$
- **Quantitative requirements:**
  - (a) Basis: 1 ton of vinyl chloride (99.5% pure, 97% yield)
    Acetylene: 0.462 tons
    HCl: 0.60 tons
  - (b) Plant capacities: 30 – 100 tons/day
- **Process description:**
  - Acetylene and HCl in 5-10% molar excess are vapor blended by jet mixing in a pipe
  - Then passed through a tubular catalytic reactor containing carbon pellets impregnated with $HgCl_2$
  - T is maintained at 160°C and is gradually raised to 215°C as catalyst deteriorates

Now, we discuss other process of vinyl chloride monomer preparation that is production by acetylene HCl reaction. If you see the reaction acetylene react with HCl at 160 to 200 degrees centigrade and then gives vinyl chloride monomer. Quantitative requirements basis 1 ton of vinyl chloride 99.5% pure at 97% yield if you want to produce. Acetylene you required 0.462 tons, hydrochloric acid you required 0.6 tons, plant capacity usually 30 to 100 tons per day. Process description acetylene and HCl in 5 to 10% molar excess are vapor blended by jet mixing in a pipe. Then passed through a tubular catalytic reactor containing carbon pellets impregnated with mercury chloride temperature is maintained at 160 degrees centigrade and is gradually raised to 215 degrees centigrade. So, that is the reason temperature should not be you know beyond 215 degrees centigrade as the reaction temperature is between 160 to 200 degrees centigrade. Why we cannot go beyond this temperature because if you go beyond this temperature catalyst deterioration takes place because these catalysts are nothing but carbon pellets impregnated with mercury chloride.

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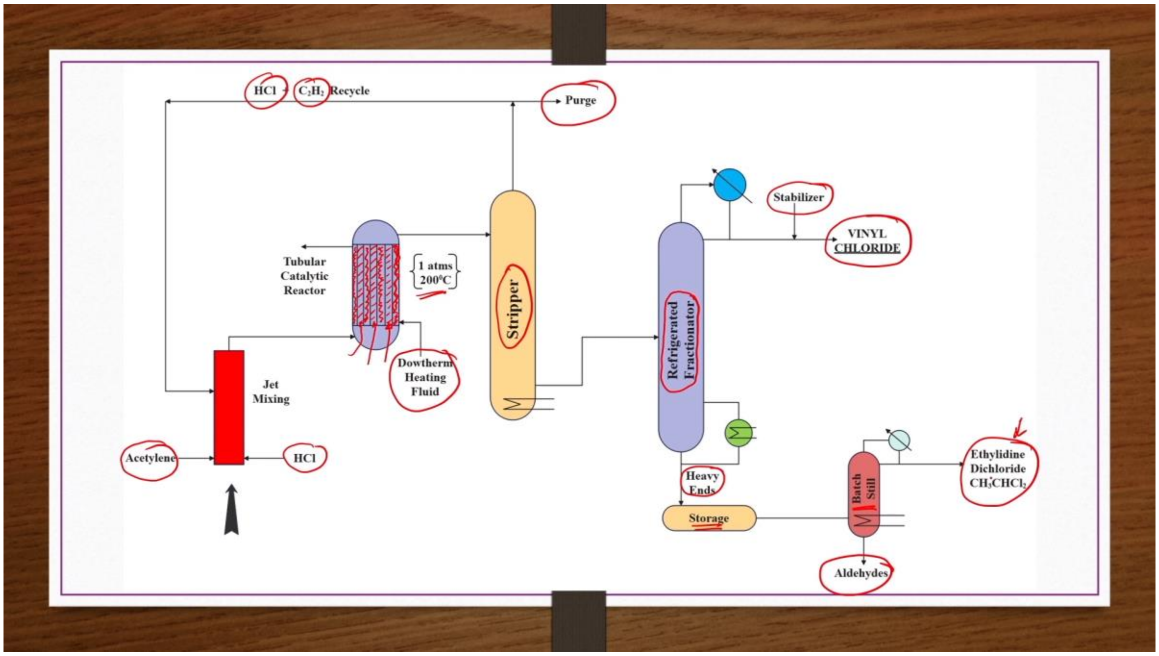

Process flowchart if you see whatever the reactant, acetylene and then hydrochloric acid are there, they are jet mixed and taken to a tubular catalytic reactor. Here these reactor again you know n number of tubes should be there. These tubes are filled with a catalyst. In this case, catalyst is nothing but carbon impregnated with mercury chloride. So, those are filled here and then this mixture of acetylene and then HCl whatever is there that is passed through these tubes in which you know the catalyst is filled in. So, the temperature is maintained 200 degrees centigrade between 160 to 200 degrees centigrade and then pressure is not allowed to go beyond one atmospheric pressure. So, whenever the such reaction takes place, so then heat would be evolved so that heat has to be controlled. So now here in this case what are we doing? We are doing Dowtherm heating fluid. We are circulating in the surroundings of these tubes that is the interstitial spaces between the tube bundles whatever is there. In those interstitial spaces, you are supplying this heat transfer fluids to control the temperature at what flow rate etc. are you supplying and all that that depends on the heat transfer engineering calculation and all those things. So, one has to do those calculations. So, now here the fluid is given and then from the top it is taken and then regenerated and recirculated back that is all conventional process. So, product mixture whatever is there that would be having not only vinyl chloride but also unreacted acetylene and then hydrochloric acid also. So, that product mixture is taken to the stripper where you separate the HCl and then C2H2 acetylene that you can take it as a recycle by passing through jet mixer and then to the reactor. If required that you can do if you cannot handle that much of recycle some of this mixture or unreacted mixture of HCl and C2H2 whatever is there that you can do the purging also. From the bottom of the stripper whatever the remaining product mixture is there that is taken to a refrigerated fractionator. So, that to get vinyl chloride as the top product after condensing and then stabilizing with the stabilizers. From the bottom of the fractionators you will get heavy ends which you can take to the storage or you can take them to batch still where you can get the ethylidene dichloride as top product and then early heads as the bottom product either options you can do if these are required. So, this is not EDC this is ethylidene dichloride CH3 CHCl2.

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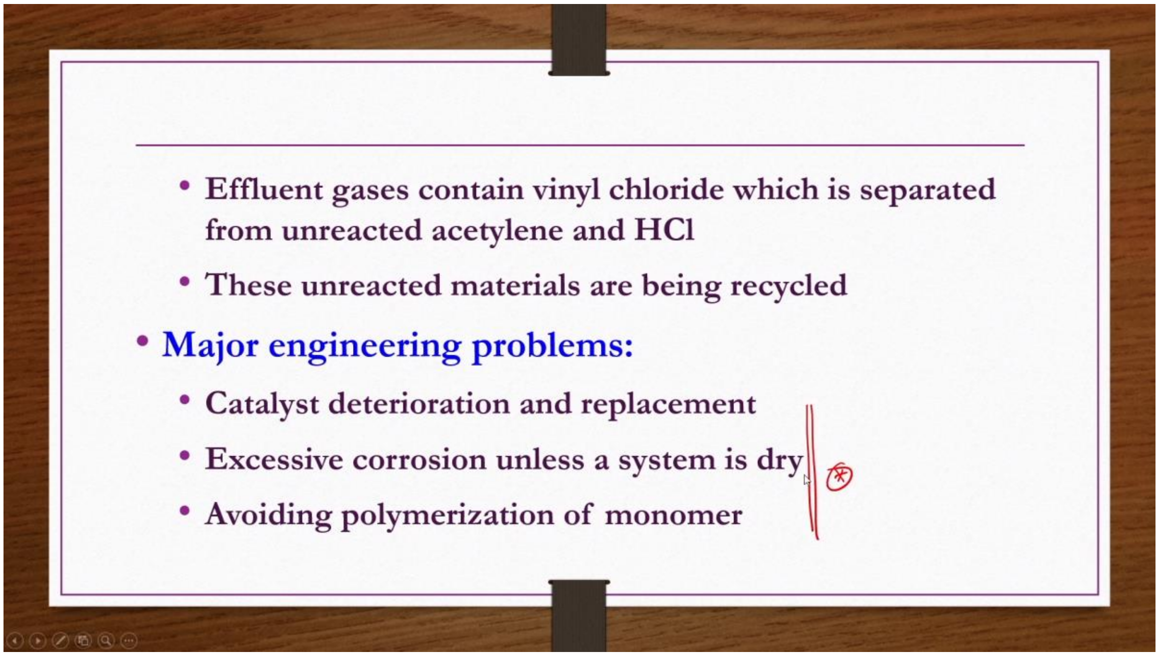

- Effluent gases contain vinyl chloride which is separated from unreacted acetylene and HCl
- These unreacted materials are being recycled
- Major engineering problems:
  - Catalyst deterioration and replacement
  - Excessive corrosion unless a system is dry
  - Avoiding polymerization of monomer

Effluent gases contain vinyl chloride which is separated from unreacted acetylene and then HCl. These unreacted materials are being recycled. Major engineering problems catalyst deterioration and replacement is one of the important issue because you have carbon or charcoal and then you are going beyond 200 degrees centigrade. So, then combustion of such particles will also take place. So, you cannot go higher temperature so then catalyst deterioration and replacement is one of the engineering problem. Excessive corrosion unless a system is dry, avoiding polymerization of monomer these are the important engineering problems you have to look into.

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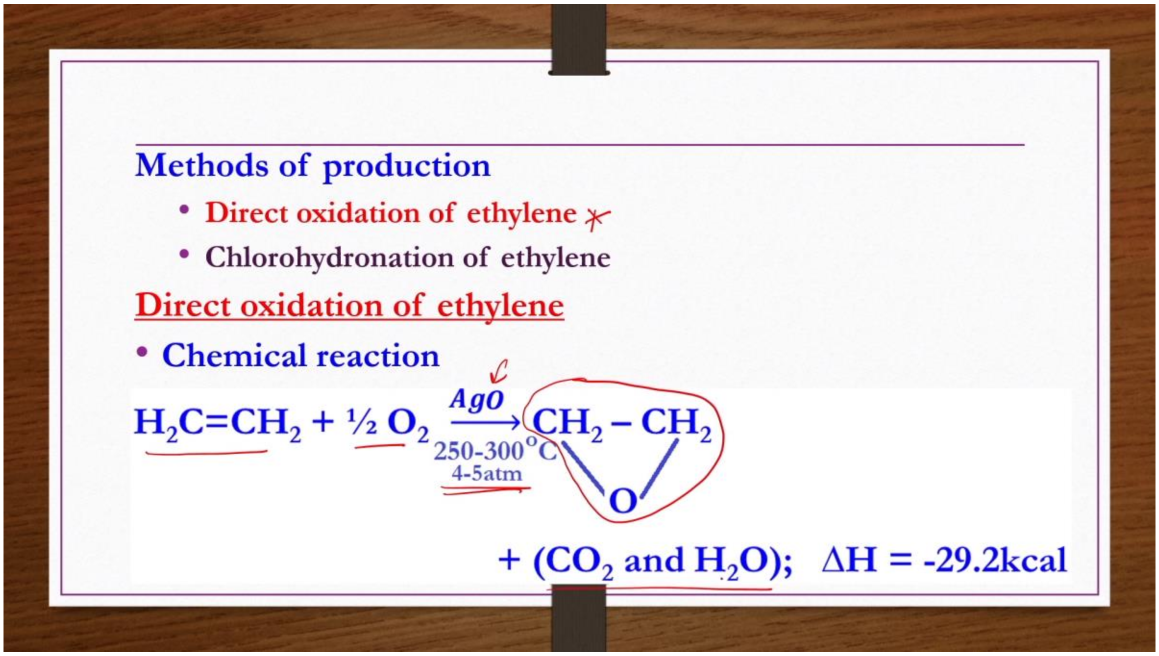

Methods of production

- Direct oxidation of ethylene *
- Chlorohydronation of ethylene

Direct oxidation of ethylene

- Chemical reaction

$$H_2C{=}CH_2 + \frac{1}{2} O_2 \xrightarrow[\text{250-300}^\circ\text{C, 4-5atm}]{AgO} CH_2 - CH_2 \text{ (with O bridge)}$$

$+ (CO_2 \text{ and } H_2O)$; $\Delta H = -29.2\text{kcal}$

Now the last topic of today's lecture is production of ethylene oxide. Ethylene oxide as the name indicates you can get by the oxidation of ethylene. You take ethylene and then do the oxidation you get ethylene oxide. So, what is the use of this one is that primarily it is used to produce ethylene glycol. Nowadays it is also used in the detergents etcetera also but otherwise primarily it is intermediate to produce ethylene glycol. So, we start with the pertinent properties of ethylene oxide. Molecular weight 44.05, melting point minus 111.7 degrees centigrades, boiling point 10.7 degrees centigrades, density at 0 degrees centigrade is 0.896 gram per cc, flash point is minus 15 degrees centigrades, ignition temperature is 430 degrees centigrades, maximum toxic limit is 25 to 100 ppm. Consumption pattern if you see primarily produced to serve as feedstock for production of ethylene glycol. In India it is also used for production of ethylene glycol polyesters, non-ionic detergents and ethanol amines also. In the next lecture we are going to discuss the production of ethanol amines as well. If you remember ethanol amines are used as a solvents to do absorption to remove undesired gases from the mixture ethanol amines are used and then some undesired gases are being absorbed in the ethanol amines. For that purpose, ethanol amines are in general used. So, production of ethanol amines from the ethylene oxide will be discussing in the next lecture. Methods of production, direct oxidation of ethylene to get ethylene oxides, chlorohydronation of ethylene, 2 processes are there but we select this process direct oxidation of ethylene. Chemical reaction, you take ethylene and do the oxidation in the presence of silver oxide at 250 to 300 degree centigrade and 4 to 5 atmosphere then you get the product ethylene oxide along with the byproducts or impurities like CO2 and then water vapor, its exothermic reaction.

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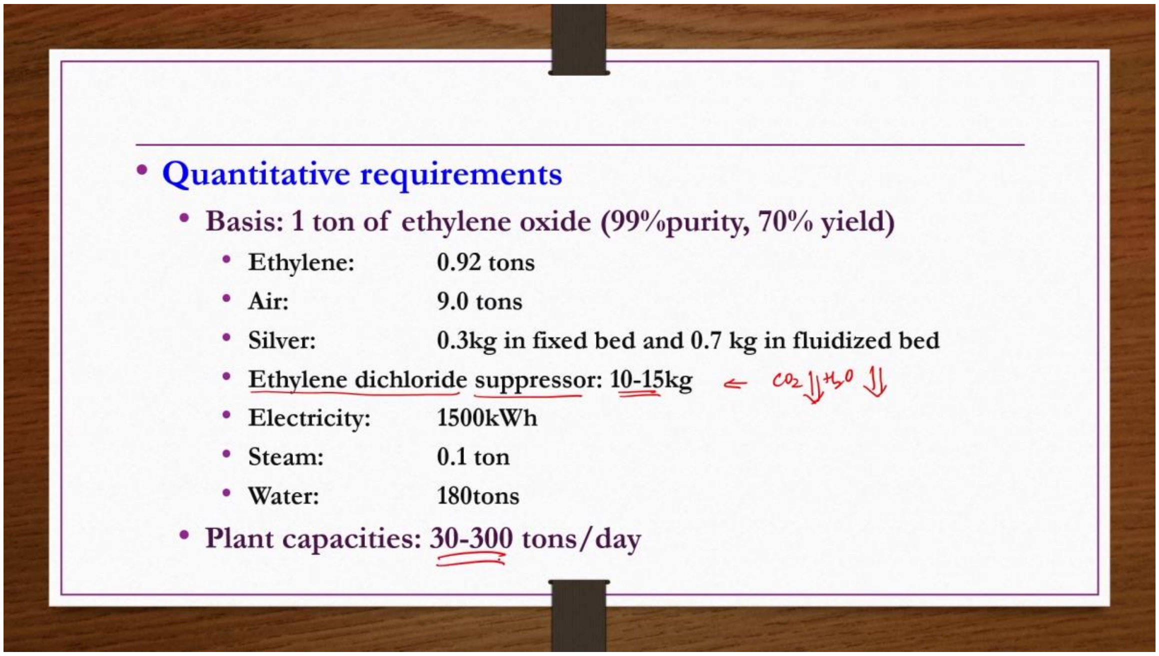

- **Quantitative requirements**
  - Basis: 1 ton of ethylene oxide (99%purity, 70% yield)
    - Ethylene: 0.92 tons
    - Air: 9.0 tons
    - Silver: 0.3kg in fixed bed and 0.7 kg in fluidized bed
    - Ethylene dichloride suppressor: 10-15kg ← CO_2 ⇓ H_2O ⇓
    - Electricity: 1500kWh
    - Steam: 0.1 ton
    - Water: 180tons
  - Plant capacities: 30-300 tons/day

Quantitative requirements, basis 1 ton of ethylene oxide of 99 purity at 70% yield if you want to produce. Ethylene 0.92 tons you require, air 9 tons you require, silver 0.3 kg in fixed bed and 0.7 kg in fluidized bed required. In addition to this one ethylene dichloride EDC suppressors are also used which is required 10 to 15 kgs. Why it is required? So, in the process whatever the CO2 and then H2O are forming, vapors are forming to reduce their formation this ethylene dichloride suppressors are in general used in the process. Electricity 1500 kilowatt hour, steam 0.1 tons, water 180 tons, plant capacity is usually 30 to 300 tons per day.

So, whatever the air and ethylene are there, they are separately compressed and then mixed and then sent to fixed bed tubular reactor along with the recycle amount also, some of the products are also being recycled. So, they are individually compressed, mixed and then sent to the tubular fixed bed reactor. Here also we have bundles of tubes which are filled with catalyst. In this case, the catalyst we already know that silver oxide that can be taken as it is but in general that is supported on alumina in general. So, these are taken here and then this mixture of air, ethylene and then recycle product streams or whatever are there, they are passed through these tubes in which the catalyst is there. The temperature is maintained 250 to 300 degrees centigrade. So here also the reaction is exothermic, so lot of heat would be evolved, so the temperature of the reactor has to be controlled. For that purpose again, Dowtherm heat transfer fluids are used. So, these fluids are circulated in the interstitial spaces between the tube bundles that are present. So in these spaces, you circulate this Dowtherm fluid so that the temperature is controlled. The selection of the flow, etc., those things are depends on the heat transfer calculations.

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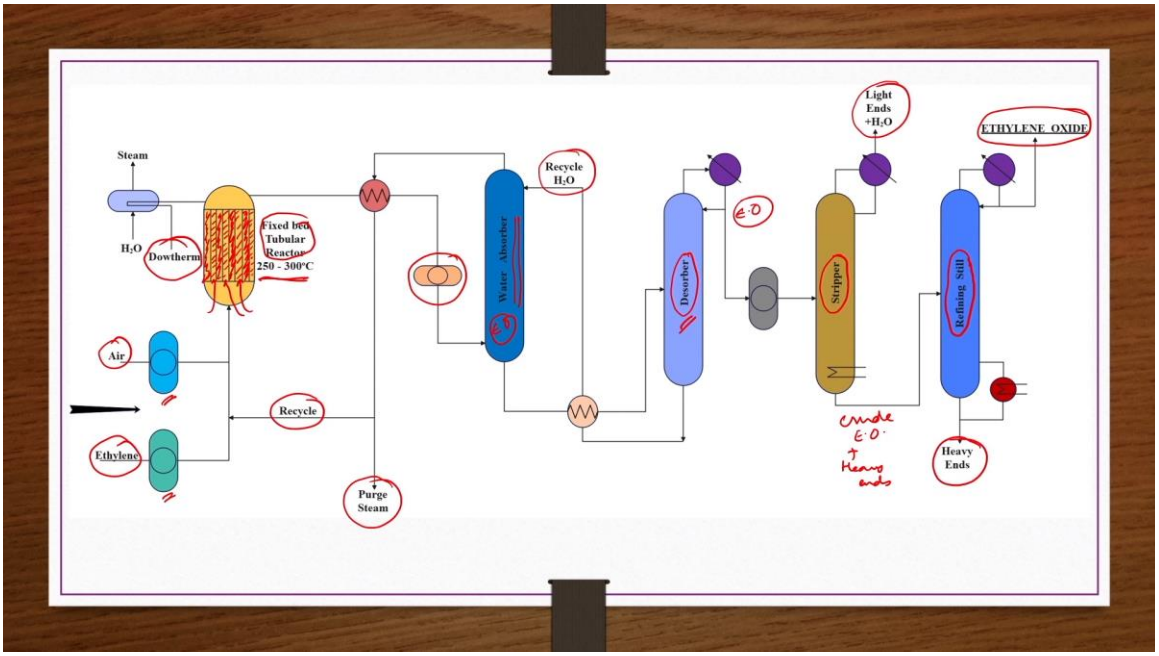

So, whatever the product mixture is there that is passed through waste steam heat boiler so that to recover some of the heat and then some of it is recycled to the reactor, some of it is taken as a purge stream. After that what it is done, it is compressed and then sent to a water absorber so that whatever ethylene oxide is there that would be absorbed in water and then whatever the unreacted ethylene, etc., are there, they will be sent back to waste heat steam boiler and then through that one it is recycled back to the reactor again. So, the solution whatever is there from the water absorber is there that you take through a heat exchanger, heat it and then take it to the desorber. So here what you do, you do the desorption of EO so that EO primarily you can get it as a product. So here when you pass through heat exchanger, some amount of water is recovered and then that is recycled back to the water absorber. So, whatever the degree of desorption you do here along with the product some amount of moisture and then light ends would be there. So, what you do, you take the top product of the desorber which is primarily ethylene oxide, but it is not pure ethylene oxide, it will be having light ends and then moisture, etc. So that you compress and then take to a stripper, do the fractionation so that you get these light ends and water as top product and then bottom ones you get as a crude ethylene oxide because it will also be containing some heavy ends also. So, this mixture you take to refining steel where you do the refining of the crude to get ethylene oxide as a top product of required purity whereas the bottom products would be nothing but heavy ends.

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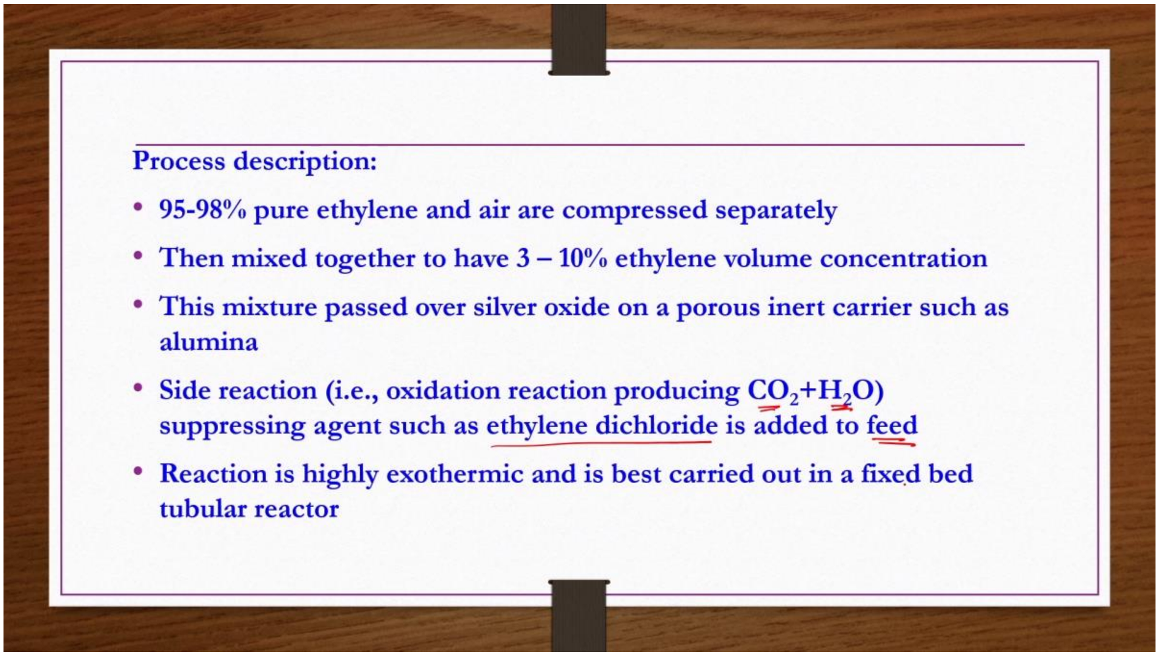

Process description:

- 95-98% pure ethylene and air are compressed separately
- Then mixed together to have 3 – 10% ethylene volume concentration
- This mixture passed over silver oxide on a porous inert carrier such as alumina
- Side reaction (i.e., oxidation reaction producing CO_2+H_2O) suppressing agent such as ethylene dichloride is added to feed
- Reaction is highly exothermic and is best carried out in a fixed bed tubular reactor

Process description 95 to 98 percent pure ethylene and air are compressed separately then mixed together to have 3 to 10 percent of ethylene volume concentration. This mixture passed over silver oxide on a porous inert carrier such as alumina. Side reaction like oxidation reaction producing CO2 and then water vapor suppressing agents such as ethylene dicloride is also added to the feed though it is not shown in the flow chart, it is in general added. Reaction is highly exothermic and is best carried out in a fixed bed tubular reactor.

For the reactor heat transfer salt or Dowtherm is pumped around the tube within the shell to maintain the temperature of 250 to 300 degrees centigrade. Heat is recovered in waste heat steam boiler. A short residence time of 1 second in plug flow with an yield of 60 to 70 percent is possible. Effluent gases from the reactor are water washed under pressure. Absorbed ethylene oxide is sent to a packed bed desorber, fractionator tower and taken as overhead product as shown in the flow chart. Even after desorption it still contains large amount of water vapor along with some impurities. This stream is then compressed to 4 to 5 atmosphere and fractionated twice to remove lightens, water and then high boiling polymers in 2 different columns.

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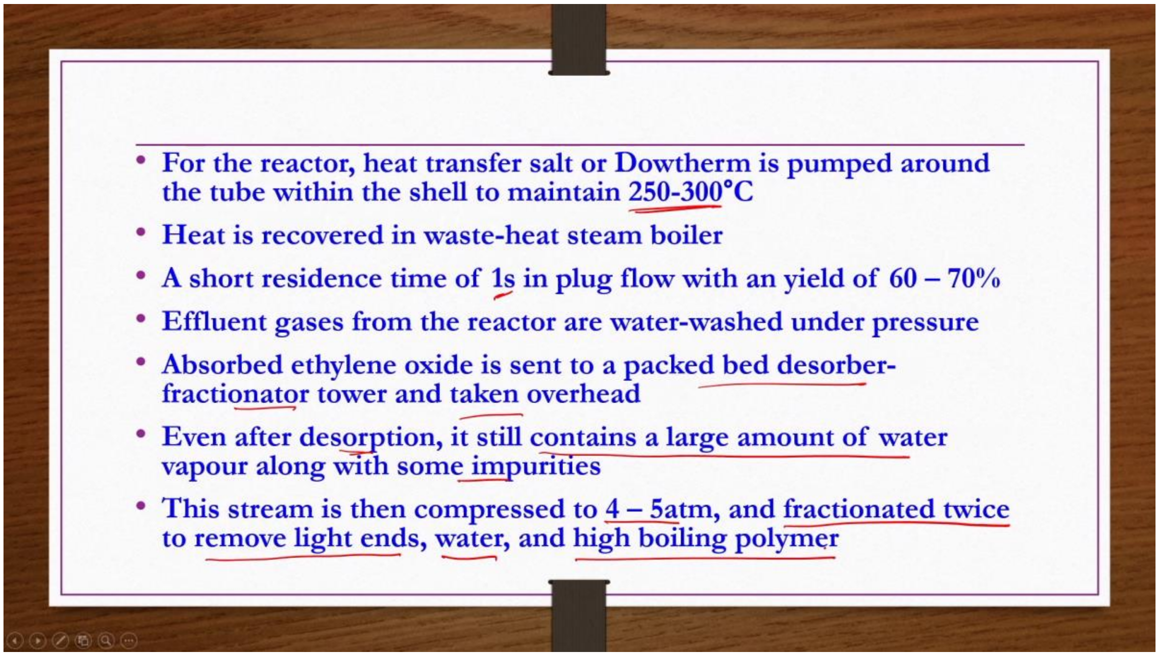

- For the reactor, heat transfer salt or Dowtherm is pumped around the tube within the shell to maintain 250-300°C
- Heat is recovered in waste-heat steam boiler
- A short residence time of 1s in plug flow with an yield of 60 – 70%
- Effluent gases from the reactor are water-washed under pressure
- Absorbed ethylene oxide is sent to a packed bed desorber-fractionator tower and taken overhead
- Even after desorption, it still contains a large amount of water vapour along with some impurities
- This stream is then compressed to 4 – 5atm, and fractionated twice to remove light ends, water, and high boiling polymer

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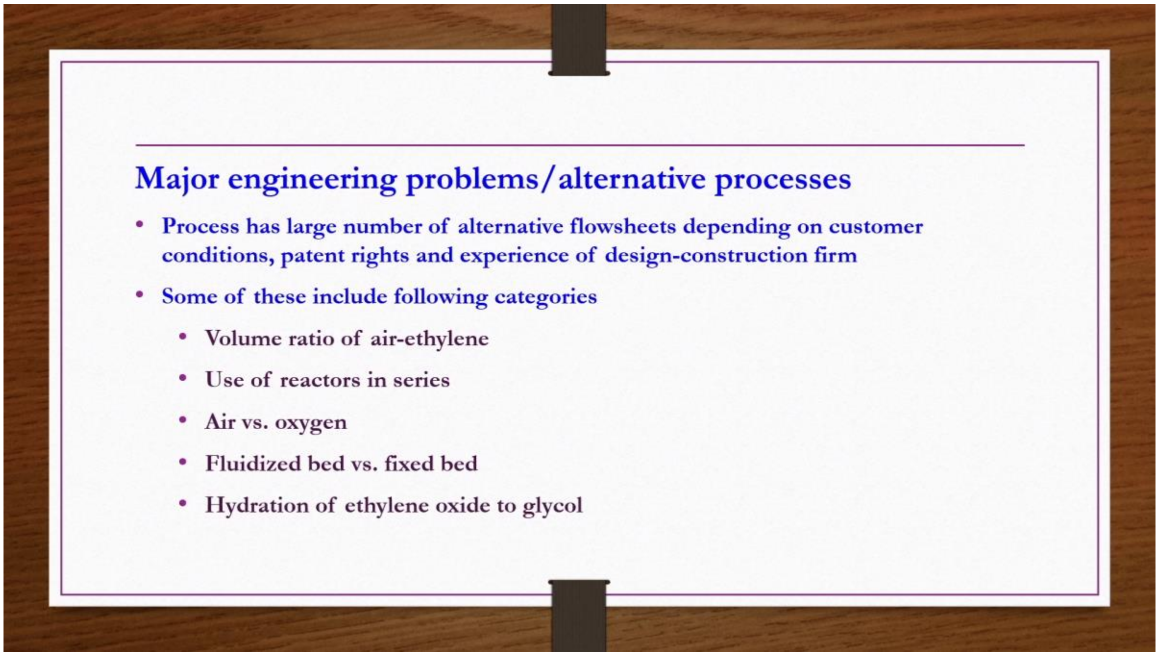

Major engineering problems/alternative processes

- Process has large number of alternative flowsheets depending on customer conditions, patent rights and experience of design-construction firm
- Some of these include following categories
  - Volume ratio of air-ethylene
  - Use of reactors in series
  - Air vs. oxygen
  - Fluidized bed vs. fixed bed
  - Hydration of ethylene oxide to glycol

Coming to the major engineering problems alternatives, process has large number of alternative flowsheets depending on customer conditions, patent, rights and then experience of design construction firm, etc. Some of them are shown here. Volume ratio of air ethylene, use of reactors in series, air versus oxygen, then fluidized bed versus fixed bed reactor, hydration of ethylene oxide to glycol are the some of the option.

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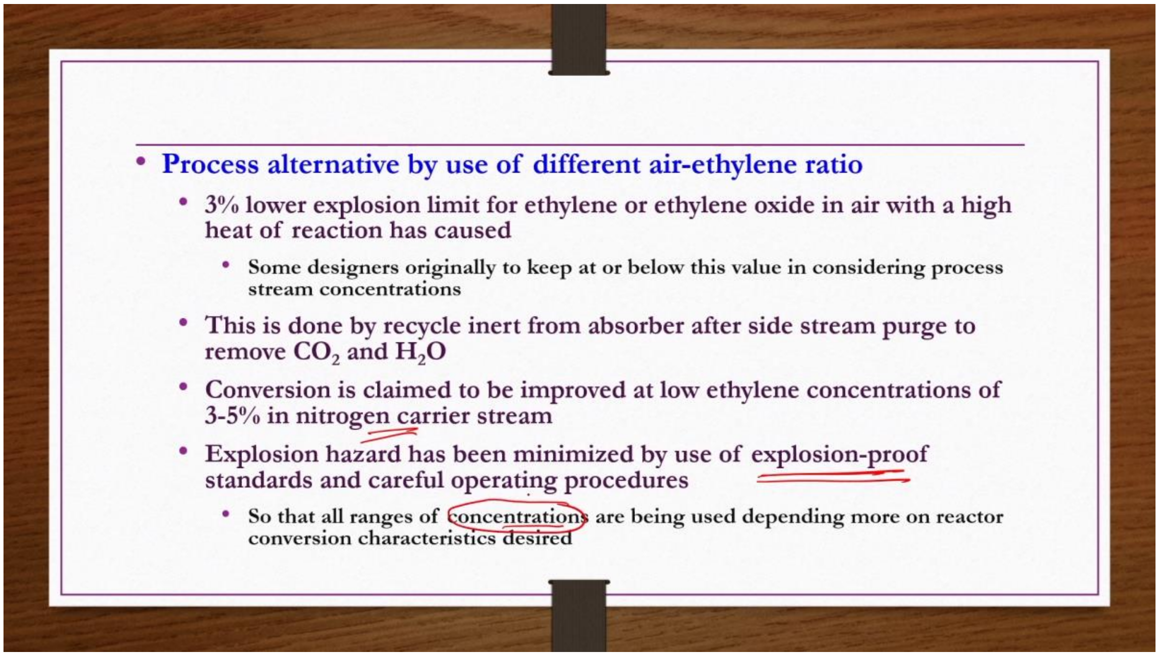

- **Process alternative by use of different air-ethylene ratio**
  - 3% lower explosion limit for ethylene or ethylene oxide in air with a high heat of reaction has caused
    - Some designers originally to keep at or below this value in considering process stream concentrations
  - This is done by recycle inert from absorber after side stream purge to remove CO_2 and H_2O
  - Conversion is claimed to be improved at low ethylene concentrations of 3-5% in nitrogen carrier stream
  - Explosion hazard has been minimized by use of explosion-proof standards and careful operating procedures
    - So that all ranges of concentrations are being used depending more on reactor conversion characteristics desired

We discussed individually about these 5 options. Let us say process alternative by use of different air ethylene ratio. 3 percent lower explosion limit for ethylene is there, ethylene or ethylene oxide in the air is there. So, you cannot go more than that one. So, 3 percent lower explosion limit for ethylene or ethylene oxide in air with a high heat of reaction has caused some designers originally to keep at or below this value in considering process stream concentrations. This is done by recycle inert from absorber after side stream pass to remove CO2 and H2O as well. Conversion is claimed to be improved at low ethylene concentration of 3 to 5 percent nitrogen carrier stream. Explosion hazard has been minimized by use of explosion proof standards and careful operation or operating procedures. So, that all ranges of concentrations are being used depending more on reactor conversion characteristics desired rather worrying about the explosion because explosion proof standards if you follow then you can work over wide range of concentrations.

Second option is process alternative by use of reactors in series. 2 reactors in series are used to convert more of ethylene with overhead gas from water absorber introduced into a second reactor. Whatever the overhead gases you are getting from the water absorber in which you know ethylene oxide is being absorbed. So, then from the top whatever the gases are there they would be involving unreacted ethylene and then air along with CO2 and then water vapor etc. So, that mixture if you take to the second reactor so then it has been found that you know yield is going to be improved. This is an economic balance between cost of ethylene and fixed charges on additional reactor. So, you have to see the balance is it better to do the recycling or you take another reactor and then see. So, that depends on the cost of ethylene and then fixed bed charges on additional reactor. One reactor is definitely is required if you have additional reactor that is more economical so then you go for the second reactor otherwise you go for the you know recycling process.

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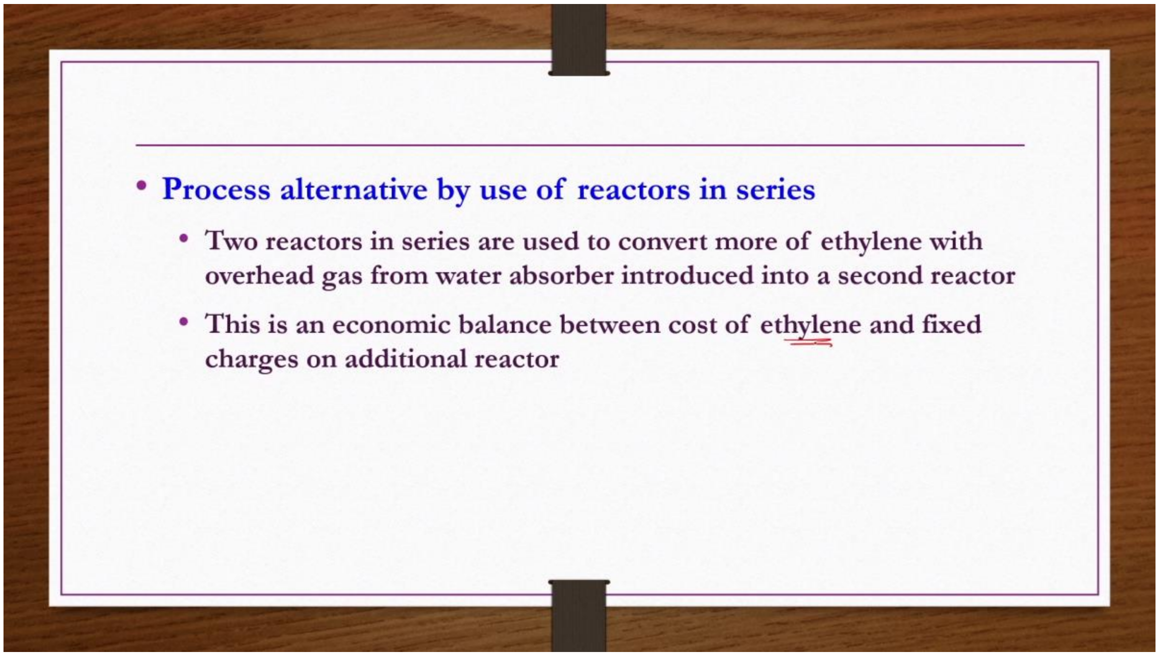

- **Process alternative by use of reactors in series**
  - Two reactors in series are used to convert more of ethylene with overhead gas from water absorber introduced into a second reactor
  - This is an economic balance between cost of ethylene and fixed charges on additional reactor

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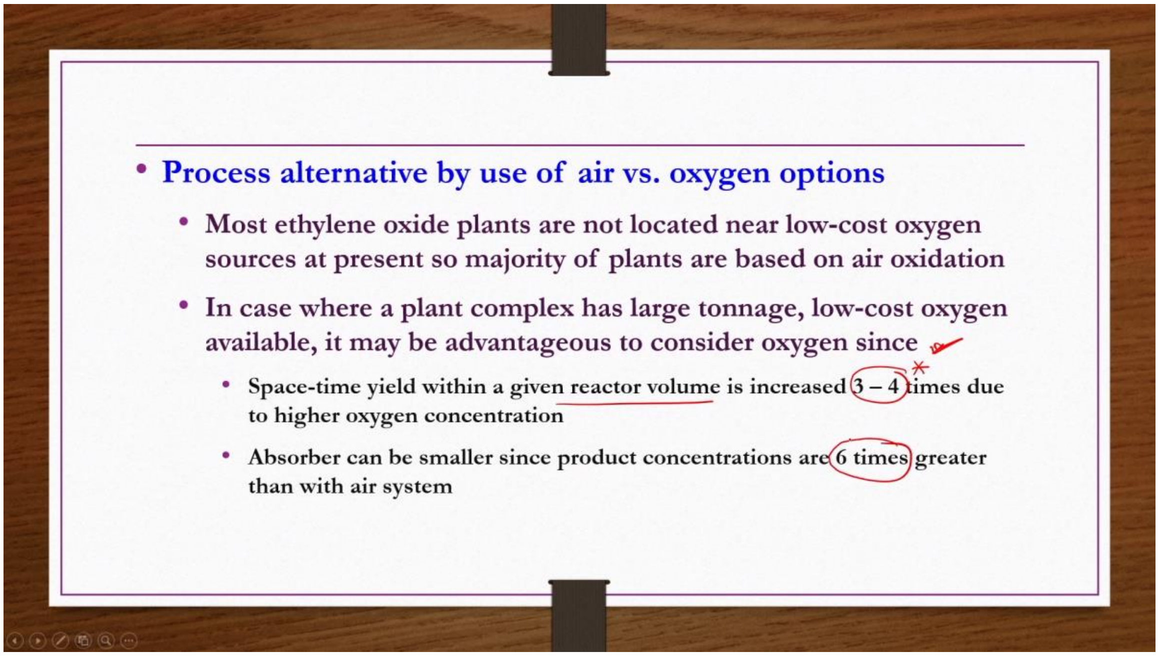

- **Process alternative by use of air vs. oxygen options**
  - Most ethylene oxide plants are not located near low-cost oxygen sources at present so majority of plants are based on air oxidation
  - In case where a plant complex has large tonnage, low-cost oxygen available, it may be advantageous to consider oxygen since
    - Space-time yield within a given reactor volume is increased 3 – 4 times due to higher oxygen concentration
    - Absorber can be smaller since product concentrations are 6 times greater than with air system

Process alternative by use of air versus oxygen options. Most of the plants in general uses air because large tonnage of oxygen is not available within the process. Mostly ethylene oxide plants are not located near low cost oxygen sources at present. So, majority of plants are based on air oxidation process. However, in case where a plant complex has a large tonnage low cost oxygen available it may be advantageous to consider oxygen rather air because space time yield within a given reactor volume is increased 3 to 4 times if you use oxygen rather air. In addition, absorber can be smaller since product concentration is 6 times greater. The product you know concentration of product is higher so then you do not need to do much absorption of you know absorption process so they can be smaller.

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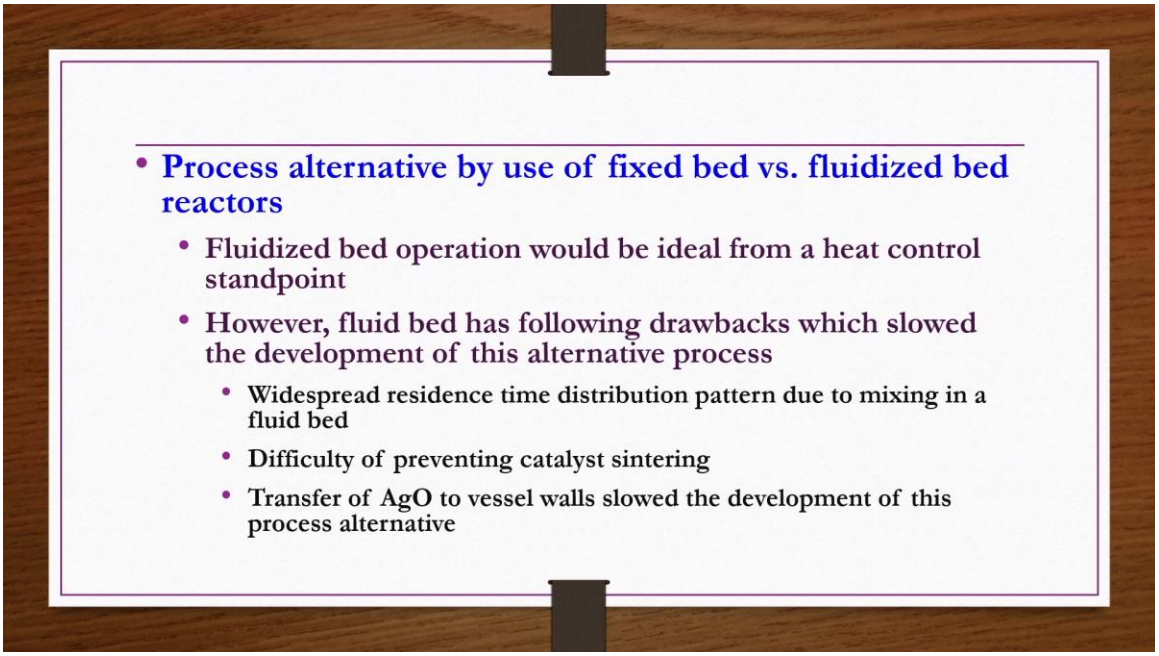

- Process alternative by use of fixed bed vs. fluidized bed reactors
  - Fluidized bed operation would be ideal from a heat control standpoint
  - However, fluid bed has following drawbacks which slowed the development of this alternative process
    - Widespread residence time distribution pattern due to mixing in a fluid bed
    - Difficulty of preventing catalyst sintering
    - Transfer of AgO to vessel walls slowed the development of this process alternative

Process alternative by use of fixed bed versus fluidized bed reactors is another alternative process alternative. Obviously, fluidized bed operations would be ideal from heat control standpoint of view. However, in this process fluidized bed reactors having certain drawbacks such as widespread residence time distribution pattern due to mixing in a fluid bed whereas you need plug flow kind of flow for fraction of second or 1 second for the reaction to take place. So, this is one disadvantage which you cannot overcome in fluidized beds. Difficulty of preventing catalyst sintering is another problem in the fluidized beds. Transfer of silver oxide to vessel walls slowed the development of this process alternative as well.

And then final engineering problem or alternative is process alternatives by hydration of ethylene oxide to glycol.

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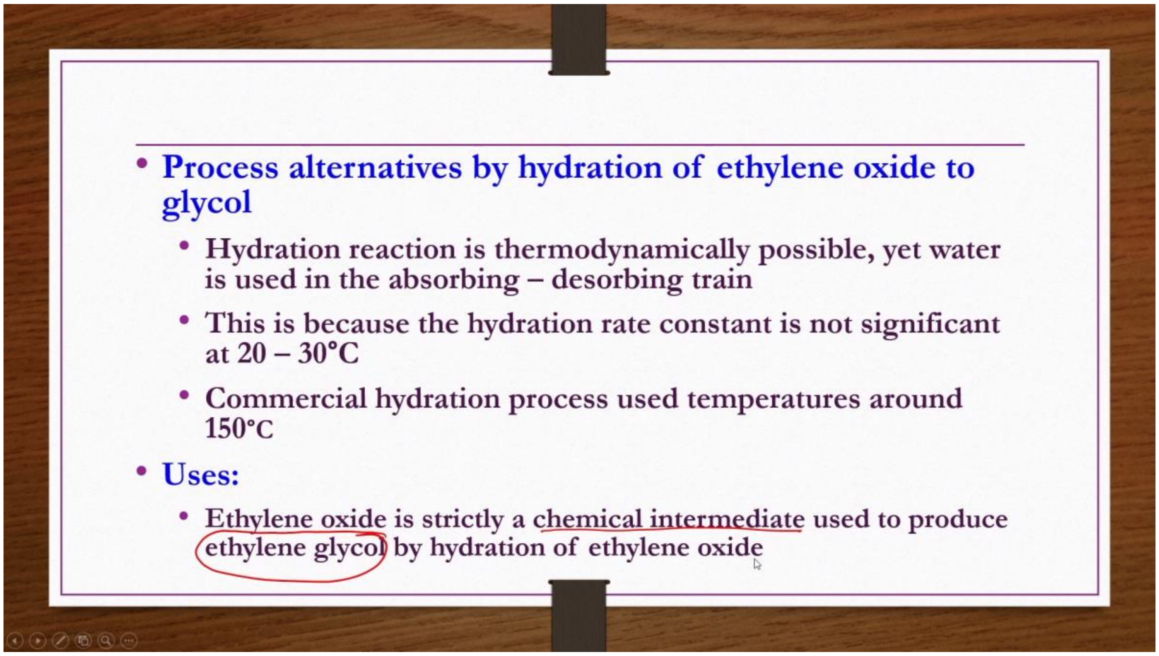

- **Process alternatives by hydration of ethylene oxide to glycol**
  - Hydration reaction is thermodynamically possible, yet water is used in the absorbing – desorbing train
  - This is because the hydration rate constant is not significant at 20 – 30°C
  - Commercial hydration process used temperatures around 150°C
- **Uses:**
  - Ethylene oxide is strictly a chemical intermediate used to produce ethylene glycol by hydration of ethylene oxide

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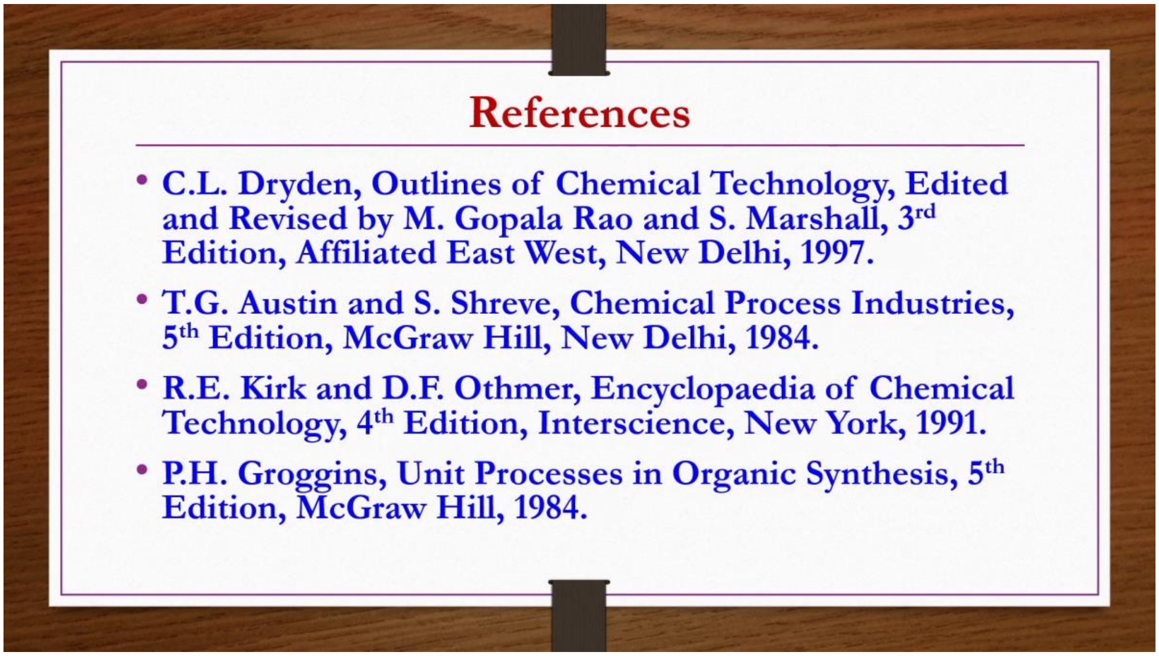

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Hydration reaction is thermodynamically possible yet water is used in the absorbing-desorbing train. This is because the hydration rate constant is not significant at low temperature. If the rate of reaction of hydration of ethylene oxide to get the ethylene glycol is happening at a better rate at atmospheric conditions of 20 to 30 degrees centigrade then you can do that one, but that is not happening because of that one absorbing and desorbing trains are used in the process. Commercial hydration process use temperatures around 150 degrees centigrade in general. Coming to the uses of ethylene oxide as already mentioned, it is strictly a chemical intermediate used to produce ethylene glycol by hydration of ethylene oxide that we subsequently studied. The references for today's lecture are provided here. Thank you.