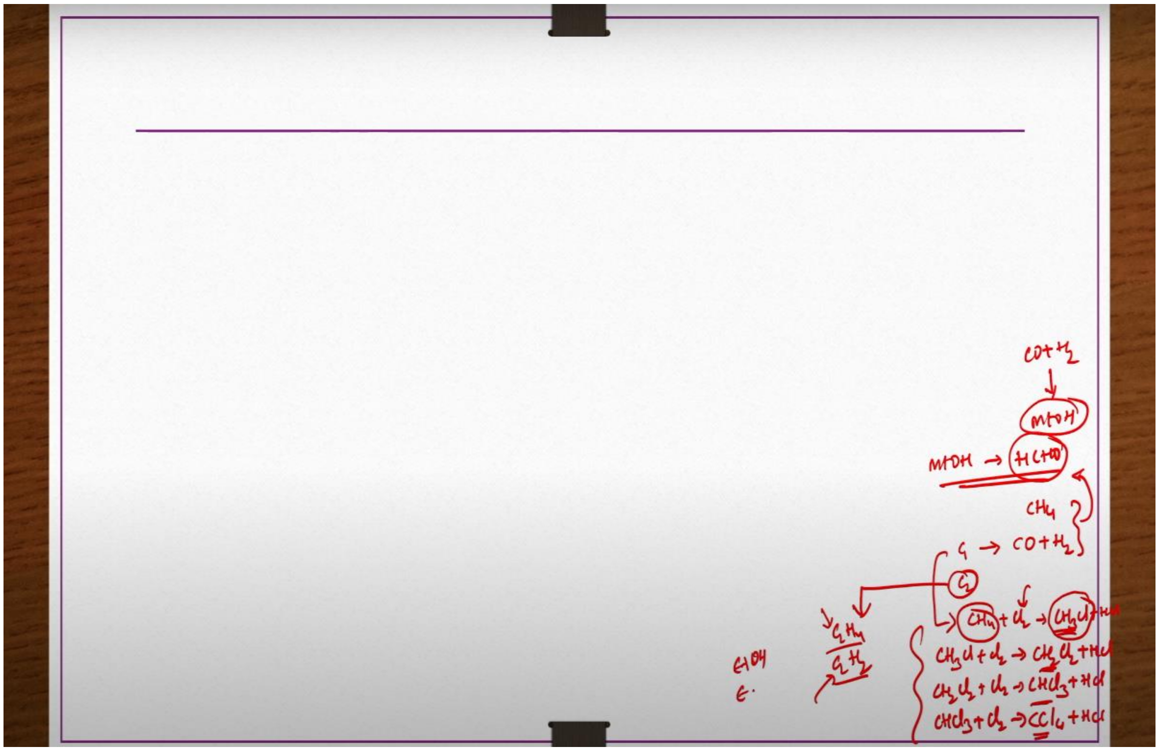
Organic Chemical Technology
Prof. Nanda Kishore
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture - 23
Chemicals from C1 & C2 Compounds

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is chemicals from C1 and C2 compounds. In the previous lecture, we started discussions on production of different types of chemicals from the C1 compounds.

(Refer Slide Time: 00:47)



What do you mean by C1 compounds or C2 compounds that we have already seen that taking the raw material whichever is having only one carbon atom then we can call them you know C1 compound like you know CO plus H2 mixture or CO alone and then doing the reaction with H_2, then methane. These are you know C1 compounds and then from here we try to produce the methanol, right?

Where CO plus H_2 reaction takes place to give the methanol and then we also have discussed like you know production of formaldehyde from methanol. These products like you know methanol as one product and then formaldehyde as another product that is what we have discussed in the previous lecture that is production of methanol and formaldehyde from C1 compounds we have seen.

In this lecture, we are going to see a few more chemicals from C1 compounds. Let us say methane we take and then do the chlorination to get chloromethane or methyl chloride plus HCl.

This CH_3Cl again will react with chlorine to give CH_2Cl_2 that is methylene chloride and then this CH_2Cl_2 will react again with Cl_2 to give $CHCl_3$ which is chloroform plus HCl you get and this $CHCl_3$ will again react with the chlorine to give CCl_4 carbon tetrachloride plus HCl that is what we are going to see in today's lecture that is production of chloromethanes from the methane we are going to see.

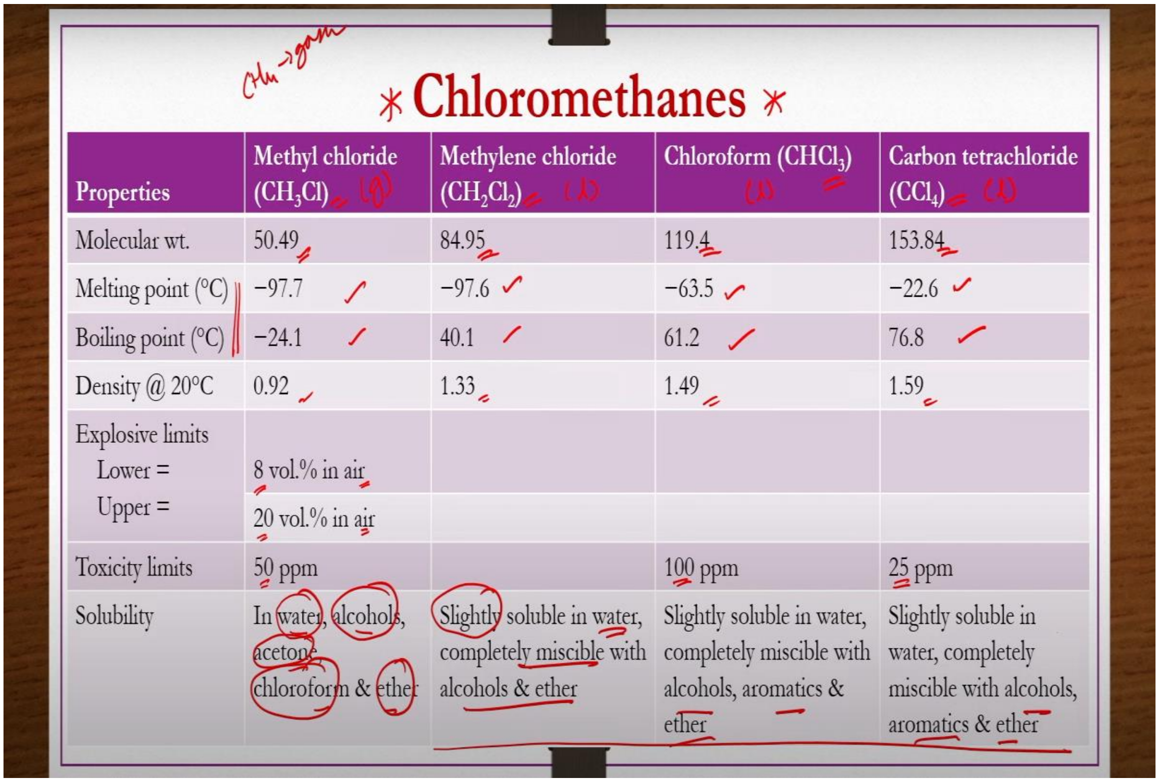
Now, you can understand that these reactions are a series initiated and then propagated reactions they are forming in series that means when you take CH_4 and Cl_2 you cannot control to have only methyl chloride or chloroform or carbon tetrachloride or methylene chloride alone.

All of them may be forming depending on what ratio of CH_4 and Cl_2 are you taking. So, these are the series reaction kind of thing and since Cl_2 is there so these reactions are highly exothermic and then if you do not control they can become even explosive reactions as well. So, that is what one topic that we are going to discuss another topic is the Cl chemicals from C2 compounds like C2 compounds what we have we have C_2H_4 ethylene and then C_2H_2 acetylene these compounds are there.

So, from here what compounds can we produce before producing chemicals from C2 compounds production of these C2 compounds like ethylene and acetylene that we discussed today and then we discuss production of some components like ethyl alcohol, ethylene oxide, etc. these kind of products production that we are going to discuss.

So, let us start with chloromethanes as explained just now, these are kind of replacement reaction that is one H atom of a methane is being replaced by 1 chlorine atom then you can get the methyl chloride if 2 hydrogen atoms are replaced by the 2 chlorine atoms then methylene chlorides would be forming if you replace 3 hydrogen atoms of methane with 3 chlorine atoms then chloroform you get if all 4 hydrogen atoms of methane are being replaced by the 4 chlorine atoms then you get the carbon tetrachloride.

(Refer Slide Time: 04:28)



$CH_4 \rightarrow$ gas

* Chloromethanes *

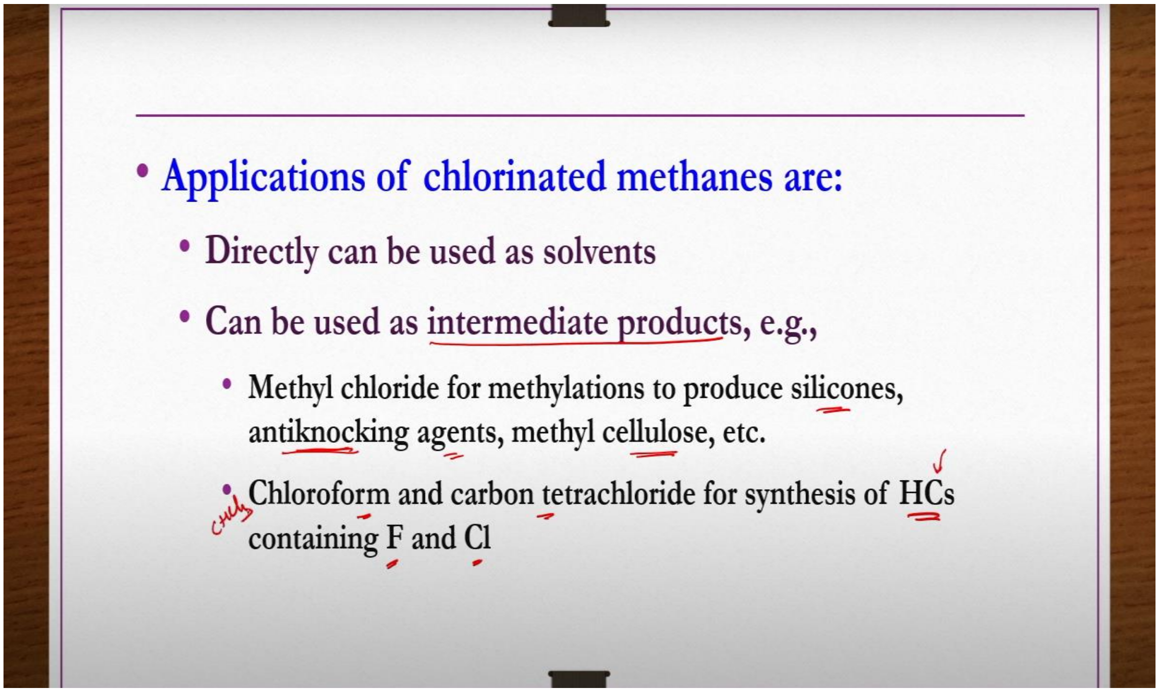
Properties	Methyl chloride (CH_3Cl) (g)	Methylene chloride (CH_2Cl_2) (l)	Chloroform ($CHCl_3$) (l)	Carbon tetrachloride (CCl_4) (l)
Molecular wt.	50.49	84.95	119.4	153.84
Melting point (°C)	−97.7	−97.6	−63.5	−22.6
Boiling point (°C)	−24.1	40.1	61.2	76.8
Density @ 20°C	0.92	1.33	1.49	1.59
Explosive limits Lower =	8 vol.% in air			
Upper =	20 vol.% in air			
Toxicity limits	50 ppm		100 ppm	25 ppm
Solubility	In water, alcohols, acetone, chloroform & ether	Slightly soluble in water, completely miscible with alcohols & ether	Slightly soluble in water, completely miscible with alcohols, aromatics & ether	Slightly soluble in water, completely miscible with alcohols, aromatics & ether

So, in the chloromethanes formation process all 4 types of chloromethanes would be forming this chloromethanes what we have methyl chloride that is CH3Cl, methylene chloride CH2Cl2 chloroform CHCl3 and then carbon tetrachloride CCl4. Now, we are going to discuss their properties. So, methane is in the gases form that we know. So, this methyl chloride whatever you get that would be in the gases form whereas the rest all 3 chloromethanes would be in the liquid form.

So, now we have discussion on the pertinent properties in a kind of tabular form so that we can compare them easily. So, lower molecular weight hydrogen atom is being replaced by the higher molecular weight chlorine atom that is the reason as you move from the methyl chloride to the methylene chloride followed by the chloroform and carbon tetrachloride your molecular weight of chloromethanes is increasing. And then coming to the melting point and boiling point of this component those things are also increasing gradually they are increasing as you move from CH3Cl to CH2Cl to CHCl3 and CCl4 because they are becoming from the gases form because methyl chloride is in gases form and then methylene chloride chloroform and then carbon tetrachloride are in the liquid form. So there are boiling point etc. gradually increasing that is because the density of these compounds are increasing gradually from increased number of hydrogen atoms being replaced by the increased number of or corresponding number of chlorine atoms.

Since methyl chloride is in gases form its presence in the air is found to be explosive and then lower and upper limits of these explosive limits are 8 and 20 volume percent respectively. Toxicity is 50 ppm for methyl chloride whereas for chloroform 100 ppm and carbon tetrachloride 25 ppm are the toxic limits. Solubility all of them are soluble in water, alcohols and then acetones, chloroform, ether and then aromatics etc. but specifically if you see methyl chloride is soluble in all of them in the water, alcohol acetone, chloroform, ether whereas the remaining three if you see these methylene chloride, chloroform and carbon tetrachloride are slightly soluble in water whereas completely miscible with alcohols and then ethers and then aromatics as well. So this is about pertinent properties of 4 different types of chloromethanes.

(Refer Slide Time: 07:28)

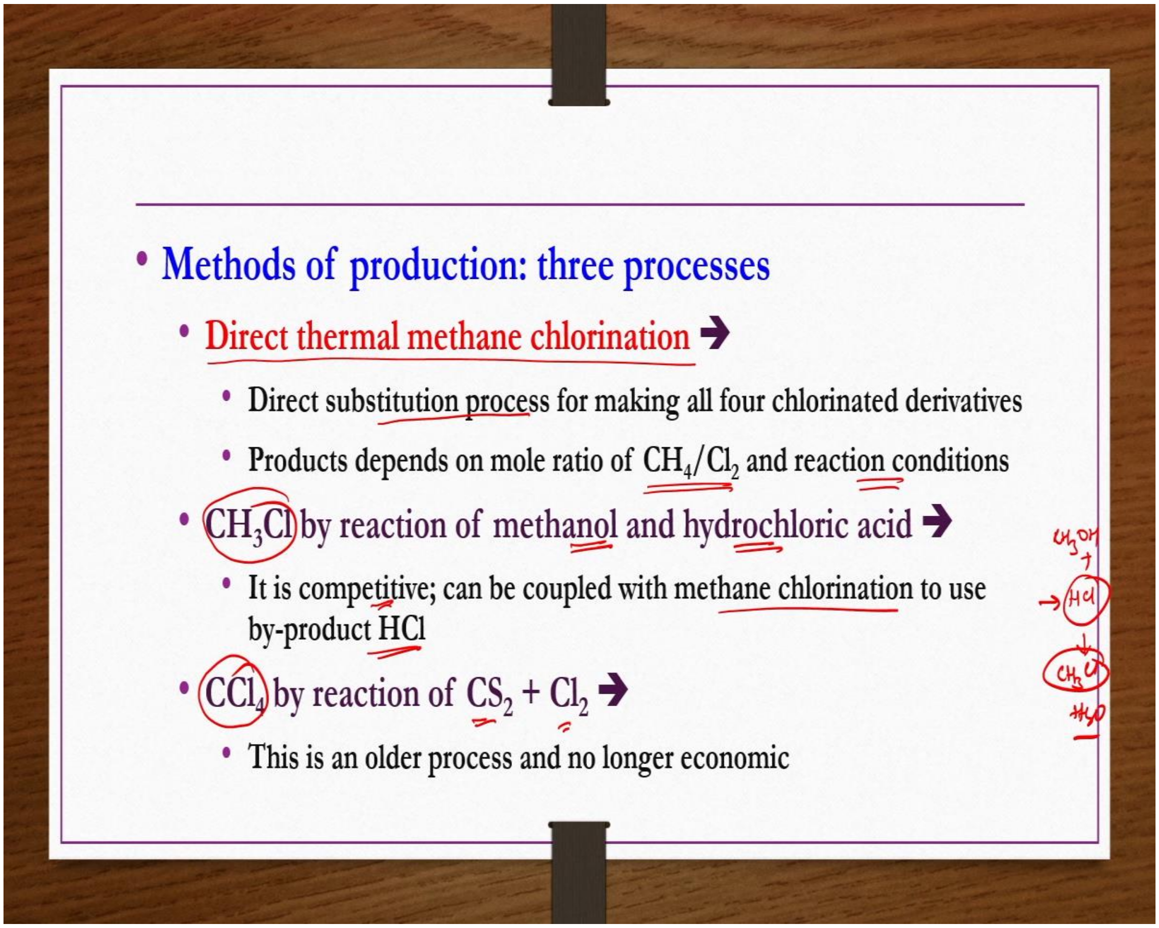


- Applications of chlorinated methanes are:
  - Directly can be used as solvents
  - Can be used as intermediate products, e.g.,
    - Methyl chloride for methylations to produce silicones, antiknocking agents, methyl cellulose, etc.
    - $CHCl_3$ Chloroform and carbon tetrachloride for synthesis of HCs ✓ containing F and Cl

Applications point of view they are used as intermediate chemicals to produce some end products as well as solvents also directly as solvents are also they are being used. So these are the two types of applications are possible for chlorinated methanes directly can be used as solvents can be used as intermediate products. Let us say methyl chloride can be used for the methylation of silicon to produce silicones like that anti-knocking agents which are essential in the automobile industries. So such anti-knocking agents can also be produced by methyl chloride by doing methylation reactions. If you do the methylation reaction of cellulose then you can get the methyl cellulose etc.

So for these production point of view also these chlorinated methanes can be used as intermediate products. Likewise chloroform and carbon tetrachlorides are also used to produce different types of hydrocarbons having fluorine and then chlorine or fluorinated or chlorinated hydrocarbons if you wanted to produce then this CHCl3 and then CCl4 are also used.

(Refer Slide Time: 08:45)



- Methods of production: three processes
  - Direct thermal methane chlorination ➔
    - Direct substitution process for making all four chlorinated derivatives
    - Products depends on mole ratio of CH_4/Cl_2 and reaction conditions
  - CH_3Cl by reaction of methanol and hydrochloric acid ➔
    - It is competitive; can be coupled with methane chlorination to use by-product HCl
  - CCl_4 by reaction of $CS_2 + Cl_2$ ➔
    - This is an older process and no longer economic

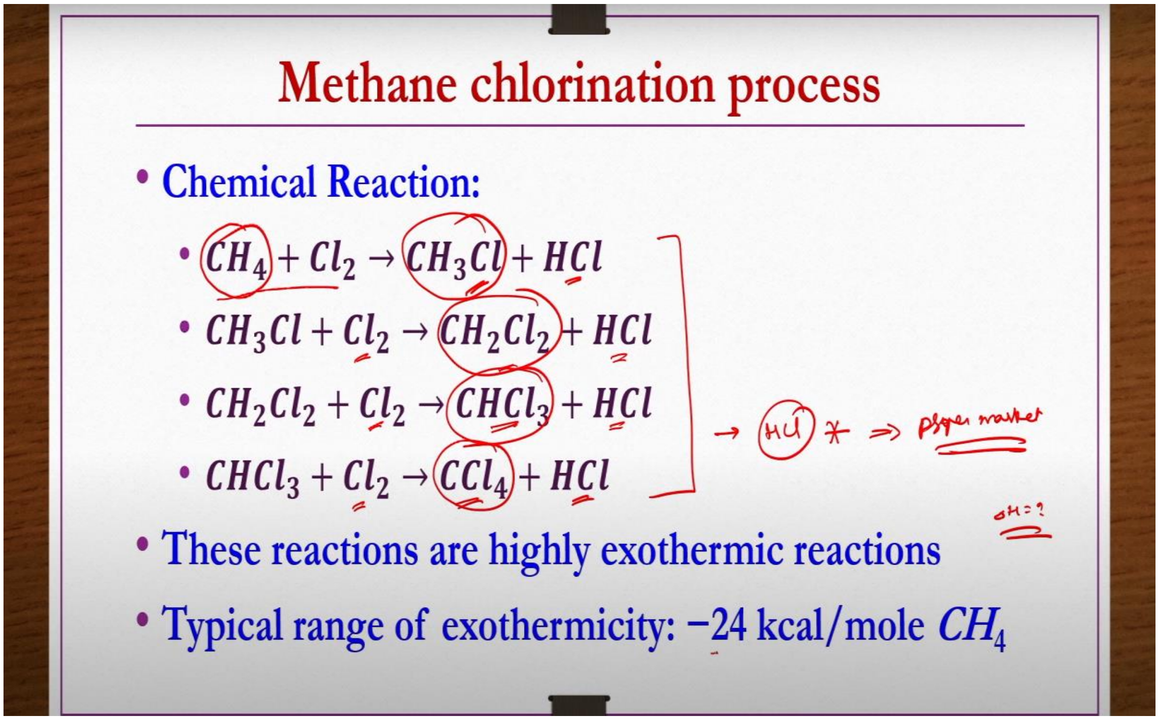
CH_3OH
+
→ HCl
↓
CH_3Cl
H_2O

Coming to the methods of production 3 processes are existing. The first one is direct thermal methane chlorination that is you just take methane and then chlorine of appropriate mole ratio as per the product distribution that you wanted to have and then do the thermal reaction. Just heat it at 370 to 400 degrees centigrade depending on the product distribution.

So process is done you get the chloromethanes that is one method which is direct substitution process for making all 4 chlorinated derivatives. Products depends on mole ratio CH4 to Cl2 what mole ratio are you taking these raw materials depending on that one your product distribution that is what percentage of a methyl chloride, what percentage of methylene chloride, what percentage of chloroform and then what percentage of carbon tetrachloride that depends on this mole ratio as well as the reaction conditions like temperature usually 370 to 410 degrees centigrades are maintained. Then methanol reacting with hydrochloric acid to give chloromethane or methyl chloride also that is one process, but it is competitive and it can be coupled with methane chlorination process to use byproduct HCl because in the reactions we have seen every one type of chloromethane when forming 1 mole of HCl is being formed. So that means lot of HCl would be forming in the process no doubt if that HCl you can utilize then these 2 process may be coupled, because this HCl will can be reacting with the methanol CH3OH to give CH3Cl plus H2O. So, for this way also the coupling of 2 process can be done where utilization of excess of HCl whatever is formed in the methane chlorination form can be utilized.

So, a kind of utilization of byproduct or co-product is taking place by coupling of these 2 processes. Third process is CCl4 production by the reaction between carbon disulphide and chlorine, but it is a older process and no more economic as well. So, we cannot go discussion about each and every process. So, what we do we discuss the manufacturing of chloromethanes by direct thermal methane chlorination reaction that is what we are going to see.

(Refer Slide Time: 11:26)



Methane chlorination process

- Chemical Reaction:
  - $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
  - $CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$
  - $CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$
  - $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$
- These reactions are highly exothermic reactions
- Typical range of exothermicity: −24 kcal/mole CH_4

→ HCl * ⇒ proper market

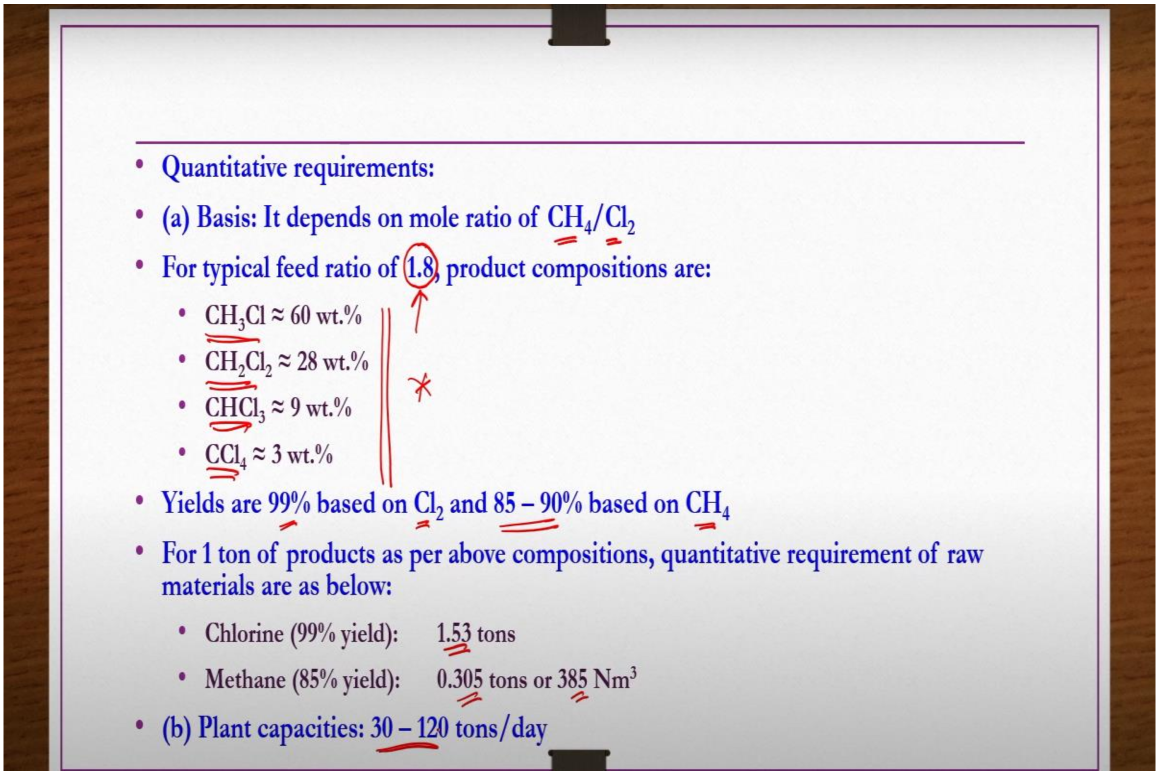
$\Delta H = ?$

So, what we do for this process we start with the chemical reactions, quantitative requirements, plant capacities, flowchart and then process description followed by what are the major engineering problems as we have been doing for almost all processes.

So, chemical reactions which I have already written so that is methane reacting with chlorine to give 1 mole of chloromethane or methyl chloride plus HCl. This methyl chloride will further react with Cl2 to give methylene chloride and then HCl and then this methylene chloride further react with the chlorine to give chloroform and then 1 mole of HCl and then this chloroform will further react with chlorine to give carbon tetrachloride and 1 mole of HCl. Now, you can see how much of HCl is being formed. So, you should have a proper market for it. These reactions are highly exothermic and then these are chain initiated and propagated reactions because of the chloride radicals present.

So, you cannot have what is the delta H for overall reaction because it depends on the mole ratio of CH4 and Cl2 and then depends on the product distribution that again depends on the reaction conditions as well. So, many factors are there because of that one having 1 single delta H for this series reaction is not possible. However, per mole of methane consumed that way if you see the exothermicity would be minus 24 kilocalories per mole of methane.

(Refer Slide Time: 13:15)

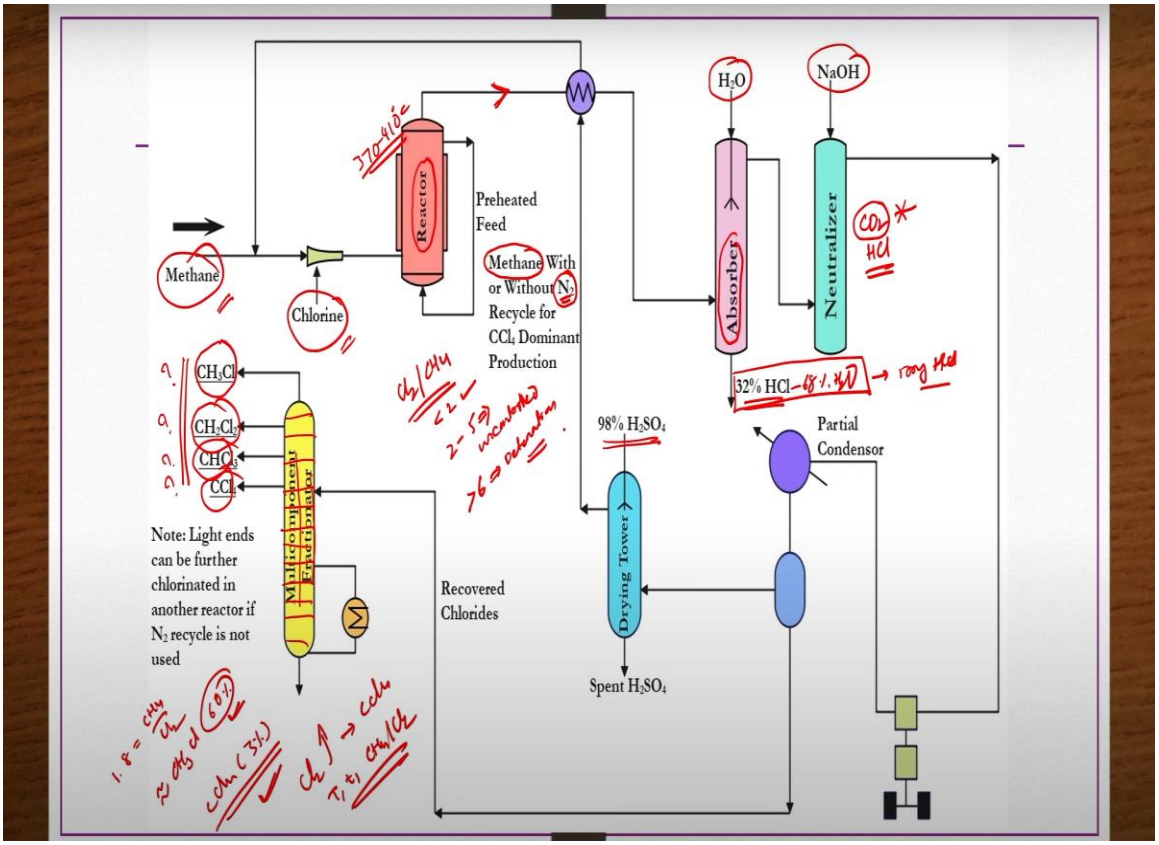


- Quantitative requirements:
- (a) Basis: It depends on mole ratio of CH_4/Cl_2
- For typical feed ratio of 1.8, product compositions are:
    - $CH_3Cl \approx 60$ wt.%
    - $CH_2Cl_2 \approx 28$ wt.%
    - $CHCl_3 \approx 9$ wt.%
    - $CCl_4 \approx 3$ wt.%
- Yields are 99% based on Cl_2 and 85 – 90% based on CH_4
- For 1 ton of products as per above compositions, quantitative requirement of raw materials are as below:
    - Chlorine (99% yield): 1.53 tons
    - Methane (85% yield): 0.305 tons or 385 Nm^3
- (b) Plant capacities: 30 – 120 tons/day

Quantitative requirements obviously depends on mole ratio of methane to chlorine as I have been discussing, but let us say typical feed ratio of 1.8 if you take whatever the CH4 to Cl2 ratio if you take 1.8, then product ratio or product composition that you get is as follows. Methyl chloride approximately 60 weight percent, methylene chloride approximately 28 weight percent, chloroform approximately 9 weight percent and carbon tetrachloride approximately 3 weight percent you can get. If you change this ratio, so these numbers would also be changing. Not only this ratio, but also temperature also plays a very important role on the formation of these products and their yields. Yields you have to calculate based on one of the raw material.

Let us say if you are calculating based on the Cl2, then 99 percent of chloromethanes you will get, but if you calculate based on the methane, then 85 to 90 percent yield of chloromethanes would take place. Let us say for 1 ton of products as per these composition that means you are maintaining 1.8 feed ratio, then quantitative requirements of raw materials if you see, chlorine 1.53 tons required, methane 0.305 tons or 385 normal cubic meters you may require, plant capacity usually 30 to 120 tons per day.

(Refer Slide Time: 14:52)



Now, we have a discussion on the flowchart of a process that is occurring in the industry to produce different types of chloromethanes. So, what you do here that methane feed whatever is there that one and then chlorine you take to a reactor, adiabatic reactor. Now, to this reactor the temperature conditions you maintain something like 370 to 410 degrees centigrade depending on your product distribution, what percentage of methyl chloride, methylene chloride, chloroform and carbon tetrachloride are you expecting depending on that one temperature variation would be there.

So, since chlorine is there and then we already know this reaction is exothermic, lot of heat would be evolved. So what happens, so whatever the unreacted methane or anything any products etc. are there, they would also be at high temperature. So, that preheated feed whatever methane is there that can be recycled back to the reactor so that to save the energy or whatever the heat that is being evolved because of this reaction that may be collected and then these reactants may be preheated before sending it to the reactor. So here this recycling of methane whatever is there that can be done with or without nitrogen inert because it is very essential to have N2 as we are going to see subsequently depending on the ratio between Cl2 to CH4 or CH4 to Cl2 the operating conditions the nature of the reaction would change. Let us say Cl2 to CH4 ratio if you consider if it is less than 2% so then it is suitable for the production of required chemicals. If you maintain it is between 2 to 5 or 8 or something like that then what happens you know uncontrolled heat would be liberated. If you maintain it more than 6 then detonation may take place, explosion may also take place in the reactor.

So, for that purpose in order to control them this nitrogen supply along with the methane or recycling of the methane along with the nitrogen is going to be useful to control these reactants that is one way. Now the ratio again like you know if you keep 1.8% of you know CH4 to Cl2 ratio as we have seen in the previous slide then more you know CH3Cl approximately 69% or 60% you are getting that is too much and then whereas CCl4 you are getting approximately 4% or something like that as we just seen in the previous slide here 3% approximately 3% you get. So this distribution is very important why because you have to see the final market.

Final market for CCl4 is very high. So you have to increase Cl2 to get more CCl4 but if you increase more CCl4 then you know explosions may takes place. So you have to design the reactor accordingly all those things we are going to discuss under major engineering problems anyway. So that is the reason the temperature, time and then CH4 to Cl2 ratio are going to be very crucial in the product distribution. So after the reaction whatever the gasses mixtures are there the product mixtures are there they will be passed through and heat exchanger and then sent to a absorber to collect 32% HCl.

In the absorber what you are doing you are spraying water so that HCl whatever is there that would be absorbed and you get the 32% HCl. So now remaining 68% is what it is nothing but H2O actually in this mixture. If you want to recycle 32% HCl that is fine in this step is fine. Otherwise if you wanted to use dry HCl then what you have to do you have to do in azeotropic distillation or extractive distillation to get the dry HCl and then that dry HCl you can be you can recycle for the process. So once this HCl is removed the product mixture is scrubbed with NaOH solution in neutralization section where CO2 etc. and then traces of HCl if at all still present they will be removed. This CO2 has to be removed by this neutralization step it is very important otherwise what happens it will be accumulating as inert gas within the reaction chamber or within the process which is not good.

After neutralization the mixture is compressed and then partially condensed and then sent to a multi component fractionator. So fractionator something like you know distillation column you have different trays like this. So for one of the particular tray you will be sending the feed material and then you maintain the temperature pressure condition such a way that you know you have to keep in mind the boiling point. So now the methyl chloride is highly volatile as per the boiling point data that we have seen in pertinent properties table.

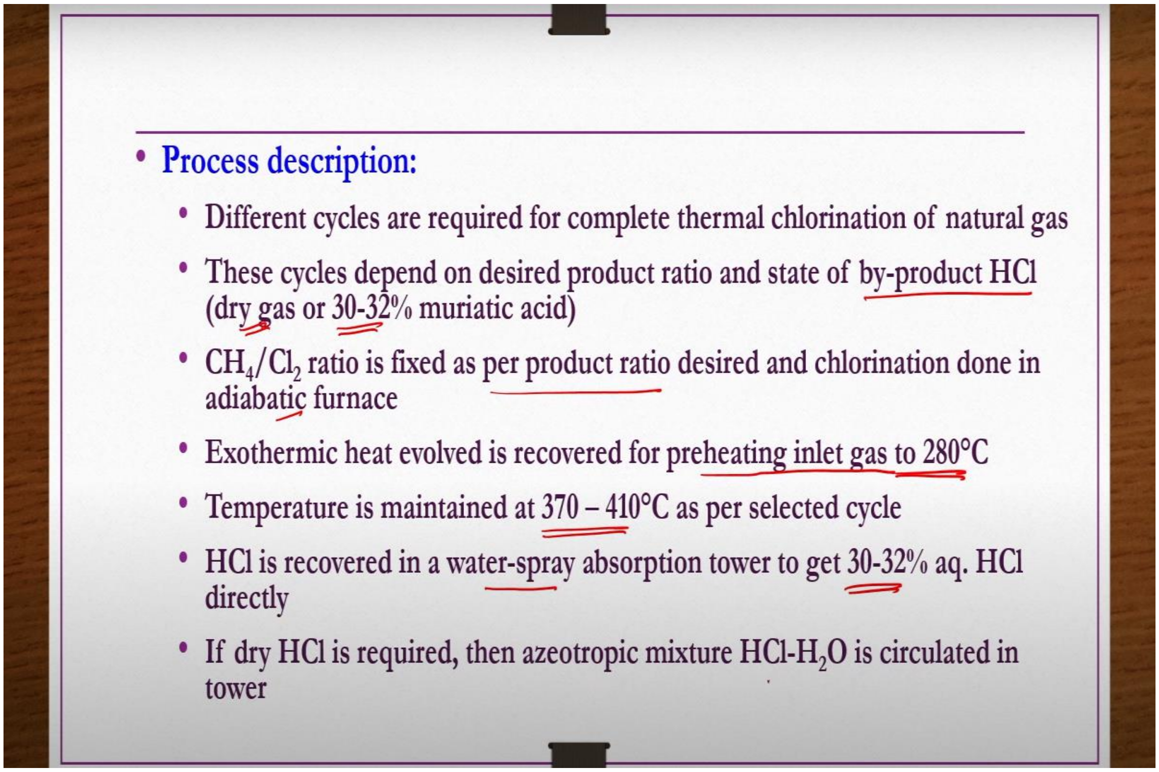
So it will be collected as top product subsequently underneath of this one as side streams you can get methylene chloride, chloroform and then carbon tetrachloride as a you know side streams. If at all you know heavy material steel are present you know they will be collected from the bottom or water etc. still present they will be removed from the bottom.

This is the process. So the mixture if at all unreacted CH4 etc. still is there. For example, methane or Cl2 etc. which are not reacted still they are present in the product mixture. So then what you can do? You can take them to a drying tower where you will be drying with

98 percent H2SO4 and then dry methane and then chlorine or some of the products may also be recycled to the reactor.

Recycling of the product is also very essential not only methane and Cl2 recycling. Recycling of a product partially product some amount of CH3Cl or CH2Cl2 may be recycled because they are present they are formed in large quantities. So that will also you can control the explosiveness of the reaction. So these are some engineering techniques that are good in order to maintain the reaction under controlled conditions.

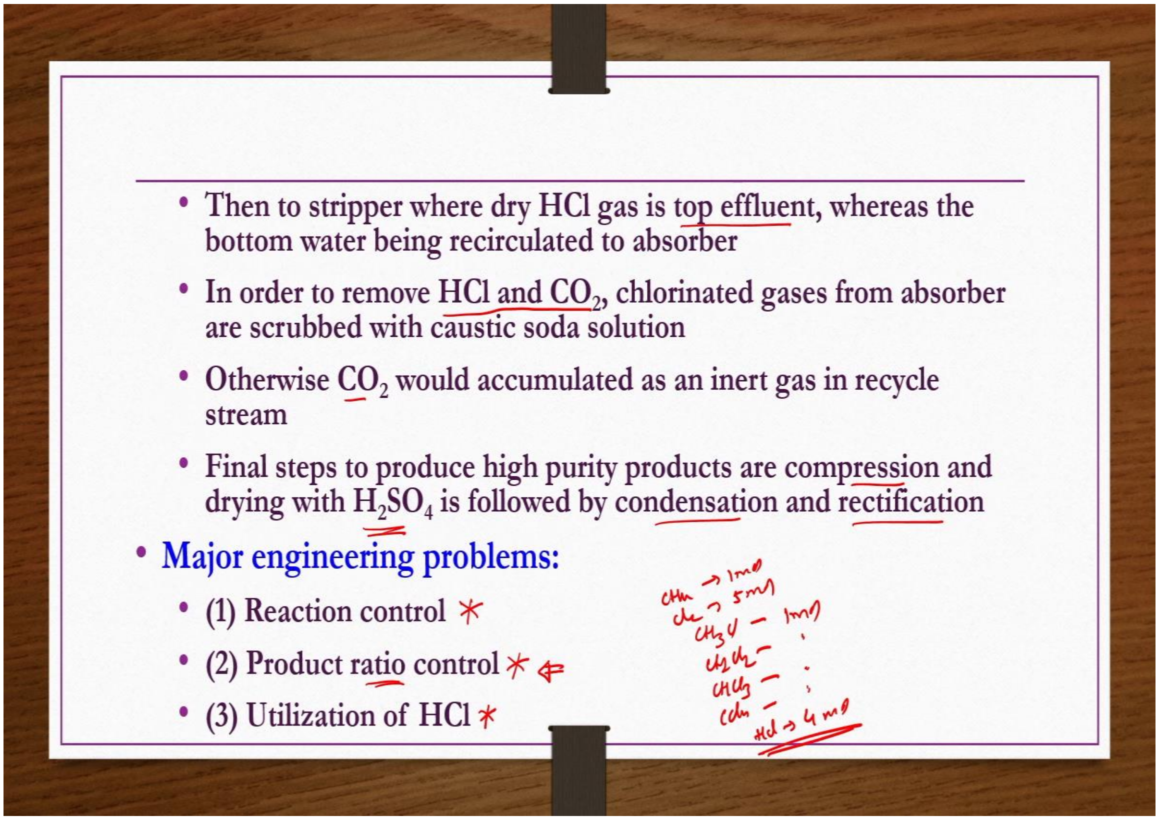
(Refer Slide Time: 21:58)



- Process description:
  - Different cycles are required for complete thermal chlorination of natural gas
  - These cycles depend on desired product ratio and state of by-product HCl (dry gas or 30-32% muriatic acid)
  - CH_4/Cl_2 ratio is fixed as per product ratio desired and chlorination done in adiabatic furnace
  - Exothermic heat evolved is recovered for preheating inlet gas to 280°C
  - Temperature is maintained at 370 – 410°C as per selected cycle
  - HCl is recovered in a water-spray absorption tower to get 30-32% aq. HCl directly
  - If dry HCl is required, then azeotropic mixture $HCl\text{-}H_2O$ is circulated in tower

Process description different cycles are required for complete thermal chlorination of natural gas. These cycles depend on desired product ratio and state of byproducts HCl required whether are you using 32 percent muriatic acid or as dry gases depending on that one different cycles are used. We have shown only one in the flowchart for the simplicity. Methane to chlorine ratio is fixed as per the product ratio desired for the consumer and chlorination done in adiabatic furnace. Exothermic heat evolved is recovered for preheating inlet gas to 280 degree centigrade. Temperature is maintained at 370 to 410 degree centigrade per selected cycle. HCl is recovered in a water spray absorption tower to get 30 to 32 percent aqueous HCl directly. If dry HCl is required then azeotropic mixture of HCl and H2O is circulated in the tower.

(Refer Slide Time: 23:02)



- Then to stripper where dry HCl gas is top effluent, whereas the bottom water being recirculated to absorber
- In order to remove HCl and CO_2, chlorinated gases from absorber are scrubbed with caustic soda solution
- Otherwise CO_2 would accumulated as an inert gas in recycle stream
- Final steps to produce high purity products are compression and drying with H_2SO_4 is followed by condensation and rectification

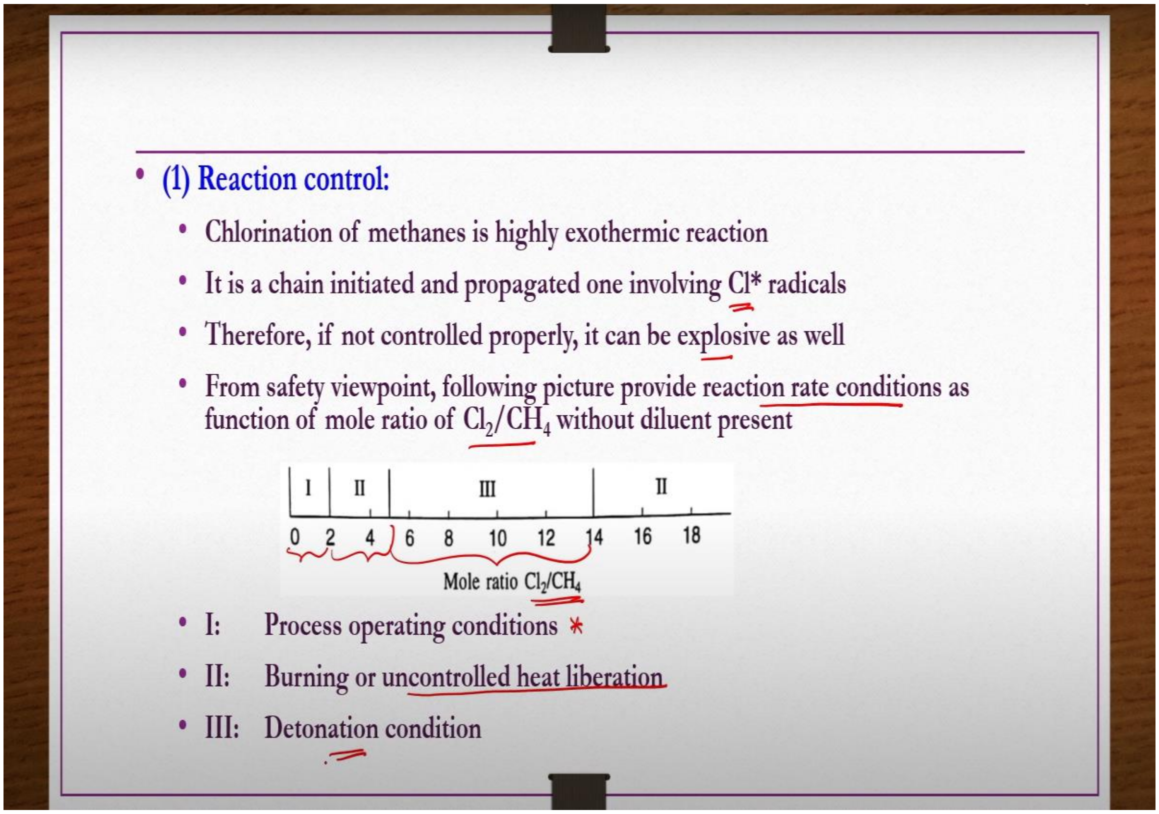
- **Major engineering problems:**
  - (1) Reaction control *
  - (2) Product ratio control * ⇐
  - (3) Utilization of HCl *

CH_4 → 1 mol
Cl_2 → 5 mol
CH_3Cl – 1 mol
CH_2Cl_2 –
$CHCl_3$ –
CCl_4 –
HCl → 4 mol

Then to stripper where dry HCl gas is top effluent whereas the bottom water being recirculated to the absorber. In order to remove HCl and CO2, chlorinated gases from absorber are scrubbed with caustic soda solution otherwise CO2 would accumulated as an inert gas in a recycle stream. Final steps to produce high purity products are compression and drying with H2SO4 is followed by condensation and rectification.

Then you get the products as seen in the flowchart. Major engineering problems of this process if you list out first is the reaction control. How are you going to control the reaction by feed ratio by chlorination process temperature what are those things how are you going to control the reaction that is very much essential. Product ratio control is also very much essential because it should be based on the market. You produce more methyl chloride but market is less for that one so the process is not going to be good for you. Then we see that lot of HCl is being formed. So when each of CH3Cl, CH2Cl2, CHCl3 and CCl4 they are formed only 1 mole for 1 mole of methane and then 5 moles of Cl2. How many moles? 4 moles of HCl you are getting so much of HCl you are getting so that much HCl you know you should able to utilize otherwise it is not going to be economical process is not going to be economical. So it is such a good process here not only you are getting the chlorinated methane but also you are getting lot of HCl which you can get a good market for it.

(Refer Slide Time: 25:05)



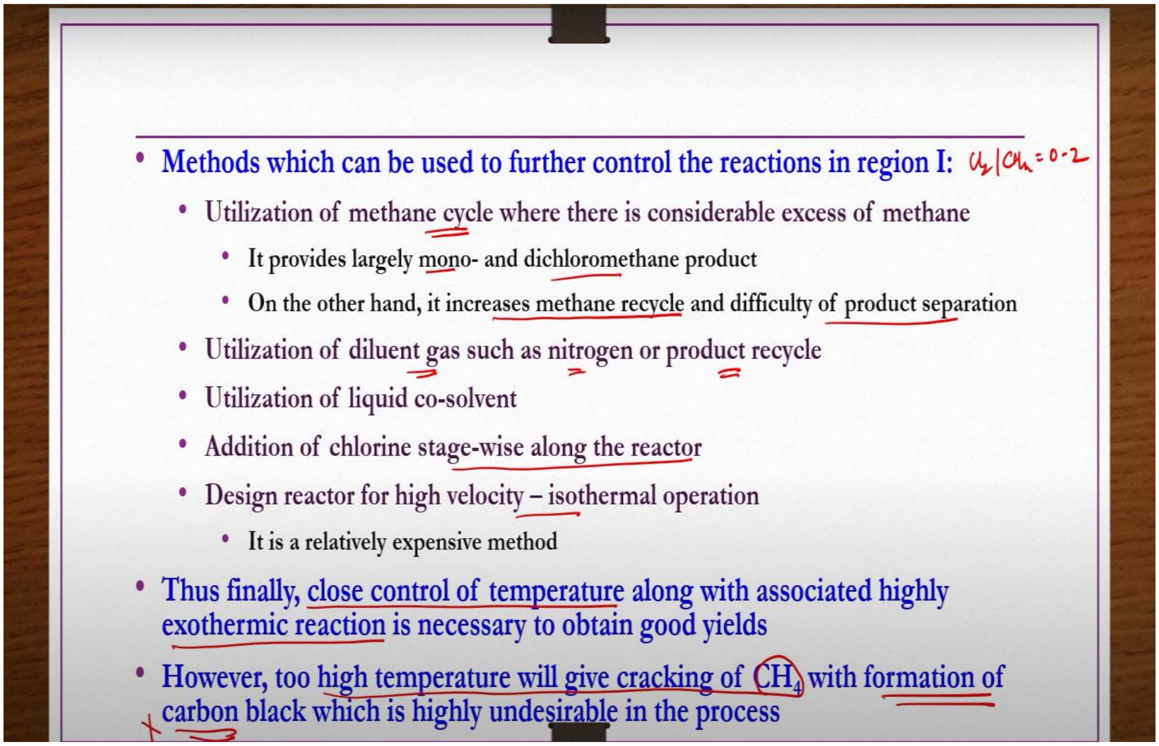
- **(1) Reaction control:**
  - Chlorination of methanes is highly exothermic reaction
  - It is a chain initiated and propagated one involving Cl* radicals
  - Therefore, if not controlled properly, it can be explosive as well
  - From safety viewpoint, following picture provide reaction rate conditions as function of mole ratio of Cl_2/CH_4 without diluent present

- I: Process operating conditions *
- II: Burning or uncontrolled heat liberation
- III: Detonation condition

Now we discussed the engineering problems under each of 3 categories. The first category is the reaction control engineering problem.Chlorination of methanes is highly exothermic reaction. It is a chain initiated and propagated one involving chloride radical so it is going to be highly exothermic and dangerous if it is not properly controlled. Therefore, if not controlled properly it can be explosive as well. From safety view point following picture provide reaction rate conditions as function of mole ratio of Cl2 to CH4 without diluent present the picture is given here. Let us say mole ratio of Cl2 to CH4 if you maintain between 0 to 2 then process operating condition that is under process operating conditions is good.

If you go towards more value of this value then more of the methane is there because this ratio is that is for the Cl2 to CH4. If more methane is there then more of the CCl4, CHCl3 may be forming and then market is for that one only. If you go for the smaller values of Cl2 to CH4 ratio then more of the methyl chloride and methylene chloride would be forming you will be having less market for that. But if you go this ratio beyond 2 and then up to 5 then what happen you know burning or uncontrolled heat liberation takes place in the process. So, that is going to be very dangerous. But if you go further higher like you know 5 to 14 then detonation condition should be there and then explosion may take place. So, you have to operate within the first regime of Cl2 to CH4 ratio of 0 to 2.

(Refer Slide Time: 26:58)



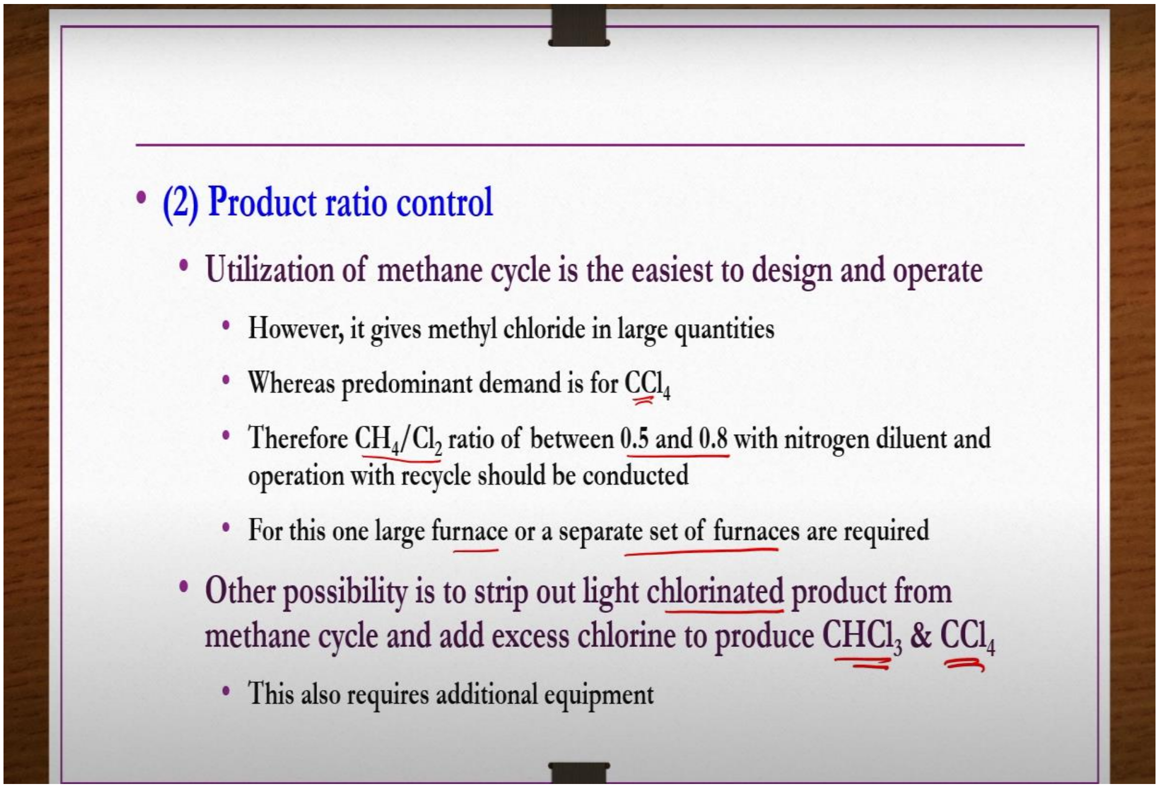
- Methods which can be used to further control the reactions in region I: $Cl_2|CH_4 = 0\text{-}2$
  - Utilization of methane cycle where there is considerable excess of methane
    - It provides largely mono- and dichloromethane product
    - On the other hand, it increases methane recycle and difficulty of product separation
  - Utilization of diluent gas such as nitrogen or product recycle
  - Utilization of liquid co-solvent
  - Addition of chlorine stage-wise along the reactor
  - Design reactor for high velocity – isothermal operation
    - It is a relatively expensive method
- Thus finally, close control of temperature along with associated highly exothermic reaction is necessary to obtain good yields
- However, too high temperature will give cracking of CH_4 with formation of carbon black which is highly undesirable in the process

Methods which can be used to further control the reaction in region where Cl2 to CH4 ratio is between 0 to 2. So, what are they utilization of methane cycle where there is considerable excess of methane is there so then more methane you can utilize. It provides largely mono and dichloromethane products that is methyl chloride and methylene chloride products you can get. But on the other hand it increases methane recycle and difficulty of product separation as well. Other option is that utilization of diluent gas such as nitrogen or product recycle.

Some portion of the product you can recycle after drying with H_2SO_4 as well as you can have the nitrogen also along with the methane recycle. Other option is that utilization of liquid co-solvent if at all suitable to control the reaction the solvent should be chosen such a way. Addition of chlorine stage wise along the reactor chlorine exothermic so rather mixing or providing high velocity chlorine or high flow rate chlorine to the reactor it would be better to allow it to the reactor slowly drop by drop or even very small flow rates.

So, that the reaction can be controlled. Then one more option is that design reactor for high velocity isothermal operations. It is relatively expensive method thus finally close control of temperature along with associated highly exothermic reaction is necessary to obtain good yields. However, too high temperature will give cracking of CH_4 with the formation of carbon black which is also highly undesirable in the products. So, you cannot go high temperature as well otherwise then this coke formation or free carbon formation takes place.

(Refer Slide Time: 29:04)

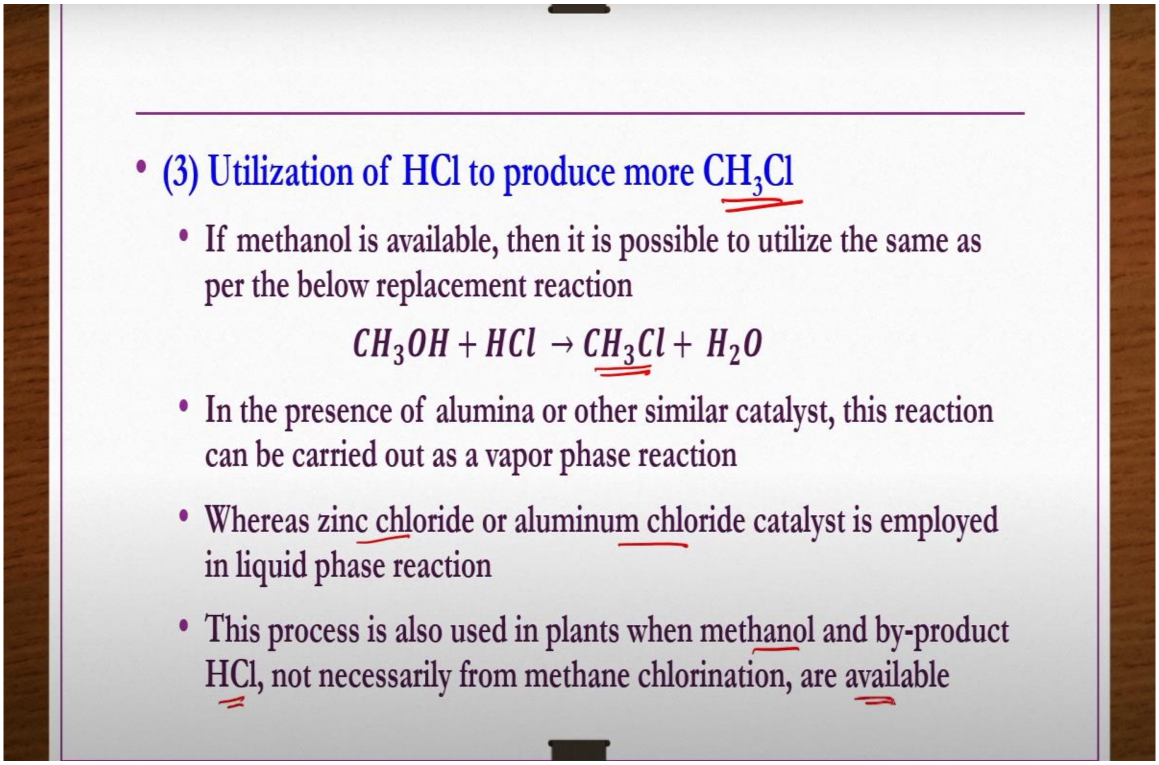


- (2) Product ratio control
  - Utilization of methane cycle is the easiest to design and operate
    - However, it gives methyl chloride in large quantities
    - Whereas predominant demand is for CCl_4
    - Therefore CH_4/Cl_2 ratio of between 0.5 and 0.8 with nitrogen diluent and operation with recycle should be conducted
    - For this one large furnace or a separate set of furnaces are required
  - Other possibility is to strip out light chlorinated product from methane cycle and add excess chlorine to produce $CHCl_3$ & CCl_4
    - This also requires additional equipment

Now coming to the major engineering problems associated with the product ratio control different methods are available utilization of methane cycle is the easiest to design and operate however it gives methyl chloride in large quantities whereas predominant demand is for CCl4.Therefore, CH4 to Cl2 ratio of between 0.5 to 0.8 with nitrogen diluent and operation with recycle should be conducted so that you know more of the carbon tetrachloride and chloroform forms rather methyl chloride and methylene chlorides. For this one large furnace or a separate set of furnaces are required.

Other possibility is to strip out a light chlorinated product that is methyl chloride or methylene chloride from the methane cycle and add excess chlorine to produce chloroform and then carbon tetrachloride. Excess of chlorine will give you carbon tetrachloride or chloroform formation. This also requires additional equipment.

(Refer Slide Time: 30:10)



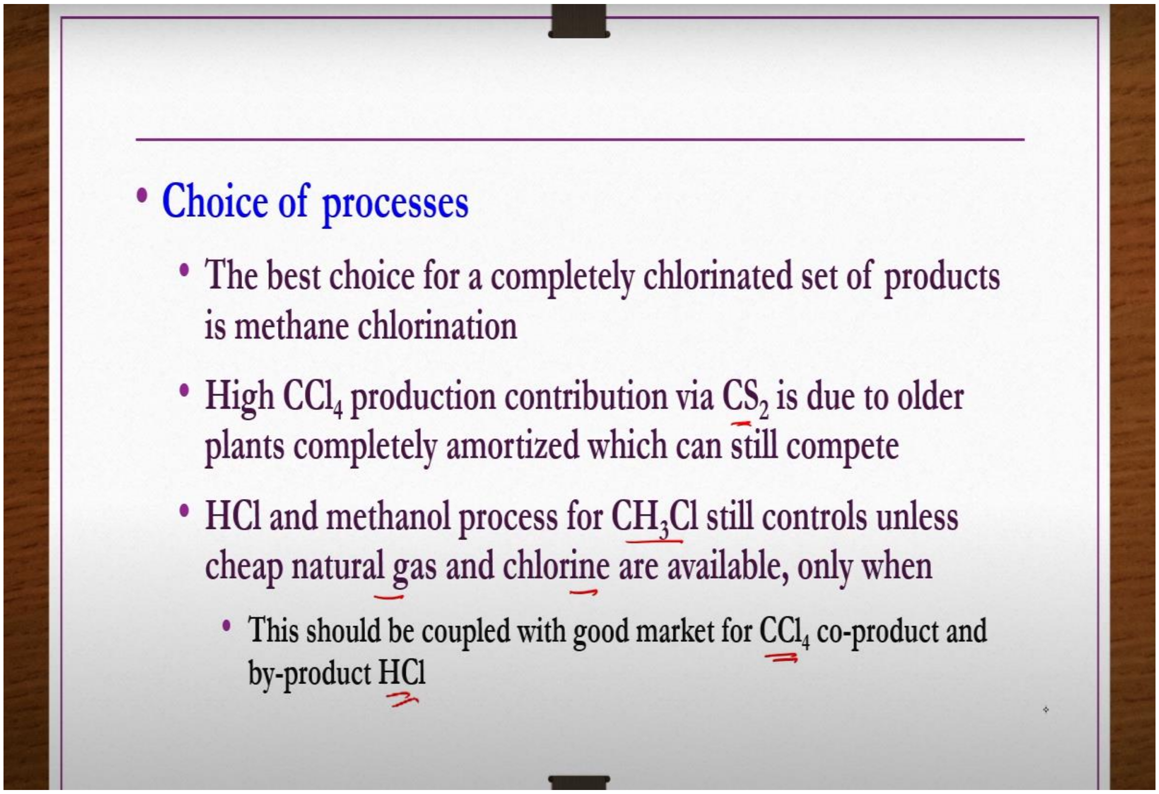
- (3) Utilization of HCl to produce more CH_3Cl
  - If methanol is available, then it is possible to utilize the same as per the below replacement reaction

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

  - In the presence of alumina or other similar catalyst, this reaction can be carried out as a vapor phase reaction
  - Whereas zinc chloride or aluminum chloride catalyst is employed in liquid phase reaction
  - This process is also used in plants when methanol and by-product HCl, not necessarily from methane chlorination, are available

Third category of major engineering problem for this direct chlorination of methane processes utilization of HCl to produce chloromethane or methyl chloride. So how it is possible? Methanol if you react with HCl then you will get this one. So in this presence of alumina or similar catalyst this reaction can be carried out in a vapor phase reaction or otherwise if you use zinc chloride or aluminum chloride catalyst then you can do this reaction in the liquid phase as well. This process is also used in plants when methanol and byproduct HCl are available.

(Refer Slide Time: 30:58)



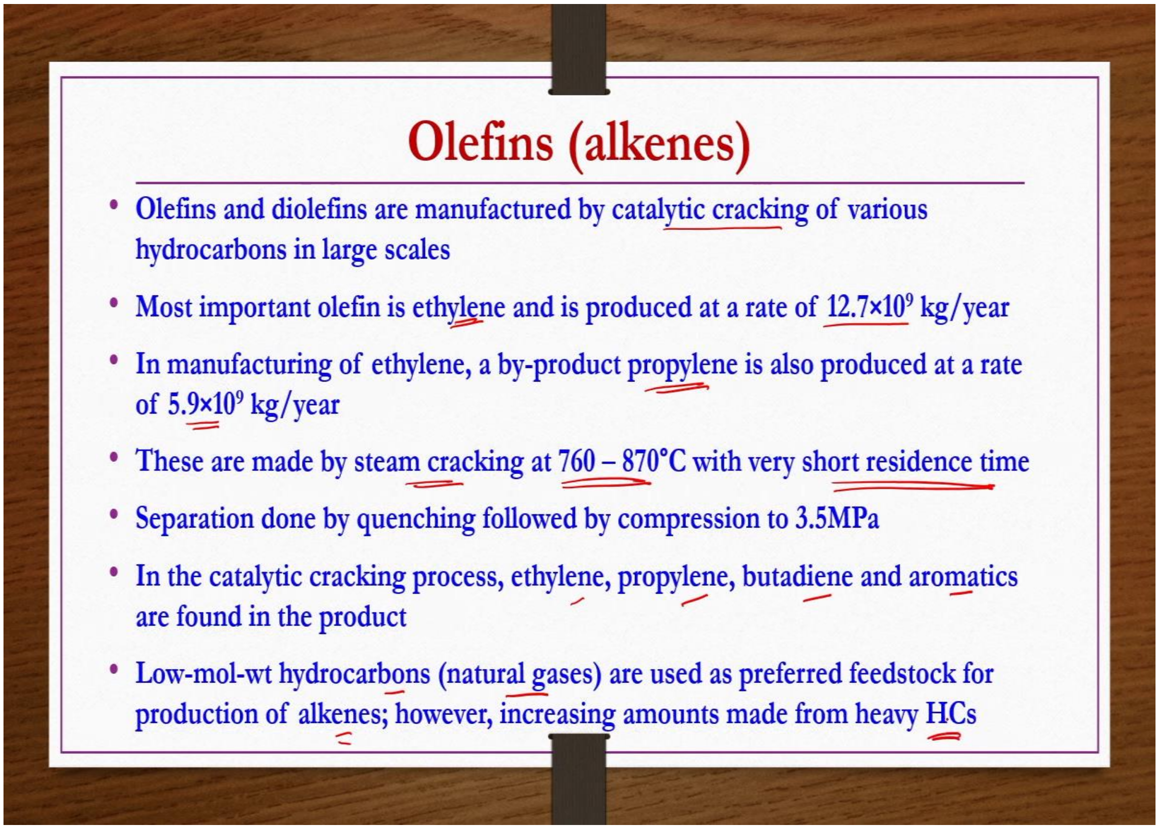
- Choice of processes
  - The best choice for a completely chlorinated set of products is methane chlorination
  - High CCl_4 production contribution via CS_2 is due to older plants completely amortized which can still compete
  - HCl and methanol process for CH_3Cl still controls unless cheap natural gas and chlorine are available, only when
    - This should be coupled with good market for CCl_4 co-product and by-product HCl

Choice of processes when different processes are available so then you have to select a process which is going to be more economical and safe for you to handle. The best choice for a completely chlorinated set of products is methane chlorination process which we just discussed. High CCl4 production contribution via CH2 is due to older plants completely amortized which can still compete. HCl and methanol process for CH3Cl still controls unless economical natural gas and chlorine are available. But only when this should be coupled with good market for CCl4 co-product and byproduct HCl. So that is all about chlorinated methanes or chloromethanes production.

With this we complete production of chemicals from C1 compounds like CO plus H2 and CH4 we have utilized and different types of chemicals we produce like methanol, formaldehyde and chloromethanes. In fact, in the previous lecture we have seen a slide where variety number of products can be produced. We cannot go into all such kind of productions of intermediate and then end products from C1 compounds. Selectively we have discussed a few.

Now we are going to discuss chemicals from C2 compounds, right? So that is from ethylene and acetylene what kind of chemicals can be produced that is what we are going to discuss. However, before producing chemicals from this ethylene and acetylene we will be having a few basics about this ethylene and acetylene and their production, okay?

(Refer Slide Time: 32:38)



Olefins (alkenes)

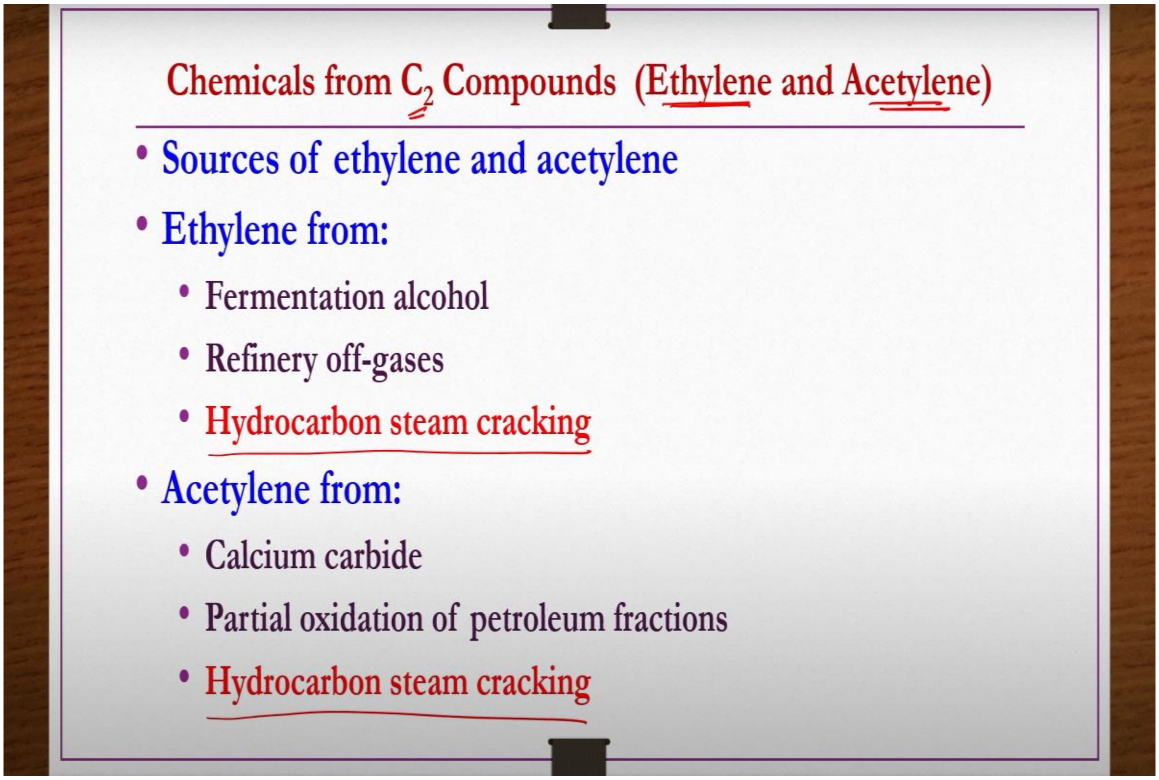
- Olefins and diolefins are manufactured by catalytic cracking of various hydrocarbons in large scales
- Most important olefin is ethylene and is produced at a rate of 12.7×10^9 kg/year
- In manufacturing of ethylene, a by-product propylene is also produced at a rate of 5.9×10^9 kg/year
- These are made by steam cracking at 760 – 870°C with very short residence time
- Separation done by quenching followed by compression to 3.5MPa
- In the catalytic cracking process, ethylene, propylene, butadiene and aromatics are found in the product
- Low-mol-wt hydrocarbons (natural gases) are used as preferred feedstock for production of alkenes; however, increasing amounts made from heavy HCs

So let us have a brief introduction about olefins because ethylene is one type of olefin. Olefins or diolefins are manufactured by catalytic cracking of various hydrocarbons in large scales in general. Most important olefin is ethylene based on the product distribution. You know ethylene is the one which is mostly used to produce different types of intermediates and end products. We are going to see a diagram depicting all such kind of products as well. And then this ethylene is produced at a rate of 12.7 multiplied by 10 power 9 kg per year. In the manufacturing of ethylene byproduct, propylene is also formed that is also we are going to see in the flowchart. It is produced at a rate of 5.9 multiplied by 10 power 9 kg per year.

Almost half of the quantity that much you know propylene is produced. Whatever the ethylene quantity is produced, at least 50% of that much quantity propylene is also produced in the same process, okay? That is what we are going to see in the flowchart as well. These are made by steam cracking at high temperatures, 700 to 800 or even higher degree centigrade, but with short residence time. Some of the process are occurring in fraction of seconds, some of them are occurring in few seconds like 5 seconds, 10 seconds or something like that. These timings also, temperature conditions also we have seen in one of the previous lectures. In fact, in the previous chapter, where we were discussing about the petroleum refinery industries.

Suppression of products done by quenching followed by compression to 3.5 megapascal because different products are forming, you have to separate, then only you can properly utilize them to produce different types of intermediates and then end products. In the catalytic cracking process, ethylene, propylene, butadiene, aromatics are also found in the product. Low molecular weight hydrocarbons such as natural gases are used as preferred feed stock for the production of alkenes which is good. However, increasing amounts are being made from the heavy hydrocarbons also, all those things we are going to discuss.

(Refer Slide Time: 34:58)



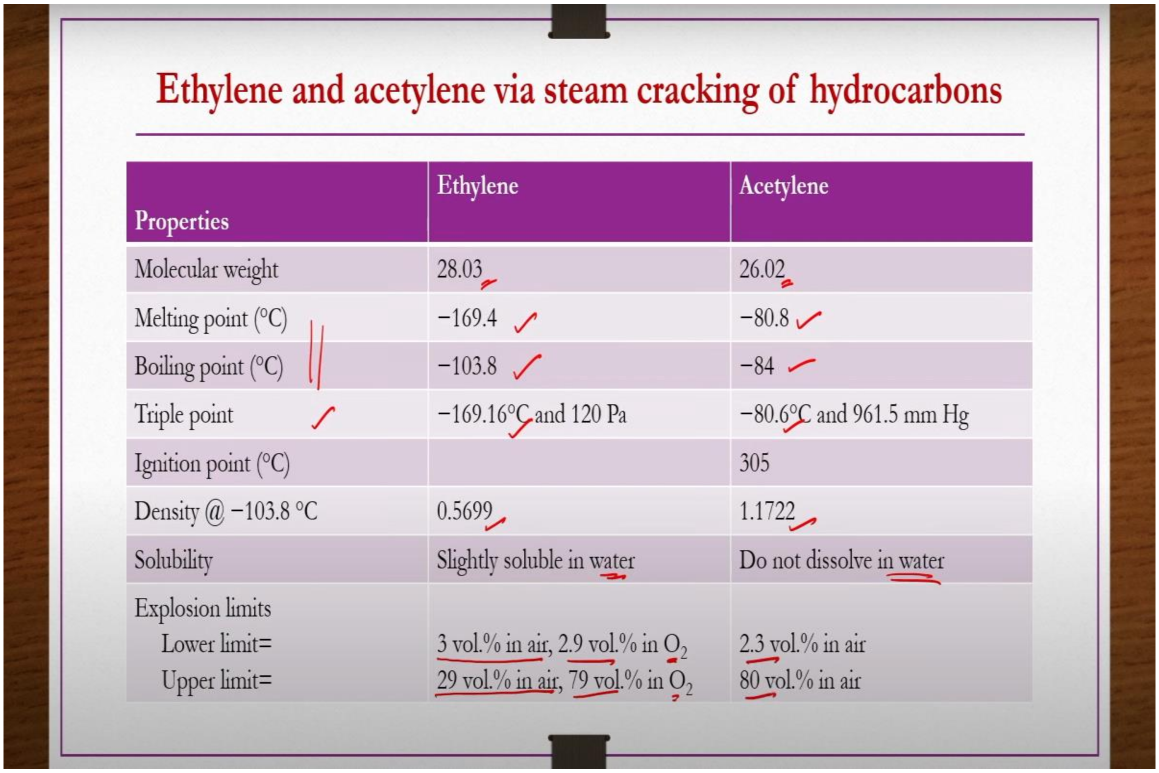
Chemicals from C_2 Compounds (Ethylene and Acetylene)

- Sources of ethylene and acetylene
- Ethylene from:
  - Fermentation alcohol
  - Refinery off-gases
  - Hydrocarbon steam cracking
- Acetylene from:
  - Calcium carbide
  - Partial oxidation of petroleum fractions
  - Hydrocarbon steam cracking

So, chemicals from C2 compounds, what are the C2 compounds we are considering in this particular lecture? Ethylene and acetylene we are going to consider, but however, making different types of chemicals from these ethylene and then acetylene, what we are going to do? We are going to see how to produce them as products.

Then we use them as raw material and then produce different types of intermediates and end products. Sources of ethylene and acetylene are provided here. Let us say ethylene can be obtained from the fermentation alcohol, from the refinery of gases, hydrocarbon steam cracking process as well can be used. Acetylene can be obtained from calcium carbide process, partial oxidation of petroleum fractions and hydrocarbon steam cracking process as well. So, we cannot discuss all of them. So, what we discuss we take a process which is common where you get both of these products, ethylene and then acetylene, right? So, hydrocarbon steam cracking we are going to discuss.

(Refer Slide Time: 36:02)



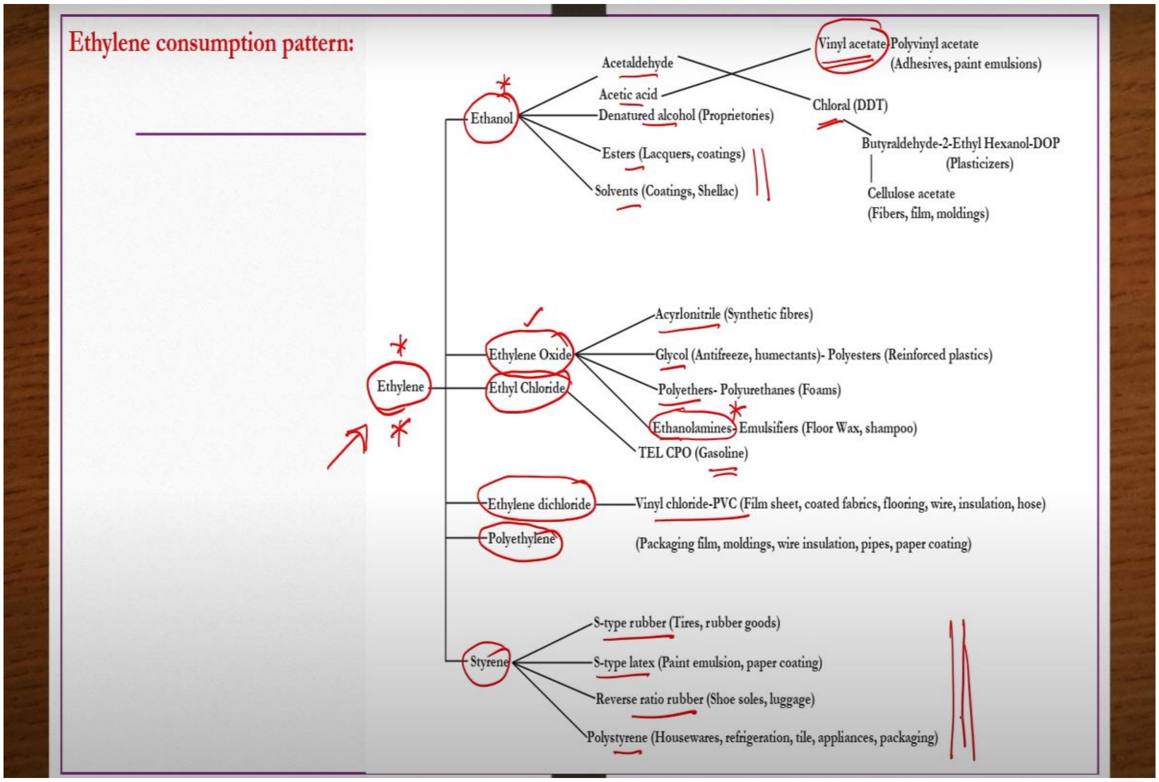
Ethylene and acetylene via steam cracking of hydrocarbons

Properties	Ethylene	Acetylene
Molecular weight	28.03	26.02
Melting point (°C)	−169.4	−80.8
Boiling point (°C)	−103.8	−84
Triple point	−169.16°C and 120 Pa	−80.6°C and 961.5 mm Hg
Ignition point (°C)		305
Density @ −103.8 °C	0.5699	1.1722
Solubility	Slightly soluble in water	Do not dissolve in water
Explosion limits Lower limit= Upper limit=	 3 vol.% in air, 2.9 vol.% in O_2 29 vol.% in air, 79 vol.% in O_2	 2.3 vol.% in air 80 vol.% in air

Before discussing process, we have pertinent properties of these materials. Molecular weight is 28.3 for the ethylene and then 26.02 for the acetylene. Melting point and then boiling points are higher for the acetylene and lower for the ethylene. Same is true for the triple point as well, okay? Density also, ethylene is having lower density compared to the acetylene. Solubility, ethylene is slightly soluble in water, but acetylene does not dissolve in water. Since both of them are in gases form, they can be explosive also.

Lower limits and upper limits of these components are provided here. For example, ethylene 3 volume percent in air and then 29 volume percent in air are lower and upper limits. Whereas, if you have pure oxygen, then 2.9 volume percent and 79 volume percent respectively are lower and upper limits. For the acetylene in air 2.3 volume percent and then 80 volume percent are lower and upper limits respectively.

(Refer Slide Time: 37:14)



Ethylene consumption pattern:

Ethylene

Ethanol

Acetaldehyde

Acetic acid

Denatured alcohol (Proprietories)

Esters (Lacquers, coatings)

Solvents (Coatings, Shellac)

Vinyl acetate-Polyvinyl acetate (Adhesives, paint emulsions)

Chloral (DDT)

Butyraldehyde-2-Ethyl Hexanol-DOP (Plasticizers)

Cellulose acetate (Fibers, film, moldings)

Ethylene Oxide

Ethyl Chloride

Acyrlonitrile (Synthetic fibres)

Glycol (Antifreeze, humectants)- Polyesters (Reinforced plastics)

Polyethers- Polyurethanes (Foams)

Ethanolamines- Emulsifiers (Floor Wax, shampoo)

TEL CPO (Gasoline)

Ethylene dichloride

Vinyl chloride-PVC (Film sheet, coated fabrics, flooring, wire, insulation, hose)

Polyethylene

(Packaging film, moldings, wire insulation, pipes, paper coating)

Styrene

S-type rubber (Tires, rubber goods)

S-type latex (Paint emulsion, paper coating)

Reverse ratio rubber (Shoe soles, luggage)

Polystyrene (Housewares, refrigeration, tile, appliances, packaging)

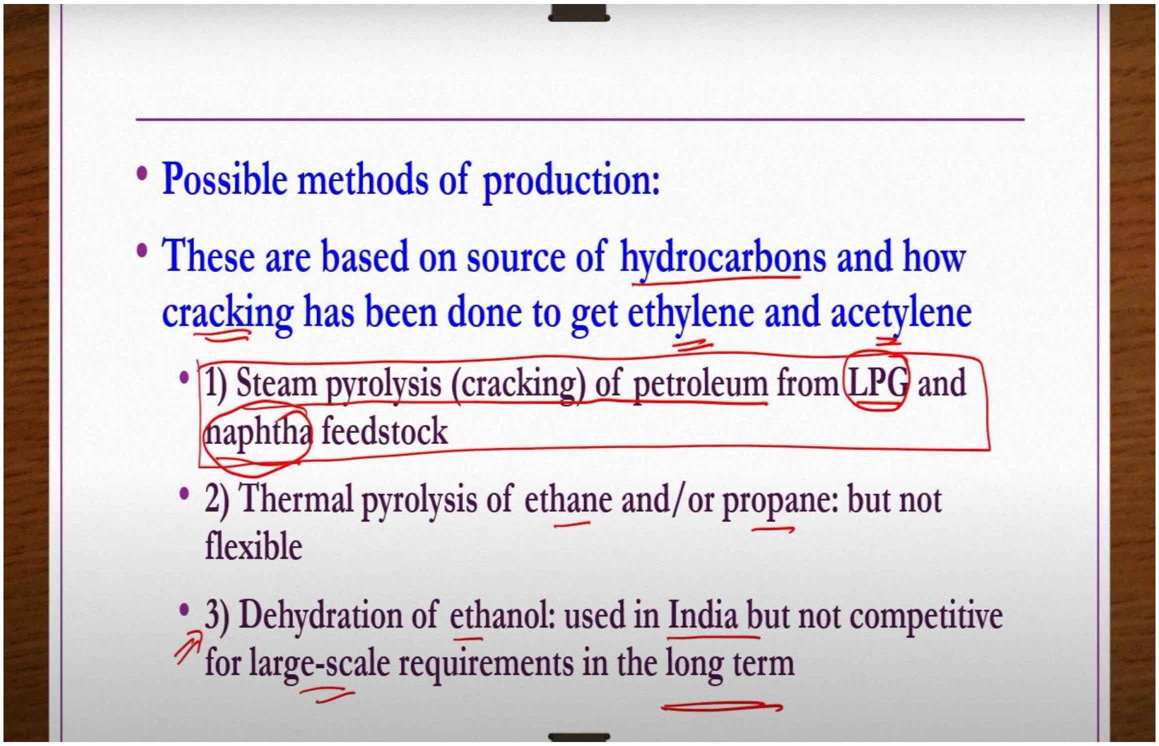
Now, we see ethylene consumption pattern. What does it mean by how many different ways ethylene can be utilized? First, we produce the ethylene. Why are we concentrating more on the production of ethylene? Because it is having so much of consumption pattern. It may be utilized to produce different types of intermediates and products as shown here. Let us say if you use ethylene as raw material or primary chemical, then you can get intermediates like ethanol, ethylene oxide, ethyl chloride, ethylene dichlorides and then end product like polyethylene, again intermediates like styrenes you can get.

So today's lecture we are going to discuss production of ethylene. In the end of the today's lecture we are going to discuss the production of ethanol as well. But in the next class we will be discussing about ethylene oxide and then other types of intermediates produced from the ethylene. So, let us say this ethanol can be further utilized to produce acetaldehyde, acetic acid, denatured alcohol, ester, solvents for different purpose it is used not only to produce some chemicals but also some end chemicals also like this. So like this, this acetic acid may be further utilized to produce vinyl acetate which we are going to discuss in the next lecture.

Acetaldehyde may be used for the production of chloral and then cellulose acetate, etc. Ethylene oxide is very good intermediate for the production of different types of products like acrylonitriles, glycols, polyethers, polyurethanes or foams and then ethanol amines which we are going to discuss how is being produced in the next class. Ethyl chloride can be used as a gasoline as well. Like that different intermediates or different products can be produced. Styrene can be used to produce different types of rubbers, S type rubber, S type latex, reverse ratio rubber, polystyrene, etc.

These many end products can be produced. See now using the ethylene you can produce so many. Only a few are represented here. Again some of them are again further utilized to produce more chemicals. So, that is the reason out of the olefins ethylene is the most important one because it is utilized for production of huge number of chemicals either directly or as a basis to get some intermediates and then from those intermediates again getting more chemicals all you know wide spectrum of product is possible when the ethylene is the base or primary material.

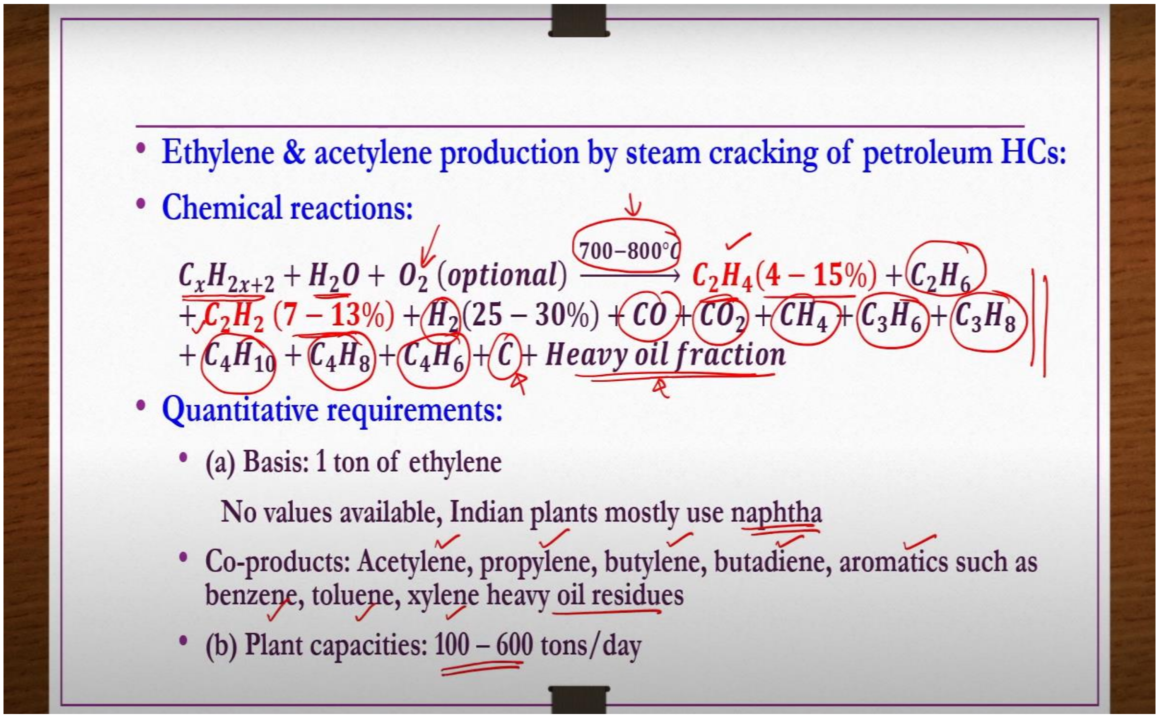
(Refer Slide Time: 40:13)



- Possible methods of production:
- These are based on source of hydrocarbons and how cracking has been done to get ethylene and acetylene
  - 1) Steam pyrolysis (cracking) of petroleum from LPG and naphtha feedstock
  - 2) Thermal pyrolysis of ethane and/or propane: but not flexible
  - 3) Dehydration of ethanol: used in India but not competitive for large-scale requirements in the long term

So, possible methods of production there are different methods are there that depends on the source of hydrocarbons and how the cracking or pyrolysis has been done and then product obviously it will be having both ethylene and then acetylene as well. One of the famous processes steam pyrolysis or cracking of petroleum from LPG and naphtha feedback. You can use LPG as well as the naphtha as feedstock to produce ethylene and acetylene depending on your resources of raw materials, but the process is same which is steam pyrolysis or steam cracking. Another process is thermal pyrolysis of ethane and or propane, but it is not flexible. We are going to discuss that one anyway. The dehydration of ethanol it is used in India, but it is not competitive for the large scale requirement in the long term. So, these are good this process is good for the small scale as well as for the short time requirements. If you want to fulfill all your long term requirement, this process is not suitable. However, we are going to discuss only one method here again that is this process using LPG or Naphtha as feedstock and doing the steam cracking to get the required ethylene and acetylene.

(Refer Slide Time: 41:40)



- Ethylene & acetylene production by steam cracking of petroleum HCs:
- Chemical reactions:

$$C_xH_{2x+2} + H_2O + O_2\,(optional) \xrightarrow{700-800°C} C_2H_4(4-15\%) + C_2H_6 + C_2H_2\,(7-13\%) + H_2(25-30\%) + CO + CO_2 + CH_4 + C_3H_6 + C_3H_8 + C_4H_{10} + C_4H_8 + C_4H_6 + C + Heavy\ oil\ fraction$$

- Quantitative requirements:
  - (a) Basis: 1 ton of ethylene

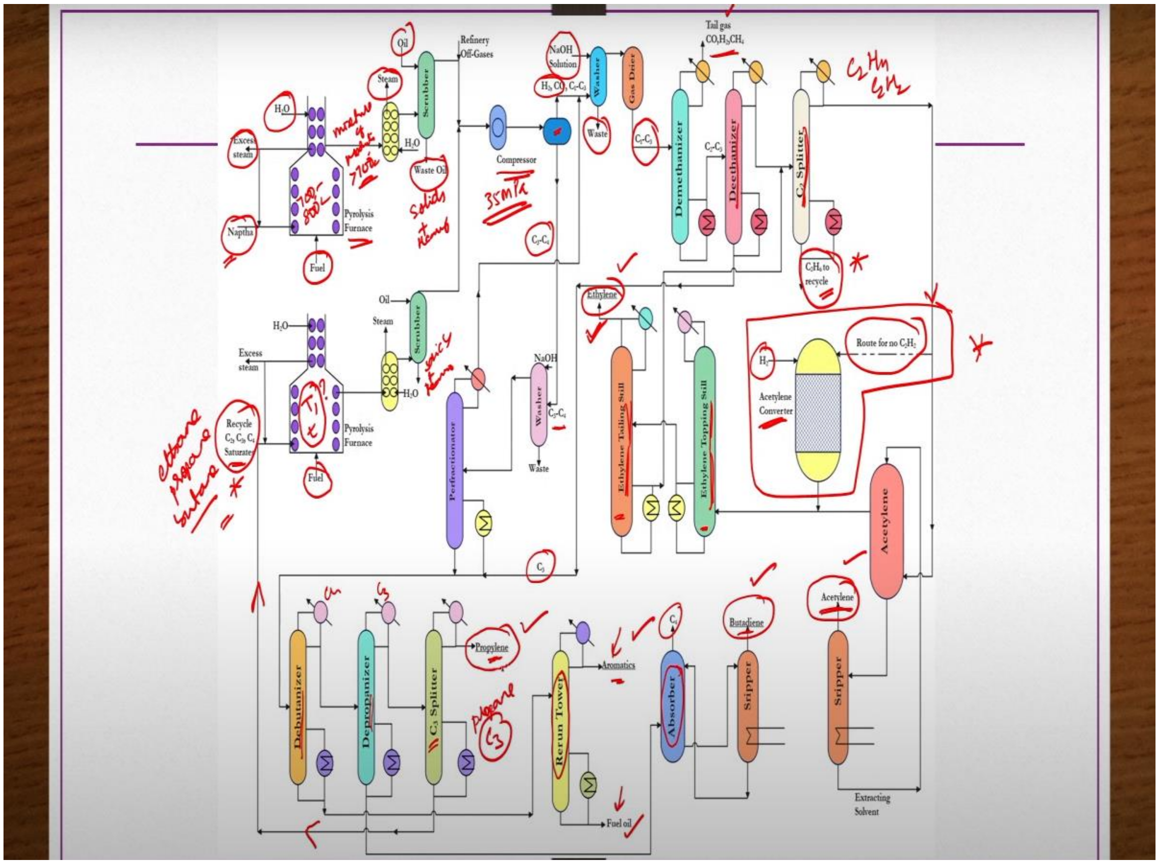
    No values available, Indian plants mostly use naphtha
  - Co-products: Acetylene, propylene, butylene, butadiene, aromatics such as benzene, toluene, xylene heavy oil residues
  - (b) Plant capacities: 100 – 600 tons/day

So, that we are going to discuss now. Chemical reaction if you see let us say whatever the LPG or naphtha that you take the generalized formula if it is represented as CxH2x plus 2, then you use the steam at high temperature 700 to 800 degrees centigrade and do the cracking O2 may be used as optional. It may not be compulsory everywhere, then you get 4 to 15% of ethylene and then 7 to 13% of acetylene. So, in addition to ethylene and then acetylene you also get ethane, propane, propylene, butane, butylene, etc. This kind of products then H2, CO, CO2, CH4, C4H6, some free carbon and then heavy oil fractions etc. also forming. So, that means there is also possibility of solid products, solids formation in the product and there is also possibility of heavy oils formation in the steam cracking process.

Quantitative requirements for 1 ton of ethylene usually the numbers are not available but Indian plants mostly they use naphtha as raw material. Co-products, acetylene, propylene, butylene, butadiene, aromatics such as benzene, toluene, xylene, heavy oil residues etc.

you will be getting as co-products as shown in the reaction, okay? So, the temperature and then reaction time are going to be very important in order to control the product distribution, okay? Plant capacity is usually 100 to 600 tons per day.

(Refer Slide Time: 43:34)



Now, we have a flowchart for the production of ethylene. So, now in this flowchart what you can see? You have a pyrolysis furnace. Let us say if you have naphtha as a feedstock, then you take it to the pyrolysis reactor from the bottom and then from the top you supply the steam. Now, in this reactor you have to maintain temperature 700 to 800 degrees centigrade. So, for that purpose fuel is also being utilized. Whatever the excess steam is there that can be collected. Now, here from this product mixture, products, co-products, etc. would be there.

So, they would be also at high temperature more than 700 degrees centigrade. So, what you do? You have to reduce the temperature so that separation can be done subsequently as shown here in the flowchart. So, for that purpose you pass through waste steam heat boiler where you recover the heat as in the form of steam. After reducing the temperature by collecting the energy in the form of steam, what you do? You take the mixture to scrubber where you scrub with the oil so that to remove solids and then heavy fractions like heavy oils, etc. would be recovered in the waste oil.

After removing the solids and then heavy fractions that would be taken to the subsequent step. Let us say if your feed is ethane, propane and then butane, these are saturated. So, then they can also be taken to the pyrolysis furnace separately. Why separately? Because here the temperature and then time of the reaction are very much different compared to this one. That is the reason separately they are being handled if you have both the feeds. So, excess steam is collected, fuel is supplied from the bottom in order to get the required energy for the reaction to take place. After the reaction, the reaction mixture is passed through waste heat steam boiler to recover the steam from the product mixtures and then after that they will be scrubbed with the oils to remove the solids and then heavy fractions as a bottoms. After removing them the gases mixture or product mixture whatever is there that is taken to the compressor. To this compressor actually along with this product mixture or refinery of gases may also be taken because the compressor is designed in such a way so that even the refinery of gases also can be taken.

Here the compression is done to 35 mega Pascal's. Then after that the mixture would be taken to flash vaporizer. This is the flash vaporizer. Here what you do? You remove like H2CO and then methane etcetera, methane H2CO etcetera that you remove as the top and then whatever the bottoms are there, there would be something like C3, C4 compounds would be there. They would be again scrubbed with NaOH separately here and then after separating whatever the top products or gases etcetera are there, they will be C2, C3 components they will be taken to another washer at the top. So here prefractionator is there in order to, this C3, C4 they would be having both propane, propylene, butane, butylene etcetera.

So then what you do? Usually prefractionation you do and then separate out whatever the C3 components etcetera are there and then remaining one you can take it to the wash. So after this flash vaporization when you separate out the methane, H2CO etcetera, then the remaining mixture whatever is there that you take to a washer where scrubbing with NaOH solution is done to remove the CO2 etcetera these kind of components. Then whatever the gas is there that would be dried using the alumina silica beds etcetera. After this primarily you will be having C1 to C3 chemicals. So here C1 chemicals are nothing but the methane etcetera, they will be removed in a demethanizer and then collected along with the CO and H2 as tail gases from the top.

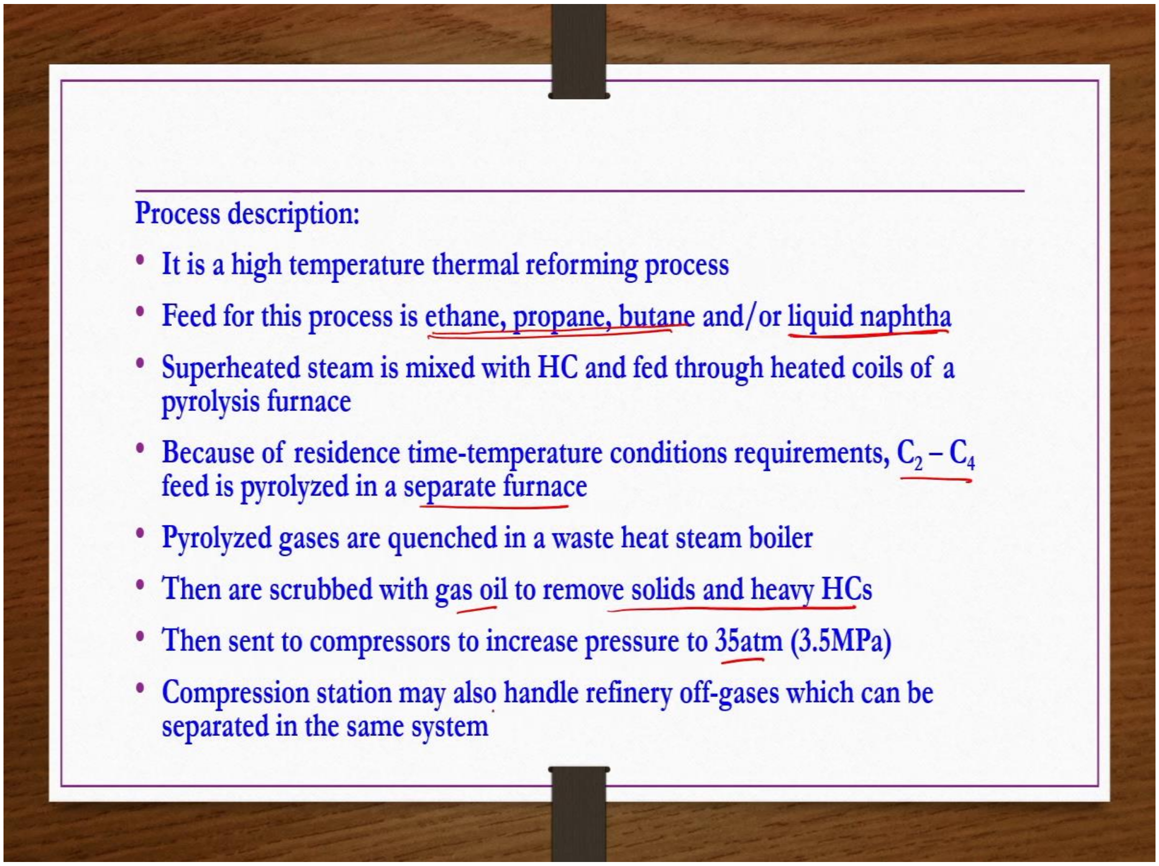
Then after removing the methane whatever the ethane and C2, C3 chemicals are there those will be taken to de-ethanizer where ethane would be separated out. So that you take it to the C2 splitter because in the ethane mixture you do not have only ethane you will be having ethylene also. So that ethylene you collect, acetylene also may be there so they will be taken back. Whereas the ethane after separating out that can be taken as a recycle, this ethane can be taken to the reactor as a recycle. Whereas after de-ethanizer whatever the mixture is there that mixture is primarily having C3 components like propane, propylene, etcetera.

This kind of components would be there some amount of butane, butylene etcetera may also be there. So that mixture would be taken to the butane to remove the butanes. After removing the butane mixture is taken to the depropanizer to remove the propanes. So those products, let us say here butane whatever you remove that you take to the rerun tower because in this one you may also having the along with the after butanes you are getting from the top from the bottom your whatever the heavy fractions are there aromatics, heavy fuels, etcetera would be there. So those things you can take to rerun tower to separate aromatics and then fuel oil as the top and bottom products. After the depropanizer, so propanes whatever are there you take from the top and then heavier fractions whatever are there they will be collected from the bottom and then sent to the absorber where if at all butane, butylene, etcetera are there, they will be absorbed and separated out as a 2 different products like butylene, etcetera.

So then after this debutanizer and depropanizer the mixture whatever is there primarily C3 mixture would be there where propylene you separate it as a product as a top product whereas the bottom one would be nothing but the propane. This propane which is nothing but C3 saturate that can be recycled back to the reactor. Now this is now here what you got? You got propylene, aromatics, butadiene as products, whereas after this C2 splitter where you separated out the ethane from the top primarily you will be having C2H4, C2H2 ethylene and acetylene would be there. So that you take to a acetylene reactor where you separate out the acetylene in a stripper using an extracting solvent. Then remaining of the mixture whatever is there that would be primarily ethylene that ethylene would be taken to ethylene topping steel and then tailing steel depending on its content how much ethylene is present and then it is collected as product from the top.

Let us say you do not want any acetylene as a product, then what you do? This mixture of C2H4 and C2H2 whatever is there that you take to acetylene converter where you react with hydrogen to convert that acetylene also into the ethylene and then you do the ethylene concentrating by this ethylene topping steels and then ethylene tailing steels and then get the ethylene only as the product. This step you do if you need only ethylene, you do not want acetylene, then only this step should be done. This is the flowchart now you can see either you use naphtha or you use the C3, C4, C2 saturates as a feedstock so many products not only ethylene you are getting you are getting acetylene, butadiene, aromatics, fuel oil, propylene so many products you are getting. So propylene also you are getting this is C3 chemical, okay?

(Refer Slide Time: 52:46)



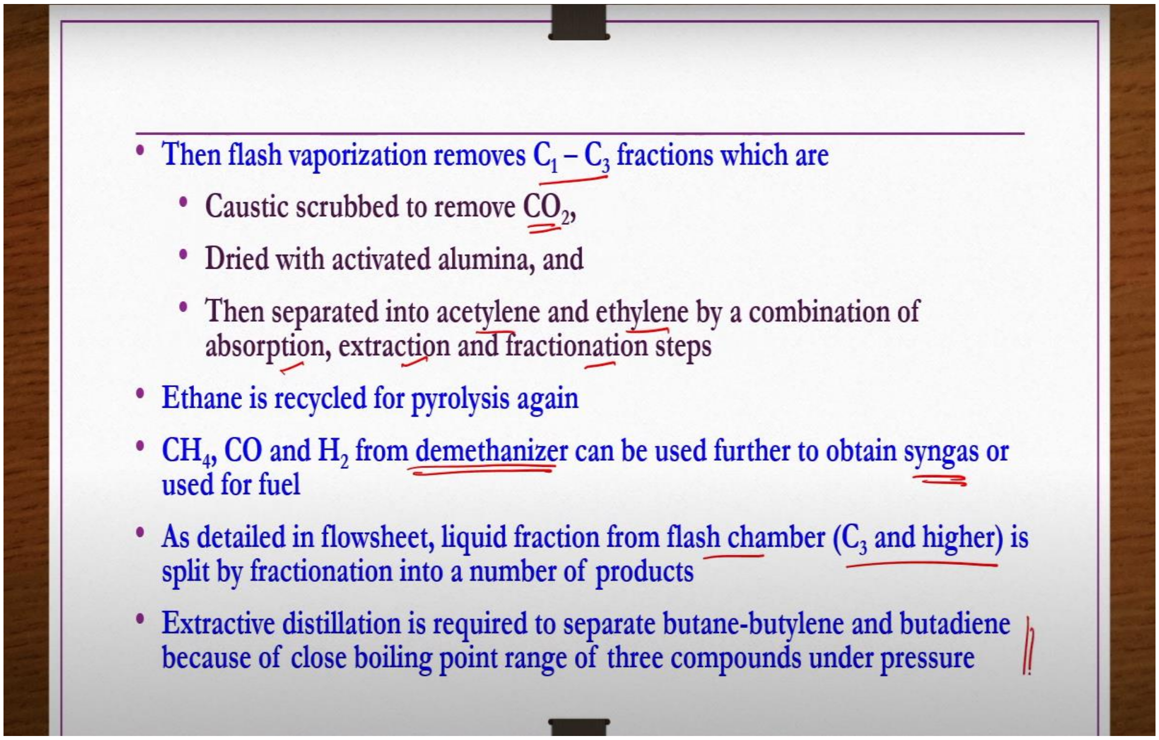
Process description:

- It is a high temperature thermal reforming process
- Feed for this process is ethane, propane, butane and/or liquid naphtha
- Superheated steam is mixed with HC and fed through heated coils of a pyrolysis furnace
- Because of residence time-temperature conditions requirements, $C_2 - C_4$ feed is pyrolyzed in a separate furnace
- Pyrolyzed gases are quenched in a waste heat steam boiler
- Then are scrubbed with gas oil to remove solids and heavy HCs
- Then sent to compressors to increase pressure to 35atm (3.5MPa)
- Compression station may also handle refinery off-gases which can be separated in the same system

Process description, it is a high temperature thermal reforming process, feed for this process is ethane, propane, butane or liquid naphtha as well. So, depending on the feed, your temperature and then reaction time are going to change that is the reason depending on the feed for these feed you have separate furnace and then for these feed you have separate furnace.

Superheated steam is mixed with hydrocarbon and fed through heated coils of a pyrolysis furnace because of residence time temperature conditions requirement which are different for both of the types of raw materials, you know C2 to C4 feed is pyrolyzed in a separate furnace. Pyrolyzed gases are quenched in a waste heat steam boiler, then are scrubbed with gas oil to remove solids and then heavy hydrocarbons, then sent to compressors to increase pressure to 35 atmosphere. Compression station may also handle refinery of gases which can be separated in the same system.

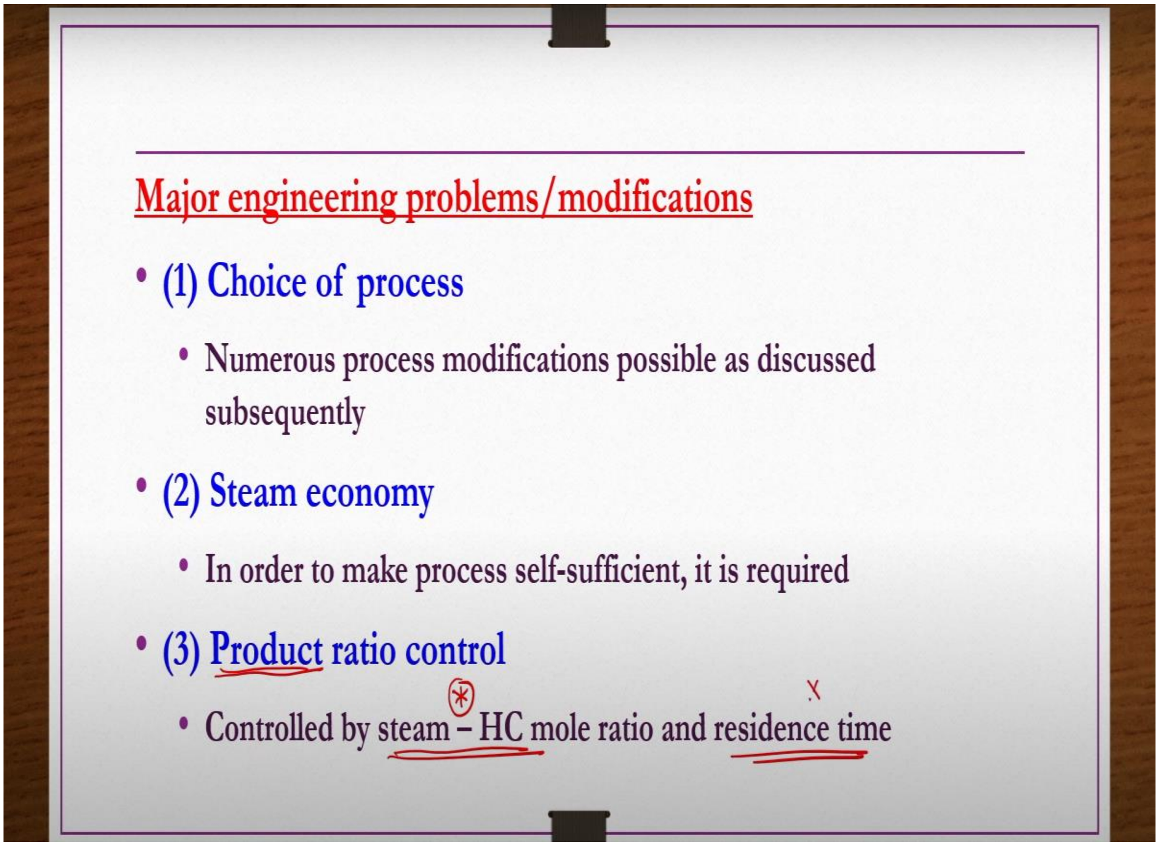
(Refer Slide Time: 53:57)



- Then flash vaporization removes $C_1 - C_3$ fractions which are
  - Caustic scrubbed to remove CO_2,
  - Dried with activated alumina, and
  - Then separated into acetylene and ethylene by a combination of absorption, extraction and fractionation steps
- Ethane is recycled for pyrolysis again
- CH_4, CO and H_2 from demethanizer can be used further to obtain syngas or used for fuel
- As detailed in flowsheet, liquid fraction from flash chamber (C_3 and higher) is split by fractionation into a number of products
- Extractive distillation is required to separate butane-butylene and butadiene because of close boiling point range of three compounds under pressure

Then flash vaporization removes C1 to C3 fractions which are caustic scrub to remove CO2 dried with activated alumina and then separated into acetylene and ethylene by a combination of absorption extraction and fractionation steps as shown in the flowchart. Ethane is recycled for pyrolysis again, whereas CH4, CO and H2 can be utilized as synthesis gas are used as a fuel because these things are you are getting as a top from the demethanizer column. As detailed in the flowchart liquid fraction from flash chamber that is C3 and then higher is split by fractionation into a number of products. Extractive distillation is required to separate butane, butylene and butadiene because of close boiling point range of 3 components under pressure. We have shown them in the flowchart.

(Refer Slide Time: 54:53)



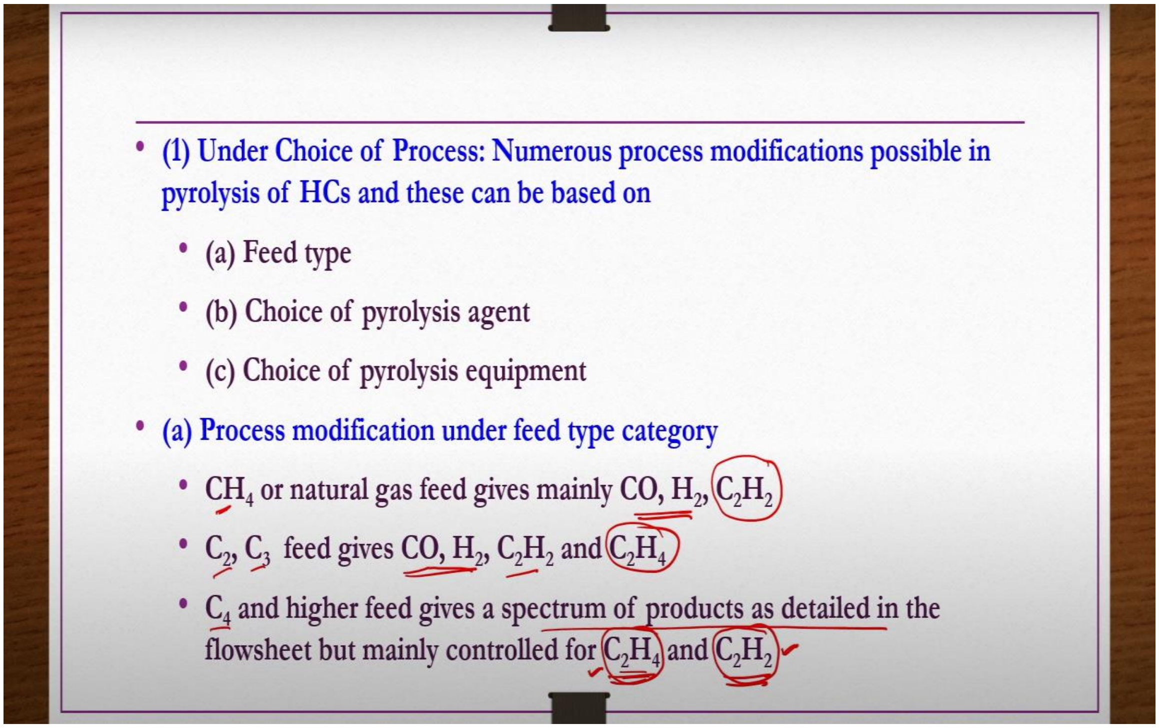
Major engineering problems/modifications

- (1) Choice of process
  - Numerous process modifications possible as discussed subsequently
- (2) Steam economy
  - In order to make process self-sufficient, it is required
- (3) Product ratio control
  - Controlled by steam – HC mole ratio and residence time

Coming to the major engineering problems or modifications that may be possible for the process are listed here. 3 types are there, first one is the choice of process, second one is the steam economy, third one is the product ratio control. We have seen that the product is having so many co-products. So, then how to control the product ratio that is also very important thing that should be based on your market for a given product or co-product. Under the choice of process, numerous modifications are possible like you know first is the feed, then how are you doing the you know so called pyrolysis or cracking whether it is catalytic, non-catalytic, whether are you using only steam or you are using oxygen also for partial combustion like different modifications are possible that we are going to discuss in the next slide.

Steam economy for any process is very much essential to make self-sufficient as well as to make an economic process or economic plant. Product ratio control, it depends on the steam hydrocarbon mole ratio. What ratio of steam to hydrocarbons are you selecting? It is one of the important parameter which is going to define your product distribution in addition to that one residence time is also an essential one.

(Refer Slide Time: 56:21)

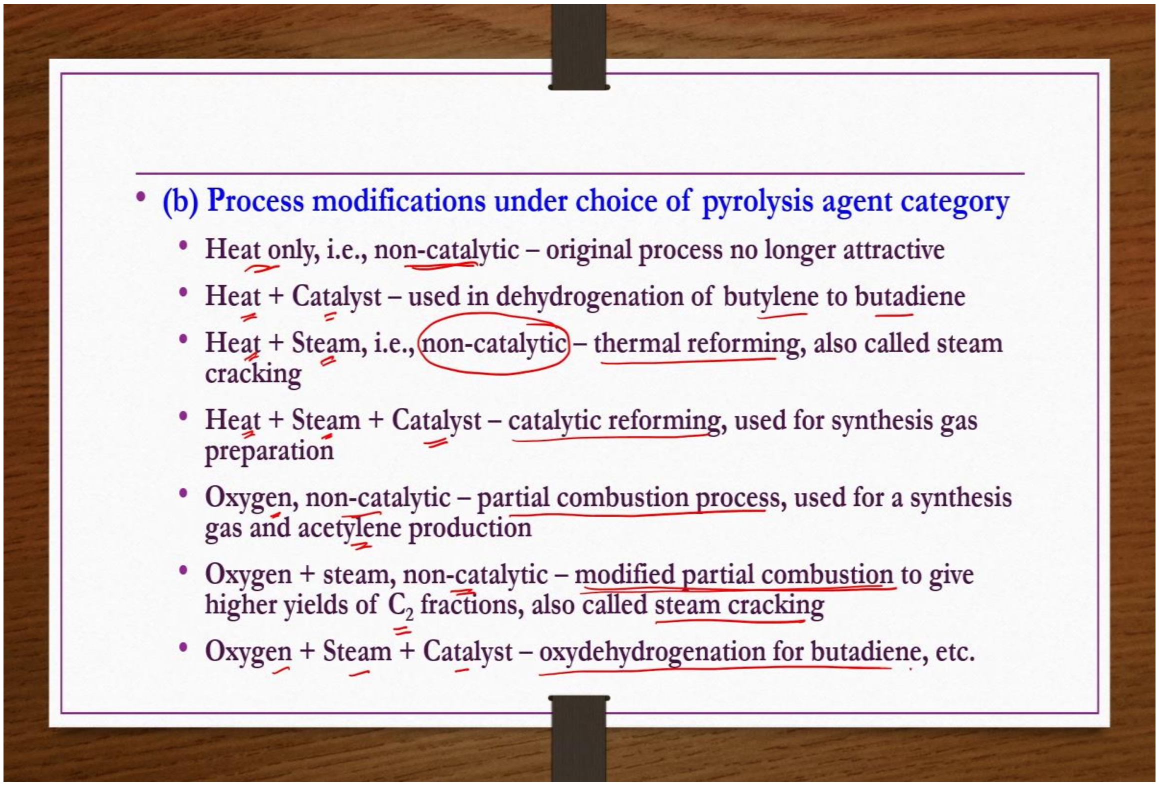


- (1) Under Choice of Process: Numerous process modifications possible in pyrolysis of HCs and these can be based on
  - (a) Feed type
  - (b) Choice of pyrolysis agent
  - (c) Choice of pyrolysis equipment
- (a) Process modification under feed type category
  - CH_4 or natural gas feed gives mainly CO, H_2, C_2H_2
  - C_2, C_3 feed gives CO, H_2, C_2H_2 and C_2H_4
  - C_4 and higher feed gives a spectrum of products as detailed in the flowsheet but mainly controlled for C_2H_4 and C_2H_2

So, under choice of process, numerous process modifications possible in pyrolysis of hydrocarbons and these can be based on feed type is one thing, then choice of pyrolysis agent, then choice of pyrolysis equipment. So, under the feed type, you can have CH4 or the natural gas as the feed, but it will give only acetylene along with the synthesis gas, but if you use C2 and C3 feed that is ethane and propane feed, then you can get in addition to this synthesis gas and acetylene, you will also get ethylene. If you use C4 or higher feed like naphtha, etc., that gives spectrum of products as detailed in the flowchart, but mainly controlled for production of these 2. Why to control these 2 products only? Because we have seen if you have ethylene, so many number of other chemicals you can produce.

Same is similar way next to the ethylene, acetylene is the most important intermediate which can be used wide variety of products. Because of that one, you have to select these ratios, feed, etc., such a way that more ethylene followed by the acetylene are forming in the product.

(Refer Slide Time: 57:46)



- (b) Process modifications under choice of pyrolysis agent category
  - Heat only, i.e., non-catalytic – original process no longer attractive
  - Heat + Catalyst – used in dehydrogenation of butylene to butadiene
  - Heat + Steam, i.e., non-catalytic – thermal reforming, also called steam cracking
  - Heat + Steam + Catalyst – catalytic reforming, used for synthesis gas preparation
  - Oxygen, non-catalytic – partial combustion process, used for a synthesis gas and acetylene production
  - Oxygen + steam, non-catalytic – modified partial combustion to give higher yields of C_2 fractions, also called steam cracking
  - Oxygen + Steam + Catalyst – oxydehydrogenation for butadiene, etc.

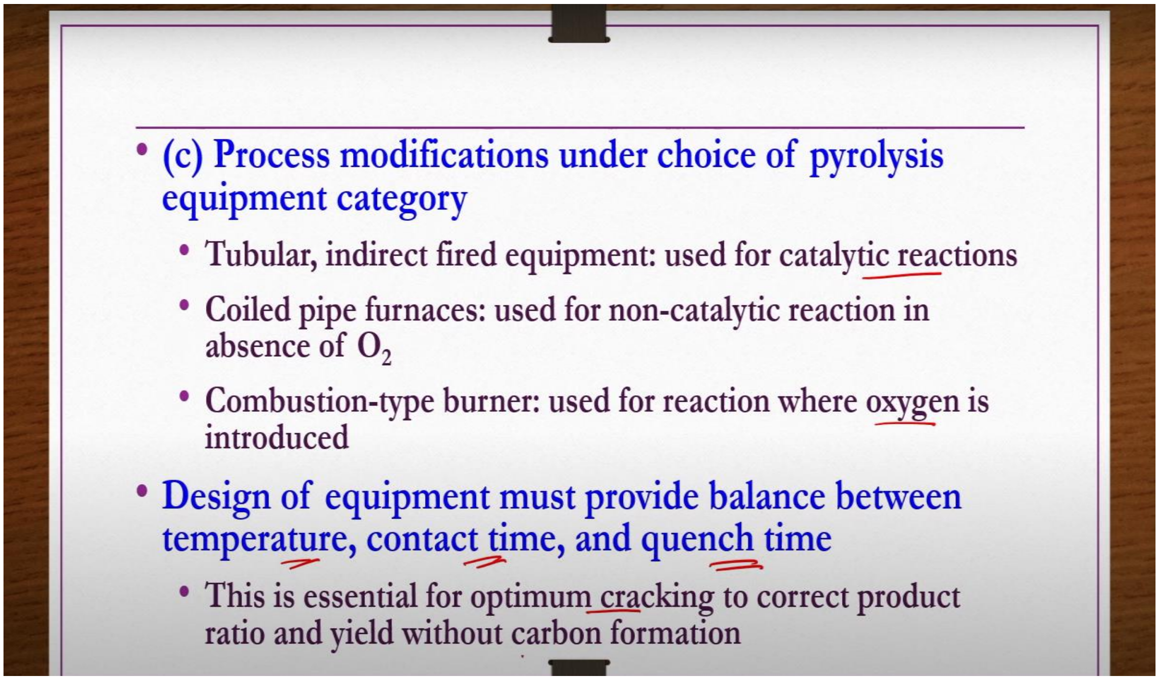
Under the choice of pyrolysis agent of process modifications, as discussed n number of possibilities are there. Let us say if you use only heat that is non-catalytic pyrolysis you are doing which is the original process but no longer attractive because it gives more gases as well as the more free carbon which is not good from the economics point of view.

Then heat and then catalyst which is known as the catalytic pyrolysis used in dehydrogenation of butylene to butadiene that is one process. Then you can have the heat plus steam which is known as the thermal reforming or steam reforming. We are not using any catalyst here, so it is a non-catalytic process. It is also known as the steam cracking. Then in addition to the heat and steam if you also have the catalyst then that is known as the catalytic reforming and it is used for synthesis gas preparation in general.

Then oxygen you are using but without any catalyst, then partial combustion will also take place because of the presence of oxygen. So then it is known as partial combustion process. It is also used for synthesis gas and acetylene production. Now oxygen plus steam but without catalytic then we call it modified partial combustion because only partial combustion is not taking place. Steam is there, so some pyrolysis would also be taking place.

So that is the reason it is known as modified partial combustion to give higher yields of C2 fractions like ethylene and acetylene. It is also called as steam cracking. So this steam cracking can be catalytic also if you are using catalyst along with the oxygen and steam which is often used for oxy dehydrogenation for butadiene.

(Refer Slide Time: 59:39)

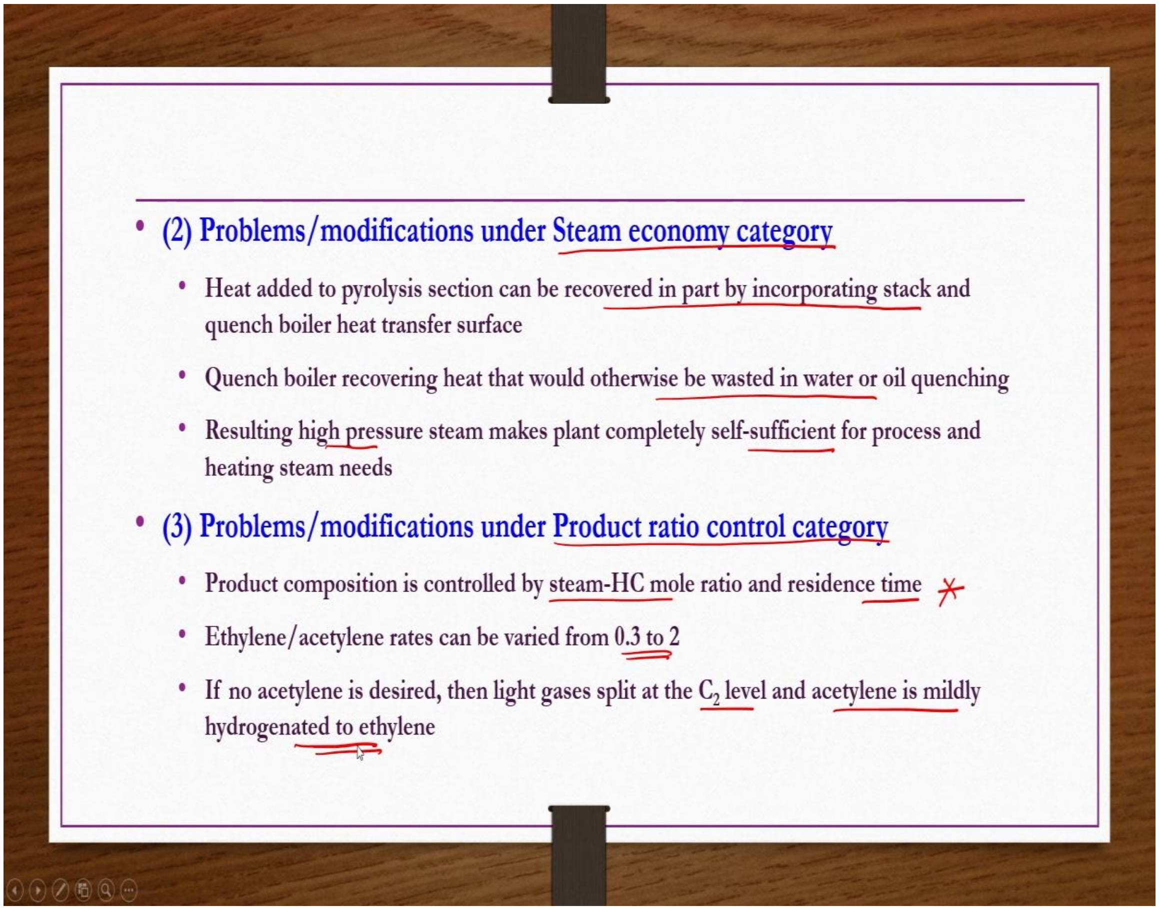


- (c) Process modifications under choice of pyrolysis equipment category
  - Tubular, indirect fired equipment: used for catalytic reactions
  - Coiled pipe furnaces: used for non-catalytic reaction in absence of O_2
  - Combustion-type burner: used for reaction where oxygen is introduced
- Design of equipment must provide balance between temperature, contact time, and quench time
  - This is essential for optimum cracking to correct product ratio and yield without carbon formation

Coming to the process modification and the choice of pyrolysis equipment category, tubular indirect fired equipment are used for catalytic reactions. Coiled pipe furnaces are used for non-catalytic reactions in the absence of oxygen and then combustion type burner are used for reaction where oxygen is introduced.

So depending on type of process are you doing you have to select the reactor also. Design of equipment must provide balance between temperature, contact time and then quench time is also because the temperature usually high 700 to 800 degrees centigrade. So product mixture whatever is coming or product gases mixture whatever is coming that has to be properly cooled to required temperature so that separation can be done easily. Otherwise free carbon formation may take place even after the reaction as well. This is essential for optimum cracking to correct product ratio and yield without carbon formation.

(Refer Slide Time: 1:00:45)

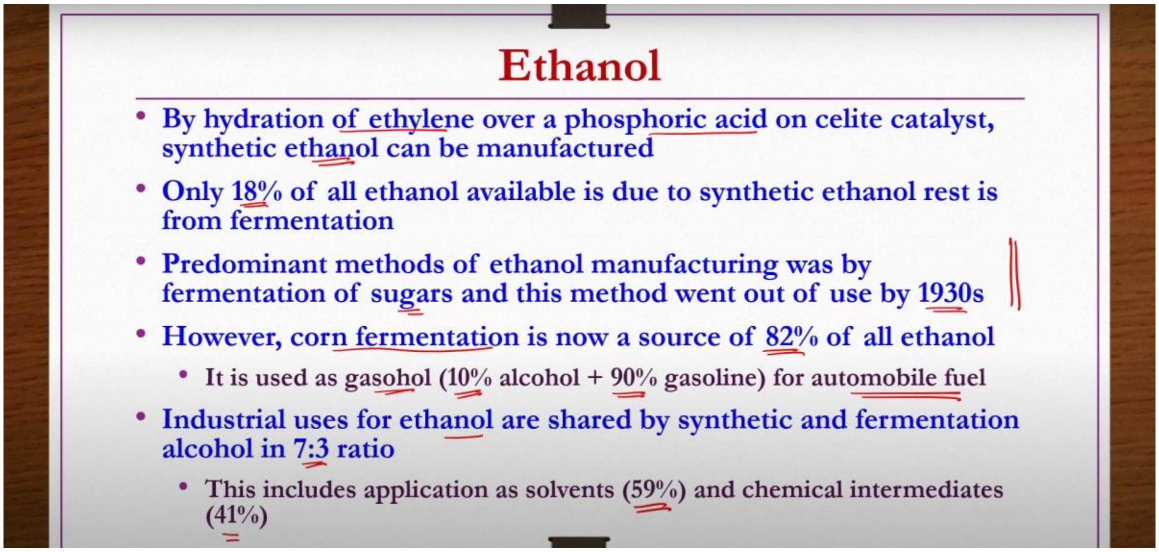


- (2) Problems/modifications under Steam economy category
  - Heat added to pyrolysis section can be recovered in part by incorporating stack and quench boiler heat transfer surface
  - Quench boiler recovering heat that would otherwise be wasted in water or oil quenching
  - Resulting high pressure steam makes plant completely self-sufficient for process and heating steam needs
- (3) Problems/modifications under Product ratio control category
  - Product composition is controlled by steam-HC mole ratio and residence time
  - Ethylene/acetylene rates can be varied from 0.3 to 2
  - If no acetylene is desired, then light gases split at the C_2 level and acetylene is mildly hydrogenated to ethylene

Now under steam economy category of major engineering problems, heat added to pyrolysis section can be recovered in part by incorporating stake and then quench boiler heat transfer surface. Quench boiler recovering heat that would otherwise be wasted in water or oil quenching. Resulting high pressure steam makes plant completely self-sufficient for process and heating steam needs. Coming to the product ratio control category of engineering problems, product composition is controlled by steam to hydrocarbon mole ratio and then residence time.

So as per your product you have to select these ratios. Ethylene to acetylene rates can be varied between 0.3 to 2. If you want more ethylene so then ratio has to be towards the lower end. If no acetylene is desired then light gases split at the C2 level and acetylene is mildly hydrogenated to ethylene as we discussed in the flow chart. So that is all about production of C2 chemicals. C2 compounds production we have seen that is production of ethylene and acetylene from the hydrocarbons. Naphtha as well as C2, C3, C4 saturates as a feed material that is what we have seen. Now we have C2 chemicals like ethylene and acetylene production. So once we have these things how we can use them to produce different types of intermediates or end products that is what we are going to discuss. But however in this lecture we are going to discuss about production of ethanol only remaining ones we will be discussing in the next lecture.

(Refer Slide Time: 1:02:36)



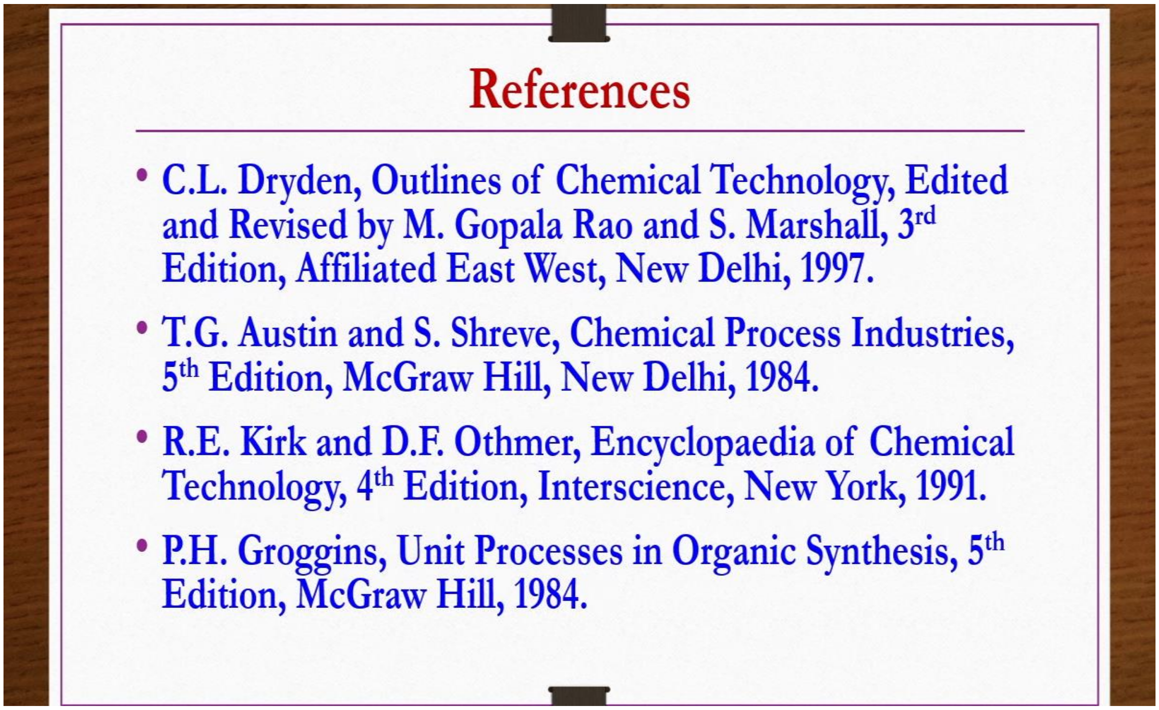
Ethanol

- By hydration of ethylene over a phosphoric acid on celite catalyst, synthetic ethanol can be manufactured
- Only 18% of all ethanol available is due to synthetic ethanol rest is from fermentation
- Predominant methods of ethanol manufacturing was by fermentation of sugars and this method went out of use by 1930s
- However, corn fermentation is now a source of 82% of all ethanol
  - It is used as gasohol (10% alcohol + 90% gasoline) for automobile fuel
- Industrial uses for ethanol are shared by synthetic and fermentation alcohol in 7:3 ratio
  - This includes application as solvents (59%) and chemical intermediates (41%)

Ethanol it can be obtained by the hydration of ethylene over a phosphoric acid on celite catalyst. So since we are producing this ethanol by the synthetic process so this is known as synthetic ethanol. But only 18% of overall ethanol that is being produced industrially is synthetic ethanol. Rest all remaining 82% is by fermentation process. Predominant methods of ethanol manufacturing was by fermentation of sugars and this method went out of use by 1930s. However, still fermentation is used to produce ethanol but not from the molasses fermentation but fermentation of corn.

Corn fermentation is now a source of 82% of all ethanol is being produced. It is used as gasohol which is nothing but mixture of 90% gasoline and 10% ethanol and used for the automobile fuels. Industrial uses for ethanol are shared by synthetic and fermentation alcohol in 7 to 3 ratio. This includes application as solvents approximately 60% and then chemical intermediates approximately 40%. So this ethanol production synthetically it is simple process you can do the hydration of ethylene using phosphoric acid on celite catalyst then you can get the synthetic alcohol. But fermentation process we have already discussed how to produce different types of chemicals from the fermentation where we have also discussed the production of ethanol. So we are not going to repeat it here again.

(Refer Slide Time: 1:04:22)



References

- C.L. Dryden, Outlines of Chemical Technology, Edited and Revised by M. Gopala Rao and S. Marshall, 3rd Edition, Affiliated East West, New Delhi, 1997.
- T.G. Austin and S. Shreve, Chemical Process Industries, 5th Edition, McGraw Hill, New Delhi, 1984.
- R.E. Kirk and D.F. Othmer, Encyclopaedia of Chemical Technology, 4th Edition, Interscience, New York, 1991.
- P.H. Groggins, Unit Processes in Organic Synthesis, 5th Edition, McGraw Hill, 1984.

References for today's lecture are provided here. Thank you.