Organic Chemical Technology
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Lecture - 22
Chemicals from C1 Compounds: Methanol & Formaldehyde

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is chemicals from C1 compounds, methanol and formaldehyde. From this lecture onwards, we are going to discuss about synthetic product industries completely and then we start first petrochemical industries where we will be discussing about the compounds that are produced from C1 compounds or chemicals produced from C1 compounds we start with, okay? However, before going into the production of such chemicals derived from C1 compounds, we have a brief introduction about synthetic industries especially towards the petrochemicals industries and then we get into the details of manufacturing processes.

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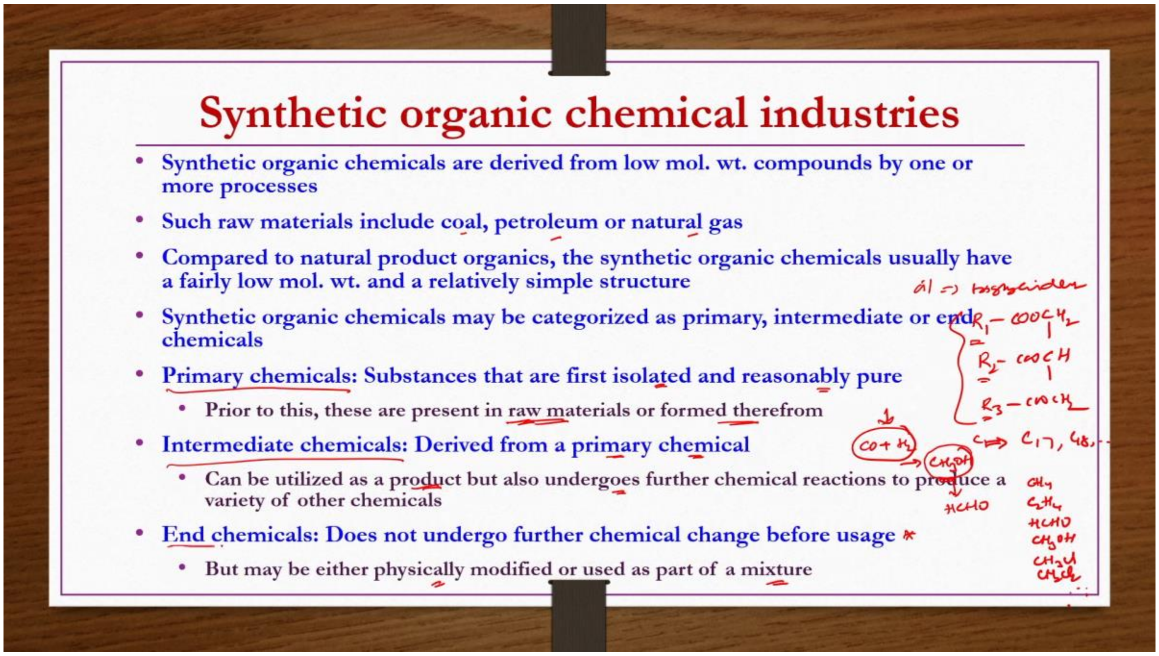

Synthetic organic chemical industries. Synthetic organic chemicals are derived from low molecular weight compounds by one or more processes. What are these low molecular weight compounds? They may be anything but in general most of the raw materials include coal, petroleum and natural gas, okay?

Compared to the natural products organics, the synthetic organic chemicals usually have a fairly low molecular weight as well as a relatively simple structure. Let us say if you remember oils and fat industry which is natural product industry which comes under the natural products industry, whatever the oil components etc. are there, they are mostly derived from the triglycerides etc. with some kind of modifications.

They have complicated structures like this, right? Something like these kinds of structures we have already seen which are very complicated and these R1, R2, R3 are also large molecular weight components like you know C number may be having something like C17 or C18 and something like that, such big molecules, so then their molecular weights are also bigger ones, right?

And their structures also very complicated. I have shown only the least complicated one, but here whatever the synthetic organic chemicals that we derive from some kind of raw materials like petroleum and natural gas etc., they will be having simple structures like you know methane, ethylene and then formaldehyde, methanol, chloromethanes, these kinds of simple structures they would be having, okay?

Synthetic organic chemicals may be categorized as primary, intermediate or end chemicals. What do you mean by primary chemicals? They are substances that are first isolated and reasonably pure. They are simply isolated from the sources itself or they may be obtained from the basic raw materials.

Prior to this, these are present in raw materials as it is or formed from thereof. If they are present as it is, so they can be obtained by the separation. Something like natural gas when you do the petroleum crude extraction or production of petroleum crude, then you know natural gas is also present there. So, petrol fractions are also present in there. So those you can directly separate.

So those things are known as the primary chemicals which are available within the source. So from the source if you are separating them and then getting in a purer form, then they may be known as the primary chemicals or they may be formed from such kind of raw materials, then also they can be known as the primary chemicals, okay?

Then what do you mean by intermediate chemicals? These are derived from primary chemicals. Let us say today we are discussing CO plus H2 synthesis gas and then from here we try to get the methanol. So synthesis gas maybe you can obtain in the natural resources. So then that can be taken as a kind of primary chemicals and then methanol maybe intermediate one because this methanol can be taken as a product itself or it can be further converted into the different chemicals like formaldehyde, etc., okay?

So the chemicals which can be utilized as product but also undergoes further chemical reactions to produce a variety of other chemicals, we can call them intermediate chemicals, okay? End chemicals does not undergo further chemical change before usage, like you know you have a basic raw materials and then from that basic raw material if you are producing some of the chemicals, you know those chemicals you can call as a primary chemicals.

If those chemicals can further undergo and then produce on a variety of other chemicals, then we can call them intermediate chemicals and then the sequence may be continuous, right? So those and then there would be a stage further conversion, chemical conversion may not take place. So such chemicals are known as the end chemicals.

However, these end chemicals may be undergoing physical modification changes, etc. and they can be part of a mixture as well. So based on the reactivity further conversion level, these chemicals especially synthetic chemicals may be primary chemicals, intermediate chemicals and end chemicals.

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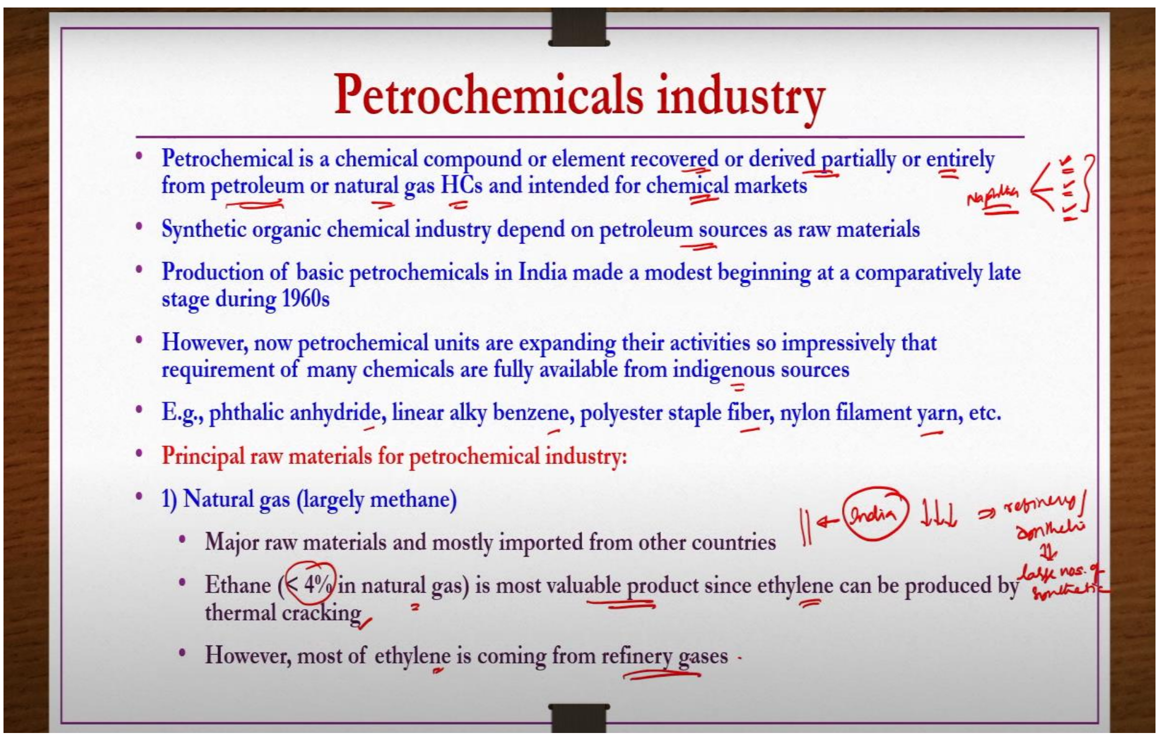

Now we start discussing about individual synthetic chemical industries. First we are talking about the petrochemicals industry. So, we have a definition of what is petrochemical, how it is derived and then how good is petrochemical industry and then we get into the manufacturing of different types of petrochemicals.

Petrochemical is a compound or element recovered or derived partially or entirely from petroleum or natural gas hydrocarbons and intended for chemical marketing, right? Let us say naphtha you are having, right? So that is available as a natural-resources, virgin naphtha is available. So, then you can do different types of processes and then you can get different types of chemicals, right?

So such kind of chemicals are usually known as the petrochemicals because the source for these petrochemicals whatever you are producing is nothing but basic petroleum crude or natural gas hydrocarbons, right? And then these products whatever that you produce, they are primarily produced from the chemical market point of view.

Synthetic organic chemical industry depend on petroleum resources as raw materials. Soon we are going to see different types of sources, petroleum resources as raw materials. There we can see huge number of resources are there from the crude petroleum as raw material for the production of n number of synthetic organic chemicals. In fact, that is what we are going to discuss in another 2 to 3 chapters that is production of different types of petrochemicals from the petroleum resources as raw materials.

Production of basic petrochemicals in India made a modest beginning at a comparatively late stage during 1960s, but however, now petrochemical units expanding their activities so impressively that requirement of many chemicals are fully available from indigenous sources for India. For example, thalic anhydride, linear alkyl benzene, polyester, fibers, nylon, filaments, etc., all of them are you know indigenously produced.

In fact, I have given only a few. Now most of the synthetic chemical industry or organic chemical industry that we are having in India mostly it is indigenous. Only that some of the raw materials may not be available, but the products, chemicals point of view, mostly we could able to produce ourselves.

Principal raw materials for petrochemical industries that is what we are going to see. The very first one is the natural gas which is primarily methane. There may be some traces of ethane also, but primarily it is methane. It is major raw material and mostly imported from other countries in general because our resources are limited.

That is what I was mentioning. The raw material resources for India may be not high, they are poor, but we are importing only primarily raw materials and then we are doing so called so many refinery processes and then synthetic processes so that to get large numbers of synthetic chemicals or organic chemicals.

Ethane which may be present less than 4% in natural gas in general is also a most valuable product since ethylene can be produced by thermal cracking, but however, most of ethylene is coming from the refinery gases also because the percentage in the natural gases is very less though it is most valuable product from the polymeric industries point of view, you know it is present less in natural gas. So, then alternative resource for the ethylene is nothing but the refinery gases.

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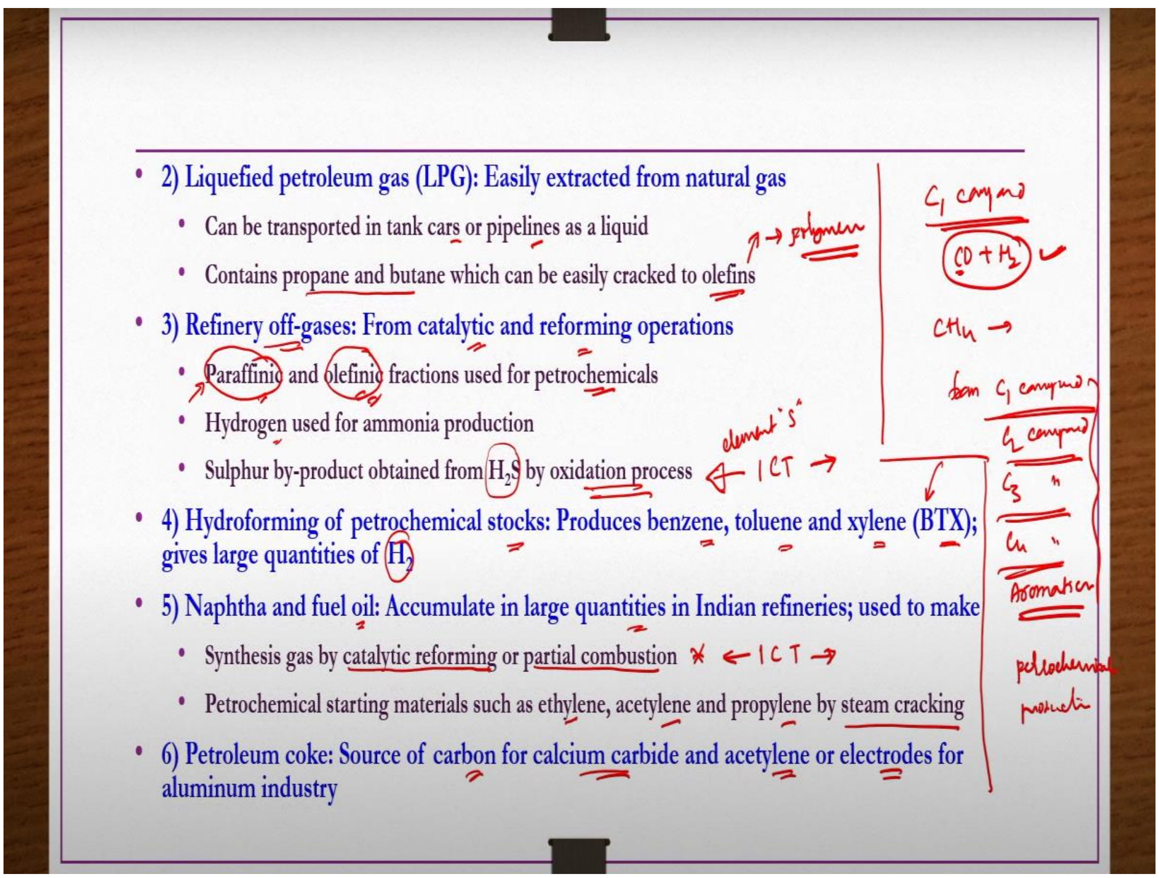

Second petroleum resource that we can use as a raw material for synthetic chemicals production or petrochemicals production is liquefied petroleum gas or LPG, easily extracted from natural gas while doing the petroleum crude extraction. It can be transported in tank cars or pipelines as a liquid, contains primarily propane and butane which can be easily cracked to olefins and then once you have the olefins, so then they can be good resource raw materials for polymers production.

Next important petroleum resources which can be utilized as a raw material for production of other petrochemicals is refinery of gases. This you can obtain in general by doing catalytic reforming operations or catalytic cracking operations of a crude petroleum, right? When you do catalytic reforming or catalytic cracking of crude petroleum, you get the refinery gases.

These primarily consist of paraffinic and olefinic fractions. So, olefinic fractions as well as the paraffinic fractions we can use for the production of petrochemicals. Paraffinic in the sense, you know if it is normal paraffins, then alkanes, if it is iso-paraffins, then iso-alkanes or isomers of these alkanes are paraffins.

Olefins are nothing but the alkanes which are having CNH2N chemical formula, right? So, these can also be used for a petrochemical production. Actually, when we use different resources, then we can produce different types of chemicals that we are going to discuss later anyway.

In this catalytic cracking as well as the catalytic reforming of crude petroleum also produces the hydrogen which can be used to produce ammonia by reacting with the nitrogen. In the crude, Sulphur may also be present in general as an impurity. So, sulphur by product obtained from H2S by oxidation process.

So, this process how to obtain elemental sulphur from H2S that we have discussed in inorganic chemical technology course which is also available in the NPTEL MOOCs portal. Hydroforming of petrochemical stocks, right? So, whatever the petrochemical stocks you have if you do the hydrogenation, right? Or hydro reforming kind of reactions, then you get several aromatics which include benzene, toluene, xylene primarily, right?

So, BTX out of this benzene, toluene, xylene, benzene is having more market compared to toluene and xylene because of its applications though all 3 of them are producing almost all equivalent yield percentages, okay? This process also produces H2. So, then H2 is again is having so many applications. Naphtha and fuel oil of crude petroleum that is also a very good resource for different types of petrochemicals production.

In India it is accumulating in large quantities in you know about a couple of decades back but however nowadays it is being utilized and then different types of chemicals are made something like synthesis gas by catalytic reforming or partial combustion. This also we have discussed in the course inorganic chemical technology which is also available on NPTEL MOOCs portal, okay?

Petrochemical starting materials such as ethylene, acetylene, propylene can be obtained by steam cracking of naphtha and fuel oil as well, right? Petroleum coke which is source of carbon, we have seen like you know whatever the residual heavy fractions that you get after doing the refining processes of any of the petroleum crude, you will definitely get a free carbon or you know char that is forming, right?

So, that free carbon or char can be source for calcium carbides, acetylene or electrodes for aluminum industry, etc. for those purpose you can use. Actually here you know whether it is natural gas or LPG or refinery gases or naphtha or fuel oil, petrol coke, whatever, only some of them are being shown from the petrochemicals that are being produced from these resources. Let us say very next slide we are going to see if you have a C-1 compound.

What do you mean by C-1 compound? Like you know in the raw materials you are having only single carbon. So, let us say CO plus H2 synthesis gas is there. From this synthesis gas where only one carbon is there, you can produce n number of chemicals, right? Likewise, methane is also there.

From this methane also you can produce methanol and then formaldehyde and then chloromethanes and so many n number of chemicals you can produce. So, all of them we are not discussing in this introductory lecture. We will be discussing you know when we talk about individual category.

We have grouped the production of petrochemicals like you know chemicals from C-1 compounds like CO plus H2 and methane, chemical from C-2 compounds like ethane, ethylene, etc. Then similarly chemicals from C-3 compounds, C-4 compounds and then chemicals from aromatics like this we grouped our petrochemicals production processes.

So here as I mentioned let us say you take C-1 compounds, n number of components can be produced. We cannot go into the manufacturing process of all of them. We selectively take 3 to 4 or something like that under each category and then we discuss. Those selection also depends on the market and then you know applications of the petrochemical that is being produced from different types of resources.

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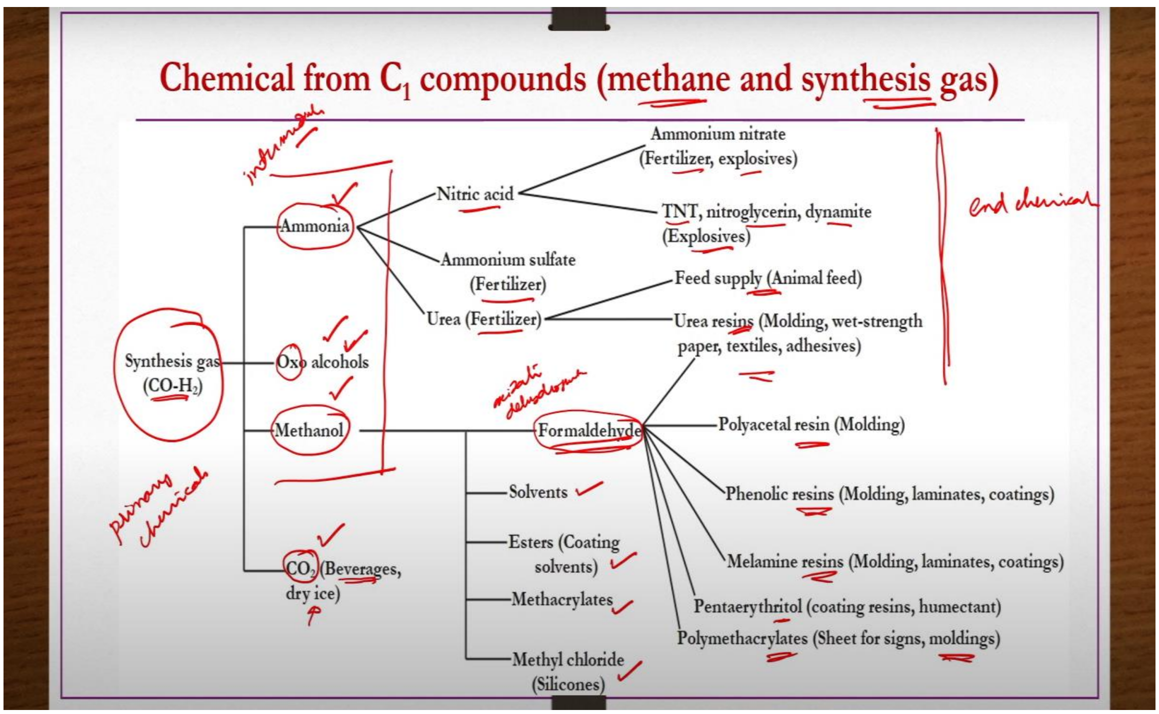

So, let us start a chemical from C-1 compounds. Let us say methane if you have only CH4, only one single carbon is there, synthesis gas CO plus H2 only one carbon atom is there. So, that is what it mean by C-1 compounds. This group supplied almost you know 25% of all petrochemicals produced.

Next slide we are going to see schematically as a chart what are the petrochemicals you can produce from C-1 compounds. So, let us say here we have that particular chart. Now we have let us say synthesis gas CO and H2 mixture as a basic raw material as a C-1 compound from which we try to produce different chemicals.

So since H2 is there if you remove CO by absorbing in some kind of appropriate inorganic solution, then you can get the H2 and then that H2 you can react with nitrogen to get ammonia. This synthesis gas can be made to undergo some kind of polymer processes like oxo processes etc. to produce different types of alcohols.

If you react this CO and H2, then you can get the methanol and then this CO H2 if you do a complete combustion then CO2 gases would be forming. So, they can be separated and then purified and then used as beverages or dry ice purpose. So primarily only 4 are shown here.

From these ammonia let us say you can produce you know fertilizers like ammonium sulfate, urea and then also you can produce explosives like nitric acid. So this nitric acid may be further converted into the ammonium nitrate which can be used as a fertilizer as well as the explosive as well as the trinitrotolvin, nitroglycerin, dynamite etc. may be produced from this nitric acid, all of them are explosives.

Whereas this urea fertilizers may be supplied as a food to the animal or can be used to make different types of resins. So you know more products are coming here. Whereas this methanol if you do the oxidation or dehydrogenation by both of the processes you get the formaldehyde.

Most of the methanol more than 50% of the methanol that has been produced industrially that is utilized for the production of formaldehyde. More than 50% of methanol is used to make formaldehyde because it can be used for making different types of resins as shown here.

Moldings and resins and then coatings etc. are being prepared from this formaldehyde. So methanol can also be used as solvents, ester coatings, methyl acrylates and then methyl chloride.

Now if you see category wise, so this may be taken as a primary chemical whereas these you can consider as intermediates or intermediate chemicals and then you can take these as end chemical, final chemical. Sometimes this classification may not be very exact, but however you know this is the basic how to make the classification of synthetic chemicals as primary, intermediate and then end chemicals.

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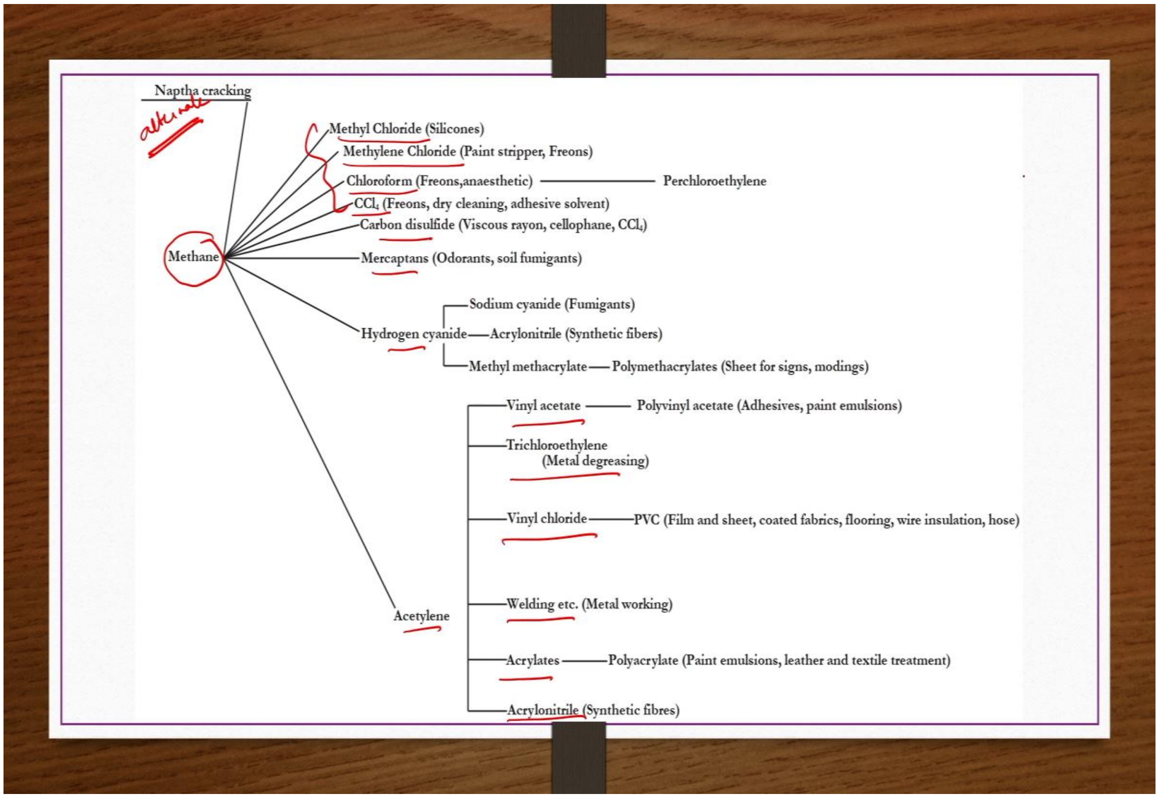

Now let us say other alternative resource for methane is naphtha cracking. When you do the naphtha cracking, you get the methane also which is present in the large fractions you can separate out, okay? So this methane can be utilized to produce methyl chloride, methylene chloride that is nothing but dichloromethane, chloroform, tetrachloromethane, carbon disulfide, mercaptans, hydrogen cyanides, etc.

Then acetylene also can be produced and these can be further utilized to produce different types of products which are mostly like polymeric kind of synthetic chemicals, right? So now you can see the spectrum of products can be produced from the source of a single carbon atom compound whether it is CO plus H2 or methane, okay?

So we cannot discuss all of them in one single chapter, so then what we do? We selectively consider production of a methanol, production of formaldehyde and then production of chloromethanes in this particular chapter where we are discussing on petrochemicals or synthetic chemicals produced from C1 compounds.

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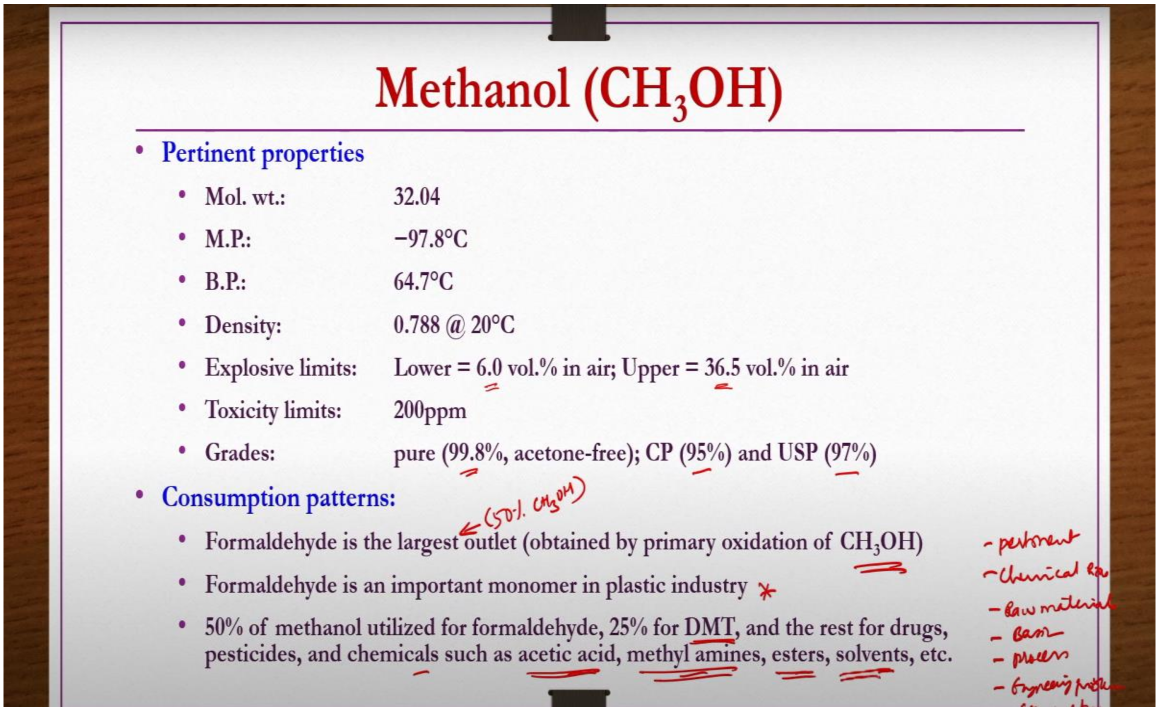

So let us start with methanol. Whenever we are discussing production of any of the chemicals, we are following a standard process of pertinent properties, chemical reactions, raw materials and then basis for the selected flowchart that is being discussed and then process, flowchart and process, then engineering problems, also consumption pattern or uses, etc. we are discussing.

So the similar basic structure we follow for petrochemicals also. So now we start with methanol. Pertinent properties, molecular weight is 32.04, melting point is minus 97.8 degrees centigrade, boiling point is 64.7 degrees centigrade, density is 0.788 gram per cc at 20 degrees centigrade, explosive limits it is explosive, lower limit is 6 volume percent and upper limit is 36.5 volume percent.

Toxicity, it should not be more than 200 ppm in the air. Grades, pure grade where 99.8 percent acetone free methanol is produced, another one is the CP with 95 percent and then USP with 97 percent purity. These are pharmacopies actually. Consumption pattern, formaldehyde is the largest outlet obtained primarily by the oxidation of methanol or dehydrogenation of methanol also if you do, then also you can get the formaldehyde, okay?

So this almost like 50 percent of methanol is used for formaldehyde production or even more because formaldehyde is an important monomer in plastic industry. So many types of resins you can produce from formaldehyde. 50 percent of methanol utilized for formaldehyde, 25 percent for DMT and then rest for the drugs, pesticides and chemicals such as acetic acid, methyl, amines, esters, solvents, etc.

See in the petrochemical spectrum that are being produced from C1 chemicals under methanol, after production of methanol from synthesis gas, we have shown only a few. Here some more applications are also there, right? N number of chemicals usually produced.

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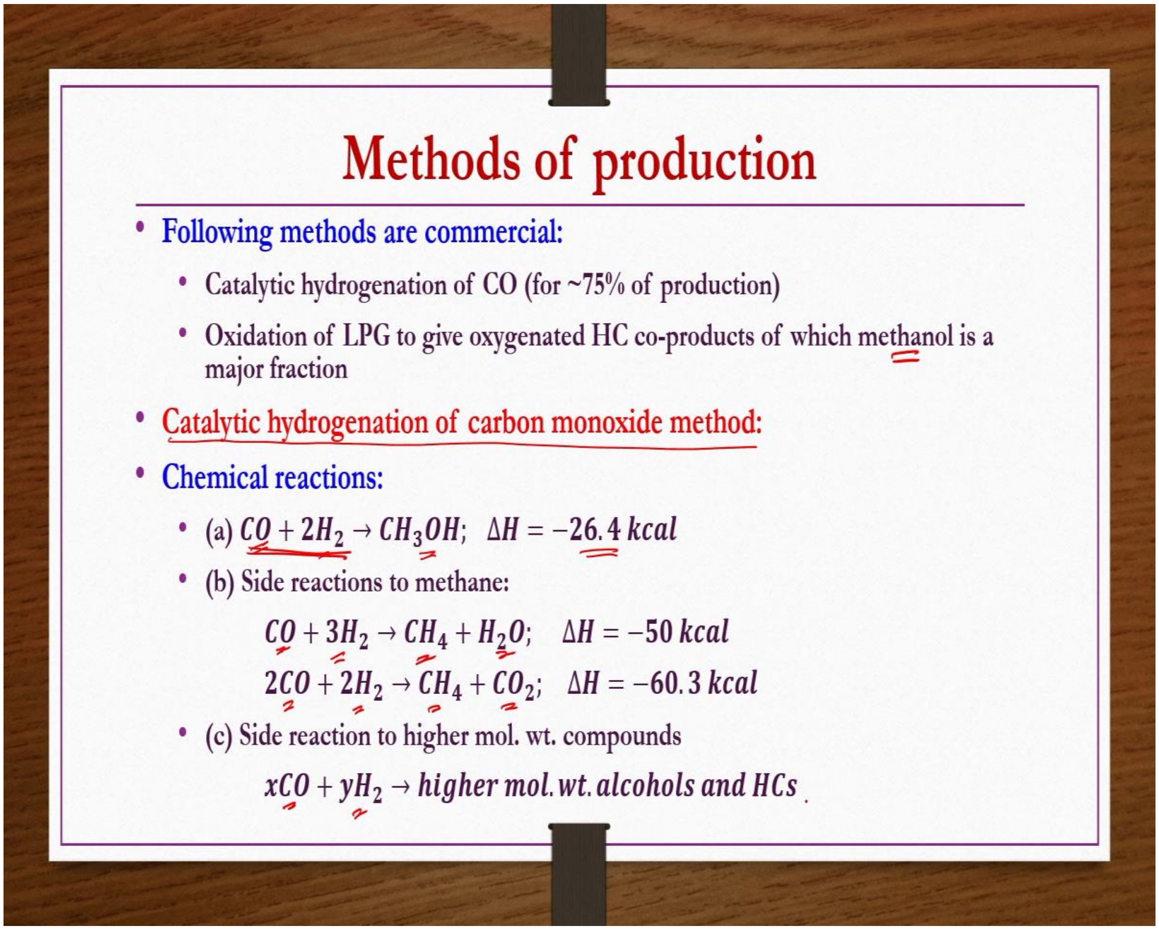

Methods of production, catalytic hydrogenation of CO is one of the important method, right? Here whatever the methanol available industrially, approximately 75 percent of methanol is produced by this method and rest is by the oxidation of LPG to give oxygenated hydrocarbon co-products of which methanol is a major fraction so that you can separate out and then take it as a product.

But now we are going to discuss about a catalytic hydrogenation of carbon monoxide method, okay? Chemical reaction, whatever carbon monoxide and hydrogen that are present in the synthesis gas you can take and then do the reaction, hydrogenation reaction or CO you react with hydrogen to get the methanol which is exothermic reaction. This reaction does not occur easily.

You need a catalyst and then temperature pressure also need to be sufficiently high that we are going to discuss, similar like ammonia synthesis process, okay? Site reactions, because of the site reactions CO may also be producing methane. What are those reactions? CO if reacting with 3 moles of H2, then methane and then water formation may take place.

2 moles of CO reacting with 2 moles of hydrogen would be producing methane again along with CO2. Main reaction if you wanted to produce methanol, you should have 1 mole of CO and 2 moles of H2, okay? Side reaction to higher molecular weight compounds also takes place. Generalized equation is xCO plus yH2 giving rise to higher molecular weight alcohols and hydrocarbons.

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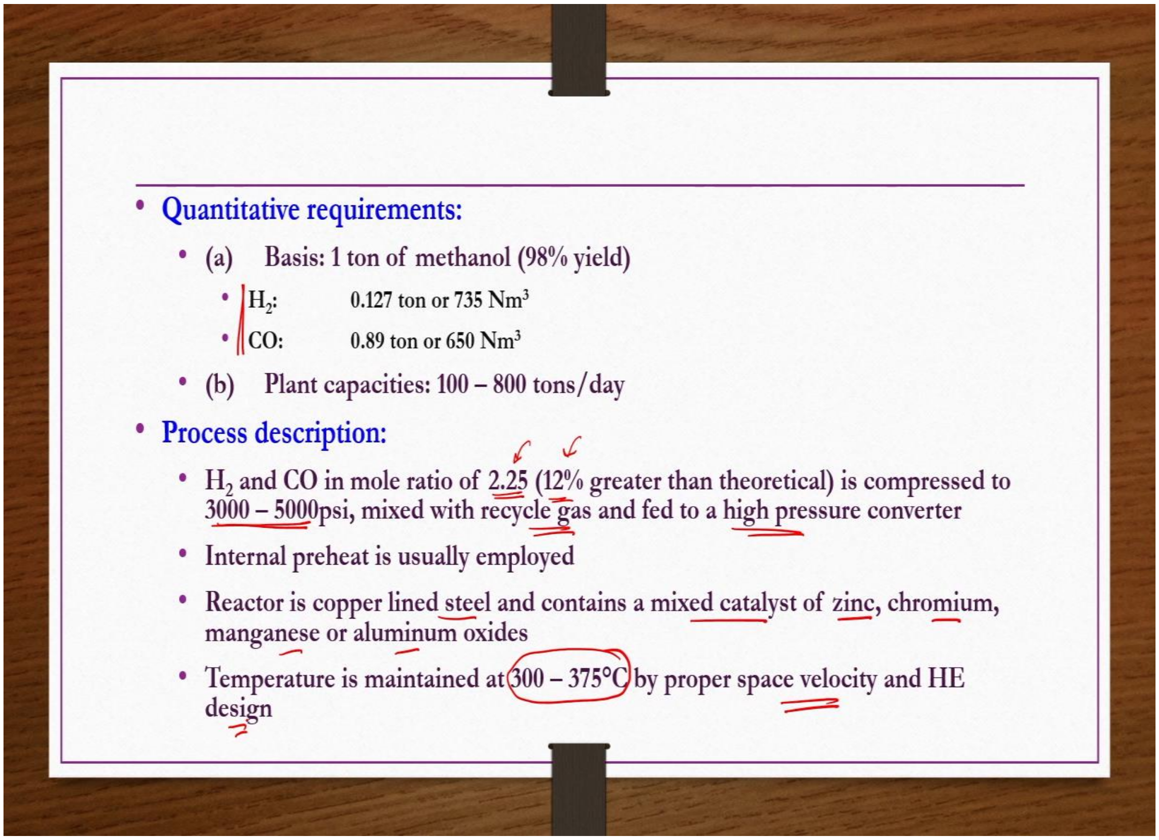

Quantitative requirements basis let us say if you wanted to produce 1 ton of methanol with 98% yield, hydrogen 0.127 tons or 735 normal cubic meters required, CO 0.89 tons or 650 normal cubic meters are required because the reaction is between these 2 only.

Catalytic hydrogenation of carbon monoxide, so carbon monoxide and hydrogen are the basic raw materials and then their quantities are required as per these numbers if you wanted to produce 1 ton of methanol with 98% yield. Plant capacities usually 100 to 800 tons per day. Now we see the process description and then we discuss the same thing through flowchart as well.

Hydrogen and CO in mole ratio of 2.25 which is 12% greater than the theoretical one actually it has to be 2, right? So 1 mole of CO reacting with 2 moles of H2, then it will give methanol, right? But here that mole ratio is 2.25 because excess of hydrogen is required, right?

So for that purpose it is 2.25 is the 12% greater than theoretical. In general, most of the theoretical numbers compared to that one excess are taken for most of the reactions especially those reactions are having side reactions also. Otherwise, you know byproducts may be forming in large quantities rather than the main component that you are intended to produce, okay?

This H2 and CO mixture is compressed to 3000 to 5000 psi mixed with recycled gas and fed to a high pressure converter where the temperature, pressure are maintained certainly high temperature and pressure, pressure more than 200 atmospheres as well as the temperature is more than 300 degree centigrade something like that so that the reaction takes place.

Internal preheat is usually employed because high temperature is required for this reaction to occur. Reactor is copper lined steel and contains a mixed catalyst of oxides of zinc, chromium, manganese or aluminum. Temperature is maintained between 300 to 375degree centigrade by proper space velocity and heat exchange design.

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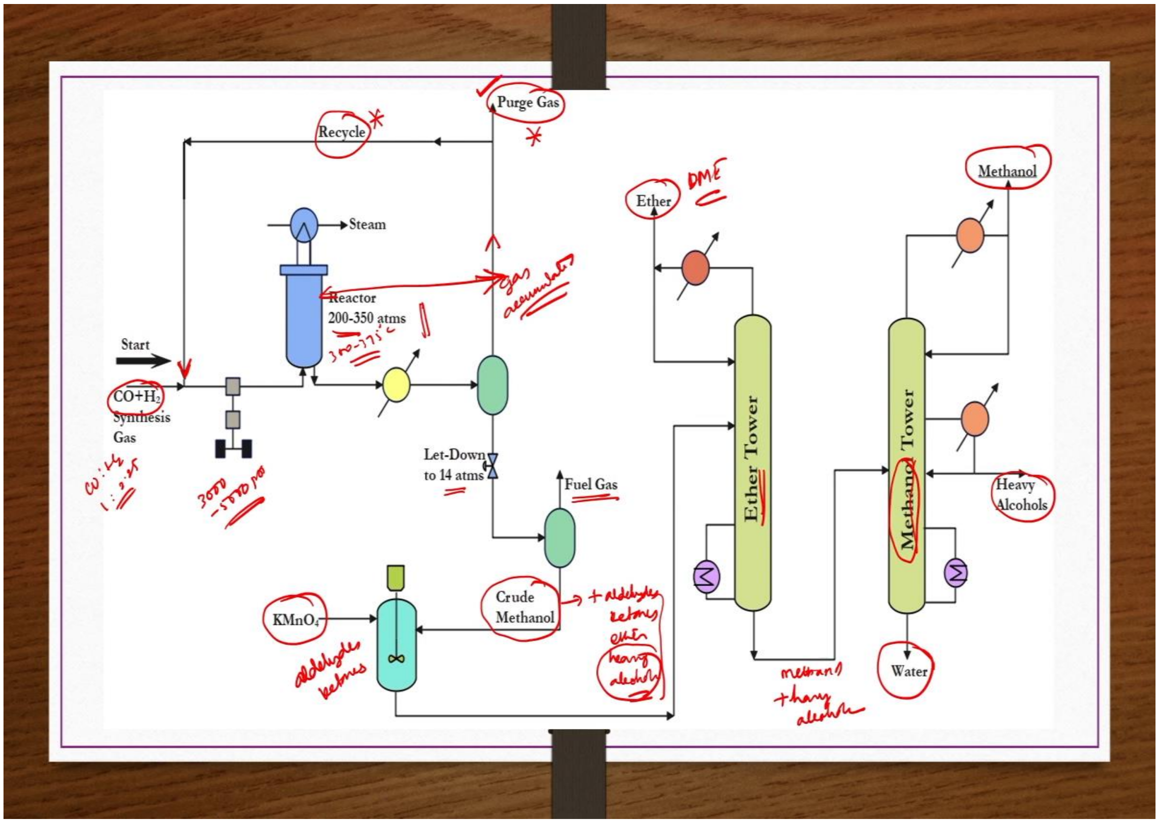

Let us say flowchart if you see here, whatever the synthesis gas is there that you take at CO2, H2 you know the ratio like let us say if you are taking 1 mole of CO at least 2.25 moles of H2 you have to take. You compress it at 3000 psi to 5000 psi and then mix with some kind of recycled gases.

Recycle is very much important here, purging is also very much important here that I will explain. So, these gases, reactant gases along with the recycle gases are compressed to such high pressure then sent to a reactor where the catalyst are present mostly oxides of metals like zinc, magnesium, aluminum, etc.

In the reactor, pressure is maintained very high 200 to 350 atmosphere and then temperature also very high 300 to 375 degree centigrade, then only reaction takes place. Otherwise, the rate of reaction is almost negligible if the temperature is less than 200 degree centigrade.

Whatever the product gases are there, they are collected and then some of them are recycled because in the single pass you do not get the enough conversion that you are intending. If you are planning for 98 percent yield, so then lot of recycle you have to do and then also you have to do the purging of the gas, some of the gas because gas may be accumulated in the reactor if you are not doing this one, recycling and then purging.

So, too much of gases are accumulated in the reactor, so then desired product may not be forming. So, that is the reason you need to do some amount of purging as well. So then after that you decrease the pressure of the mixture to something like 14 atmosphere and then you pass it through a separator where fuel gases are separated out whereas the crude methanol.

This crude methanol is also including some kind of aldehydes, ketones, ethers and then heavy alcohols also because in the reactions we have seen that you know x moles of CO and then y moles of H2 if reacts and heavy alcohols may also possible to form, okay? So, we are calling this crude methanol because of these impurities. Out of this aldehydes and then ketones are removed here.

Aldehydes and ketones are removed by absorption in potassium manganate solution in this absorption column. After removing aldehydes and ketones, the mixture is taken to ether tower where dimethyl ether kind of impurities are separated out. Then after that what you will be having?

Methanol plus heavy alcohols only you may be having in the mixtures along with some amount of water. So, that mixture will be taken to a methanol tower where methanol is taken as a top product whereas the heavy alcohols are collected as an intermediate or side stream products and then water is collected from the bottom.

Process is very simple here, okay? Only issue is that the reaction does not occur at low temperature and pressure. This is to be maintained and then gas accumulation is one other problem, okay? There are certain other problems also there like you know material of construction, etc., which are standard for any of the process in general.

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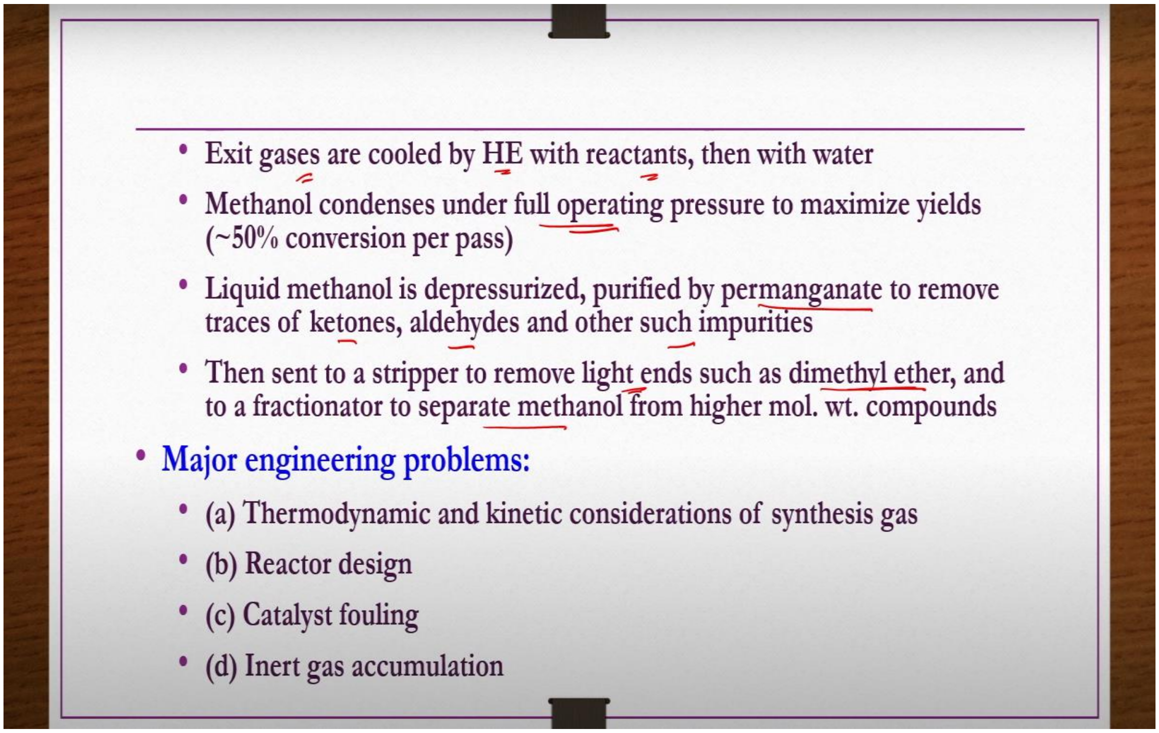

Exit gases from the reactor are cooled by heat exchangers with reactants, then with water. Methanol condenses under full operating pressure to maximize yields approximately 50% conversion per pass, so which is not sufficient. So, then you have to do recycling of the reaction gases or exit gases coming out from the reactor.

Liquid methanol is depressurized purified by permanganates to remove traces of ketones and aldehydes and other such impurities. Then sent to stripper to remove light ends such as dimethyl ether and fractionator to separate methanol from higher molecular weight components.

So, four major engineering problems are there for such kind of reactions where high temperature and high pressure are required, one has to thoroughly look at the thermodynamics and kinetics. So, that is first one thermodynamic and kinetic considerations of synthesis gas, reactor design because the temperature pressure is too high and then hydrogen is also involved.

So, then reactor design has to be done very carefully because hydrogen is very explosive and then it can be disastrous if it is not properly handled at high pressures like 200 or more than 200 atmospheres, okay? Catalyst fouling is also one issue, inert gas accumulation is the other issue that one should look in while running the plant.

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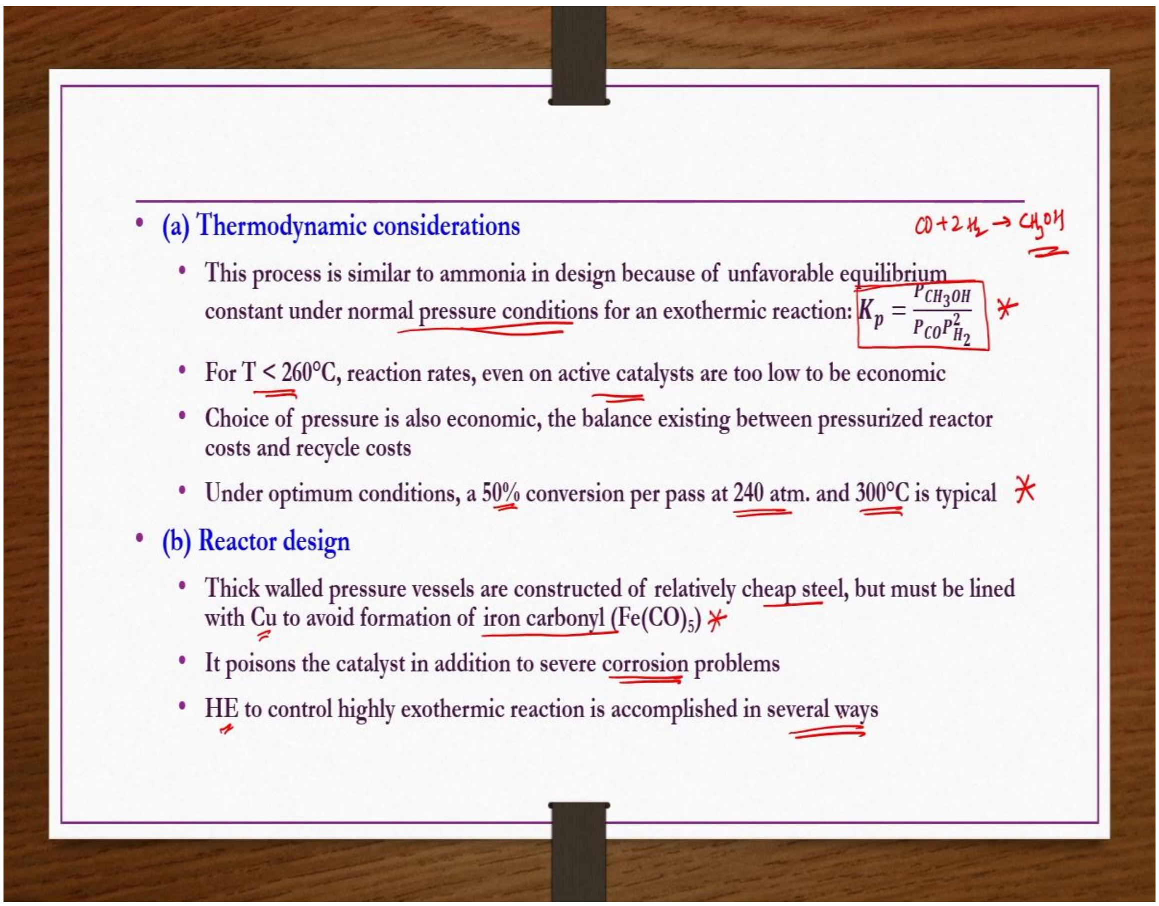

Thermodynamic considerations, this process is similar to ammonia in design because of unfavorable equilibrium constant under normal pressure conditions for an exothermic reaction. Even though it is exothermic reaction, it does not proceed forward under normal pressure conditions as well as the low temperatures.

The equilibrium constant is given by this because the reaction whatever reaction that we are having CO plus 2H2 giving rise to CH3OH, okay? Here P stands for the partial pressure of the component within the gases mixture. Actually this methanol etcetera also forming in vaporized form and then later we are condensing. For temperature less than 260 degrees centigrade, reaction rates even on active catalyst are too low to be economic.

Choice of pressure is also based on the economic that is the balance existing between pressurized reactor cost and recycle cost accordingly you have to select the pressure and then under optimum conditions for a 50% conversion per pass, 240 atmosphere and then 300 degrees centigrade are typical. These are optimized one, okay?

Reactor design, thick-walled pressure vessels are constructed of relatively cheap steel but must be lined with copper to avoid formation of iron, carbonyl. Otherwise this component what will do, it will deactivate the catalyst. In addition, it will also cause severe corrosion to the reactor.

Heat exchange to control highly exothermic reaction because the reaction is exothermic, so heat exchangers are very essential to control the temperature within the reactor. There are several ways are there, some of them are generally we have discussed for other processes but however now we are not discussing any of the methods but it is very essential to have heat exchangers to control the temperature of the reactor.

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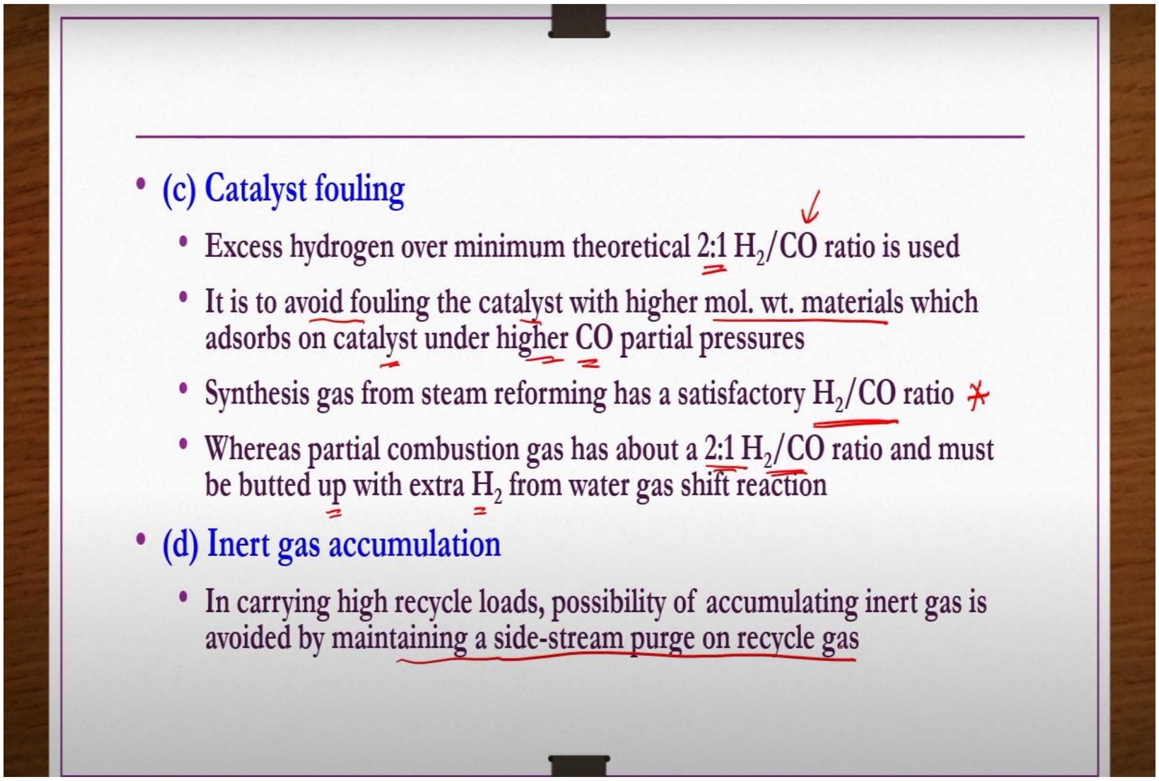

Catalyst fouling, excess hydrogen over minimum theoretical 2 is to 1 H2 to CO ratio is used so that to avoid the catalyst fouling because this excess hydrogen avoid fouling the catalyst with higher molecular weight materials which adsorb on catalyst under higher CO partial pressures.

If the CO is more, so then this is another problem. One other problem is that methane formation takes place, another problem is that catalyst fouling may also takes place. So, that is the reason you have to have excess hydrogen rather excess CO. Synthesis gas from steam reforming has a satisfactory H2 to CO ratio, so need not to worry for that.

Whereas partial combustion gas has about just 2 to 1 H2 to CO ratio and must be butted up with extra H2 from water gas shift reaction, otherwise you know side reactions will lead and then catalyst fouling may also take place.

Inert gas accumulation in carrying high recycle loads, possibility of accumulating inert gas is avoided by maintaining a side stream purge on recycled gas as we have discussed in flowchart. So, that is all about methanol production from C1 compound that is CO plus H2 reaction that we have taken.

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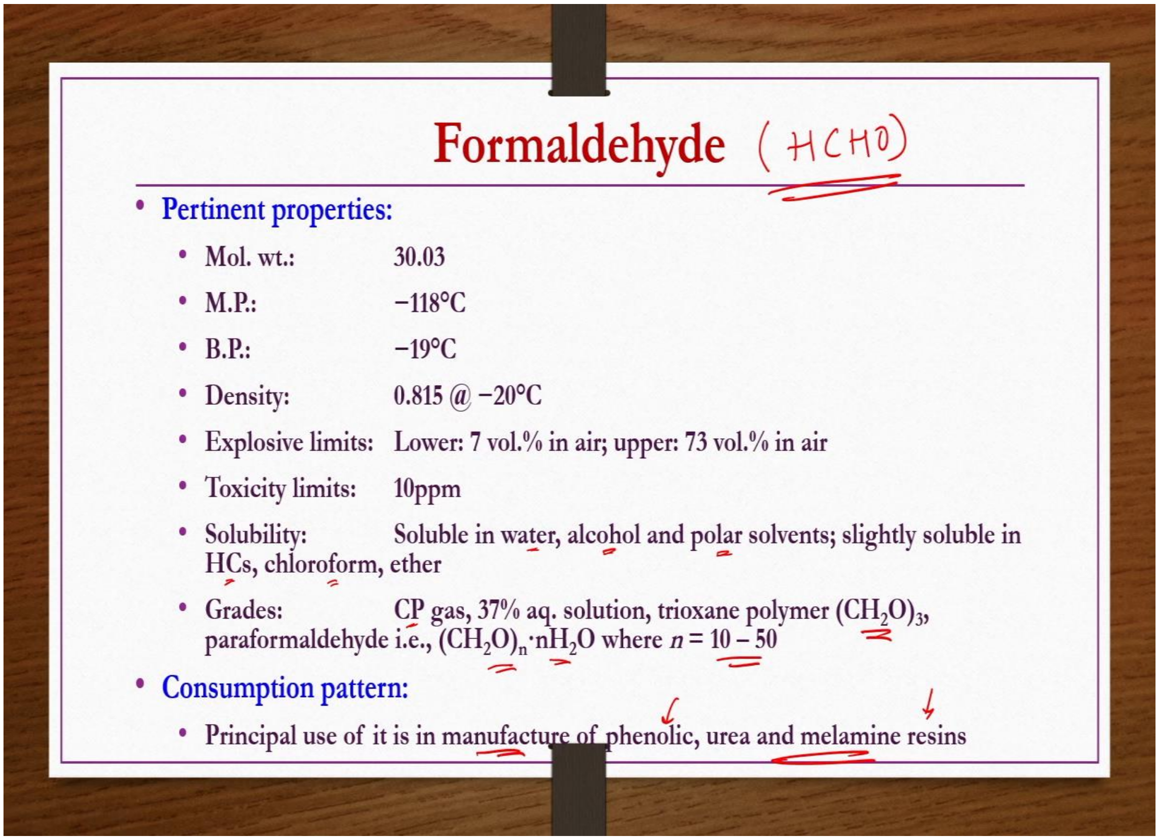

Now, we discuss about formaldehyde. Pertinent properties, molecular weight 30.03, melting point minus 118 degree centigrade, boiling point is minus 19 degree centigrade, density is 0.815 gram per cc at minus 20 degree centigrade. It is also explosive, so lower limit for the explosives is 7 volume percent and then upper limit is 73 volume percent in air and then its toxic limit is 10 ppm in air, it should not be more than 10 ppm.

Solubility, it is soluble in water, alcohols and then polar solvents, slightly soluble in some kind of hydrocarbons such as chloroform, ether, etc. Grades, CP gas grade and then 37 percent aqueous solution grade, trioxane polymer which is CH2O thrice. This formaldehyde is having chemical formula is nothing but HCHO that is nothing but CH2O. If trimer is there, so that is known as the trioxine polymer.

Like that paraformaldehyde is also possible that is nothing but hydrated polymerized component with n being 10 to 50. Consumption pattern, principal use of it is in manufacture of phenolic, urea and melamine resins as we have seen in the chart where we were discussing about different types of chemicals being produced from C1 chemicals or C1 compounds.

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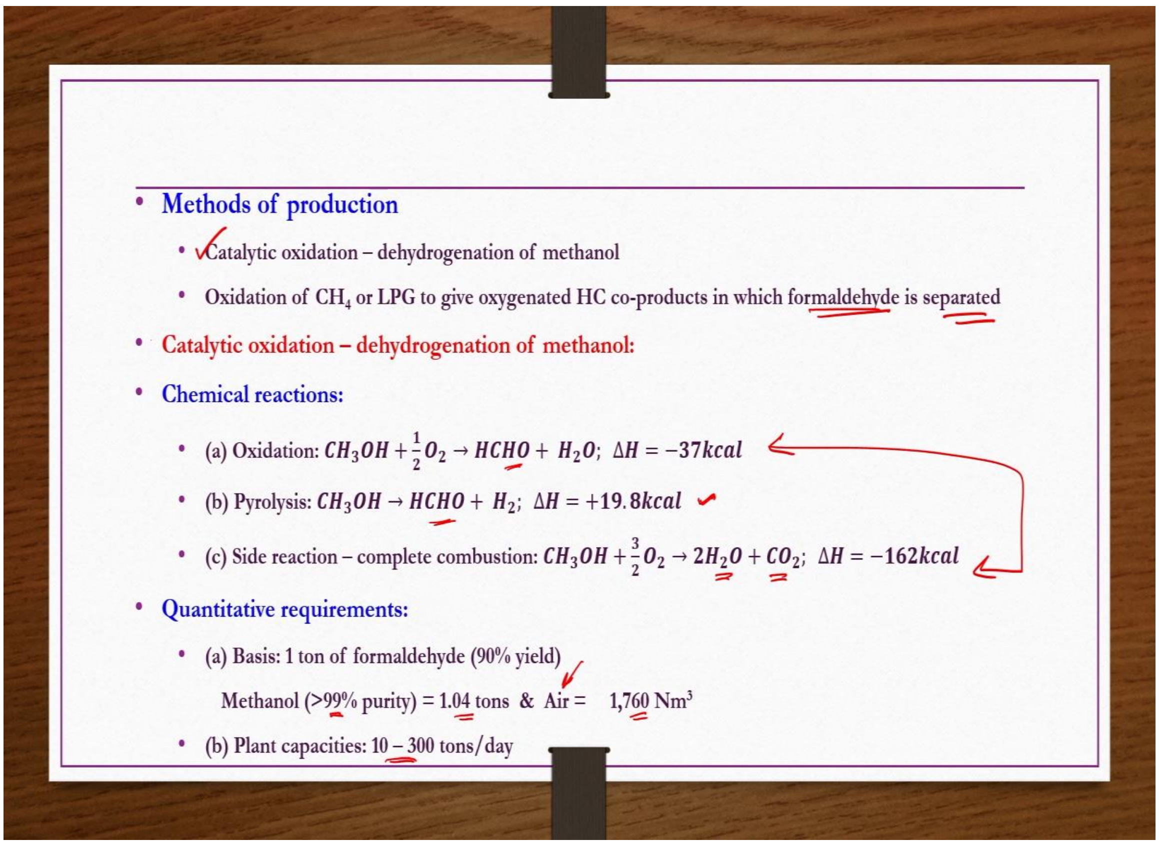

Methods of production, catalytic oxidation, dehydrogenation of methanol is one of the method. Other method is oxidation of methane or LPG to give oxygenated hydrocarbons, co-products in which formaldehyde is also present in sufficiently good quantity which can be separated, but this separation is very difficult in general.

We discussed this particular method, catalytic oxidation, dehydrogenation of methanol. Chemical reactions, if you do the oxidation of methanol, then you can get the formaldehyde and water. If you do the pyrolysis or dehydrogenation, then also you can get formaldehyde. Side reactions, if complete combustion is taking place, then it is possible that you get CO2 and then H2O, okay?

Only this reaction is endothermic and then remaining two reactions are exothermic. Quantitative requirements, basis 1 ton of formaldehyde with 90% yield, you required more than 99% pure methanol 1.04 tons, whereas 1,760 normal cubic meters of air are required because you are doing the oxidation. If you are doing the oxidation, oxygen is required, so in that place you can take the air, okay? Plant capacities usually 30 to 300 tons per day.

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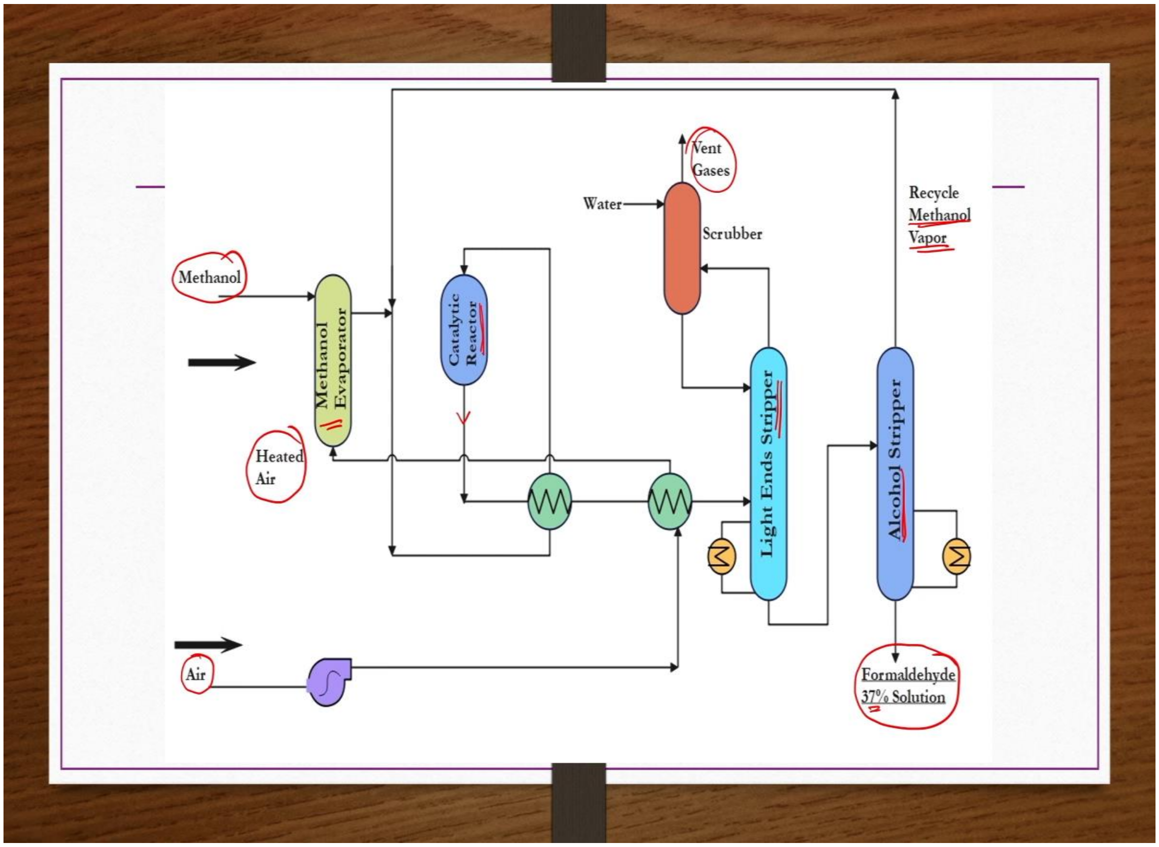

Now first we discussed the flowchart, then we discussed the same thing by text, right? So, here what we do? Whatever the air required for the reaction for the oxidation to occur, oxidation of methanol to occur that is passed through heat exchanger, preheater and then compressed and then heated air is sent to a methanol evaporator to which methanol is being supplied.

So that here with the heated air, evaporation of methanol takes place, so that this air and methanol both of them are in the vapor form and then the vapors of mixtures or these gases mixture of the reactants are passed through another heat exchanger and then sent to a catalytic reactor, right?

So, in the catalytic reactor required reaction of formaldehyde production takes place, then that crude formaldehyde along with the impurities like light fractions, other unreacted methanol, etc. are taken to a stripper where light ends are separated, vent gases are separated out from the light ends.

Then after separation of vent gases, the light ends are taken to the alcohol stripper where unreacted methanol vapors are separated out and sent back to the reactor as a recycle, right? And then from the bottom you get formaldehyde solution which is 37% pure, okay? This is the process, process is simple here.

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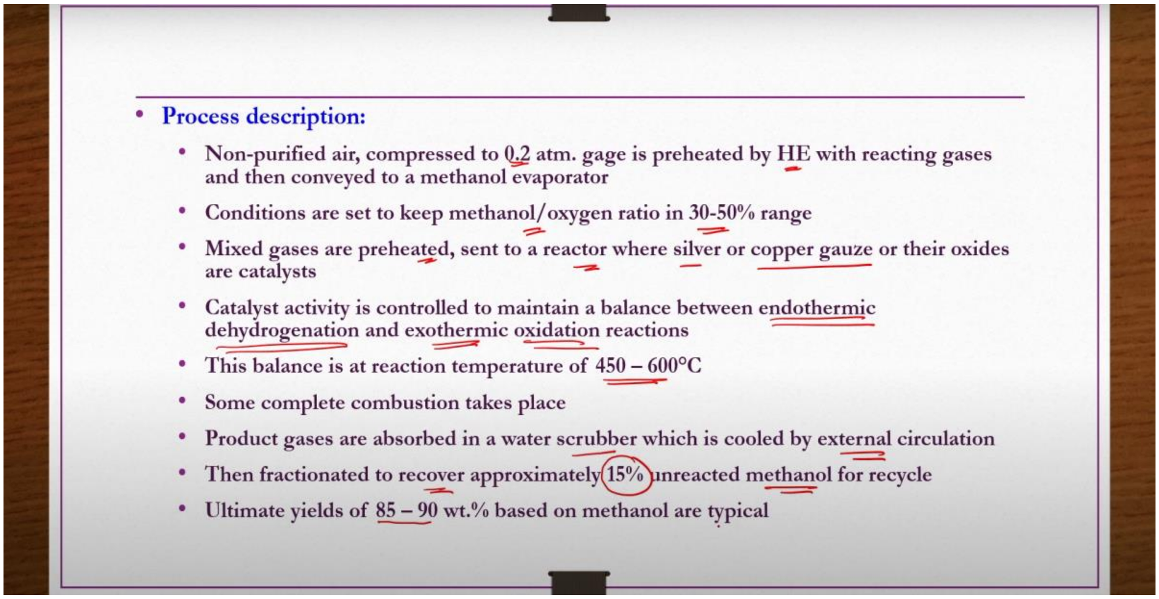

Process description, non-purified air compressed to 0.2 atmosphere gas is preheated by heat exchanger that means you compress it to 1.2 atmospheric pressure, then it is preheated by heat exchanger with reacting gases and then conveyed to a methanol evaporator. Conditions are said to keep methanol to oxygen ratio 30 to 50% range.

Mixed gases are preheated again and sent to a reactor where silver or copper gas or their oxides are utilized as catalyst. Catalyst activity is controlled to maintain a balance between endothermic dehydrogenation, dehydrogenation reaction whatever we have seen previous slide that is endothermic and then whatever the oxidation reaction is we have seen in the previous slide that is exothermic.

So between this endothermic and exothermic reactions you have to do a balance accordingly catalyst activity is controlled. This balance is at reaction temperature of 450 to 600 degrees centigrade. Sometimes complete combustion may also take place, so then CO2 possibility is there.

Product gases are absorbed in water scrubber which is cooled by external circulation, then fractionated to recover approximately 15% of unreacted methanol for the recycle. Ultimate yields of 85 to 90 weight percent based on methanol are obtained which are typical for the formaldehyde production by this process.

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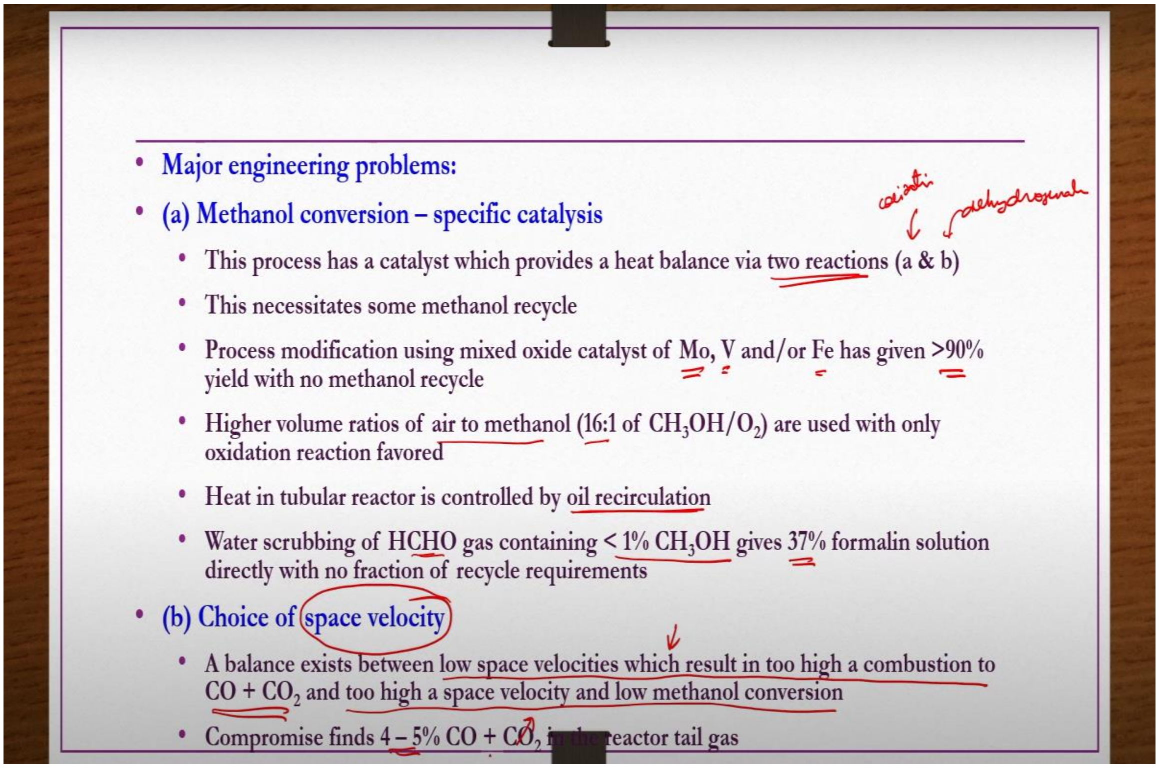

Coming to major engineering problems, two important major engineering problems are there. First one is methanol conversion specific catalysis. This process has a catalyst which provides a heat balance via two reactions. One is the oxidation of methanol and then another one is the dehydrogenation of methanol, both of them give you formaldehyde. This necessitates some methanol recycle.

Process modification using mixed oxide catalyst of molybdenum, vanadium and iron has given more than 90% yield with no methanol recycle. Higher volume ratios of air to methanol having 16 to 1 of CH3OH2O2 are used with only oxidation reaction favored because if you are doing more oxidation, then it is possible that more of the formaldehyde formation is there, yield would be higher, okay?

So for that reason, you know excess of A to methanol ratio has been taken. Heat in tubular reactor is controlled by oil recirculation. Water scrubbing of formaldehyde gas containing less than 1 percent of methanol gives 37 percent formalin solution which is nothing but the formaldehyde solution directly with no fraction of recycle requirements.

Another important engineering problem is choice of space velocity. It has to be selected based on the balance that existing between low space velocities which results in too high a combustion to CO plus CO2 and too high a space velocity and low methanol conversion. So this is one factor and this is another factor.

These two factors you have to consider and make a balance. Accordingly, you have to calculate space velocity, how much is required for the plant, okay? Usually, compromise finds 4 to 5 percent of CO plus CO2 in the reactor tail gases, okay? This is all about formaldehyde production from the methanol.

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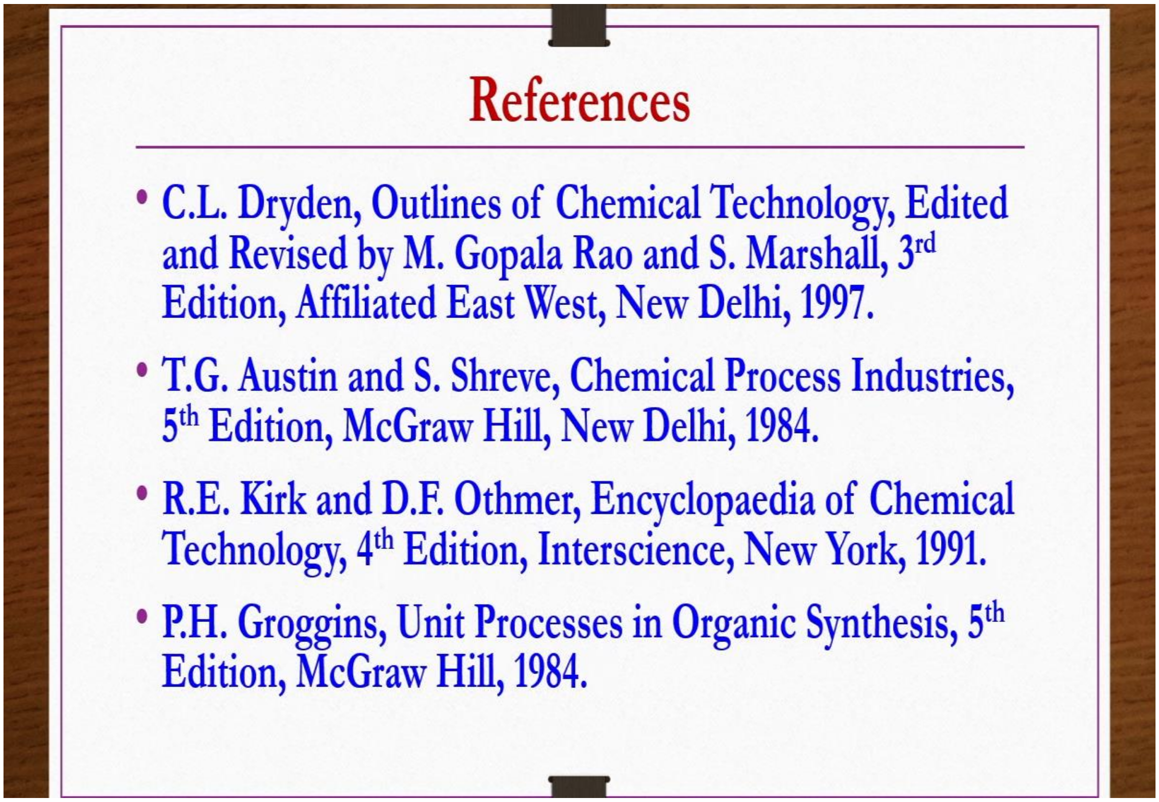

The references for today's lecture are presented here. Outlines of Chemical Technology by Dryden, edited and revised by Gopalrao and Marshall, 3rd edition. Chemical Process Industries by Austin and Shreve, 5th edition. Encyclopedia of Chemical Technology by Kirk and Othmer, 4th edition. Unit Processes in Organic Synthesis by Groggins, 5th edition. However, majority of the details you can find out in this first reference book. Thank you.