Waste to energy conversion
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Lecture - 13
Syngas Utilization-2

Hi friends, now will discuss on the second part of the module Syngas Utilization under the course Waste Energy Conversation. In the first part of this module, we have discussed on the gas clean off and Syngas conditioning as well as the production of FT fuels. In this part of this module we will discuss on the production of methanol, DME, higher alcohol, SNG and hydrogen, another important applications of Syngas is electricity productions and we have discussed in previous modules that Syngas can be used for a electricity production to steam turbine and the hot Syngas can be used for electricity productions in gas turbine followed by applications in steam turbine and different efficiency we have explained in previous modules.

Now, we will concentrate on methanol synthesis. So, methanol synthesis takes place through Syngas route and many other routes also, but here we will concentrate on methanol synthesis through Syngas routes. So, Syngas will be generated from biomass and waste and that will be reacted to convert methanol in a methanol reactor where copper base catalyst is used.

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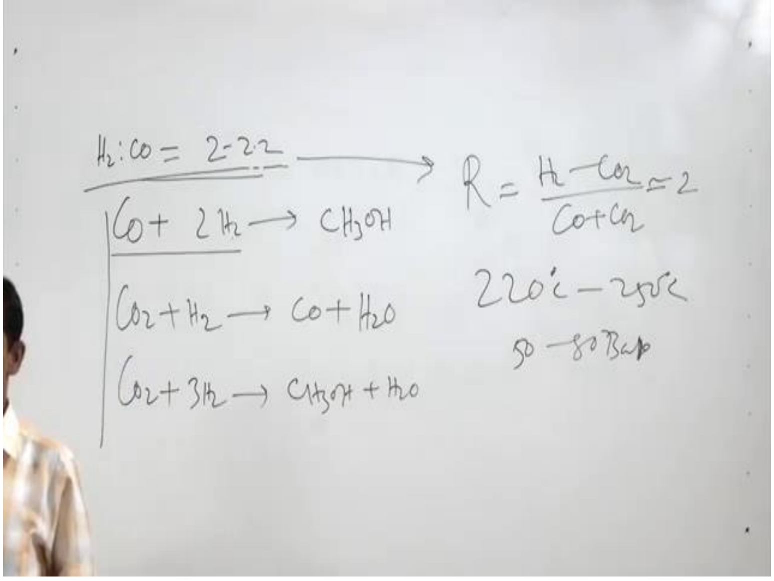

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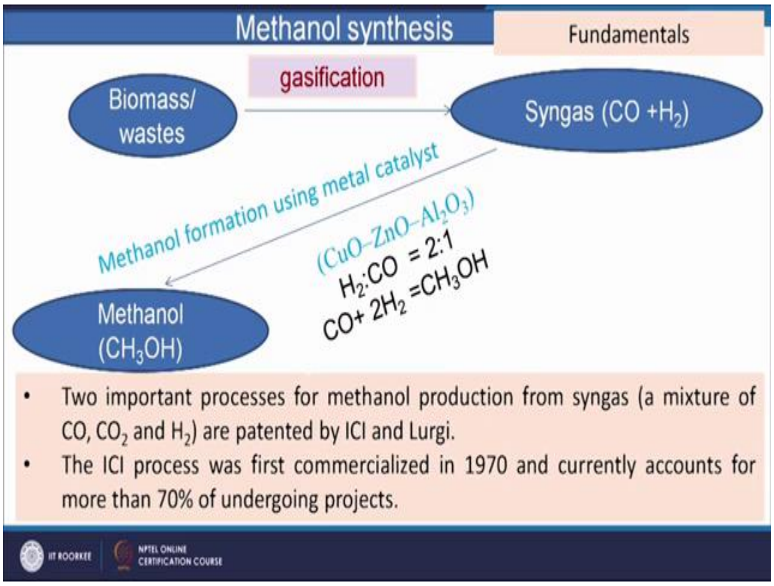

Methanol synthesis

Fundamentals

Biomass/ wastes

gasification

Syngas (CO $+H_2$)

Methanol formation using metal catalyst

($CuO-ZnO-Al_2O_3$)

$H_2:CO = 2:1$

$CO + 2H_2 = CH_3OH$

Methanol (CH_3OH)

- Two important processes for methanol production from syngas (a mixture of CO, CO_2 and H_2) are patented by ICI and Lurgi.
- The ICI process was first commercialized in 1970 and currently accounts for more than 70% of undergoing projects.

And Syngas having H 2 is to CO ratio 2 to 2 point 2 is used. And the product we get methanol and this technology is developed in nineteen seventy by ICI process and Lurgi process these 2 processes are commercial available important the processes and ICI process captures around seventy percent of the market on the methanol production.

Now, this methanol production takes place in the reactor through three main reactions that is CO plus 2 H 2 then it will give CH 3 OH and here CO 2 and HH 2 that will be converted to CO plus H2O that is reverse it reaction and CO 2 can also react with 3 H 2 then it will give us CH 3 OH plus H2O, so these 3 main reactions which are responsible for the methanol productions in the reactor.

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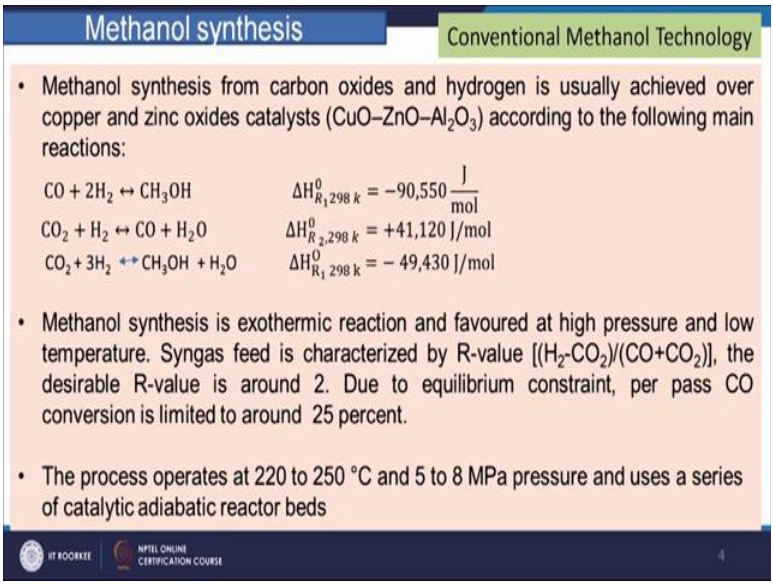

Methanol synthesis

Conventional Methanol Technology

- Methanol synthesis from carbon oxides and hydrogen is usually achieved over copper and zinc oxides catalysts ($CuO–ZnO–Al_2O_3$) according to the following main reactions:

$CO + 2H_2 \leftrightarrow CH_3OH$ $\Delta H^0_{R_1 298\,k} = -90{,}550 \frac{J}{mol}$

$CO_2 + H_2 \leftrightarrow CO + H_2O$ $\Delta H^0_{R_2,298\,k} = +41{,}120\ J/mol$

$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ $\Delta H^0_{R_1\ 298\,k} = -49{,}430\ J/mol$

- Methanol synthesis is exothermic reaction and favoured at high pressure and low temperature. Syngas feed is characterized by R-value [$(H_2$-$CO_2)/(CO$+$CO_2)$], the desirable R-value is around 2. Due to equilibrium constraint, per pass CO conversion is limited to around 25 percent.
- The process operates at 220 to 250 °C and 5 to 8 MPa pressure and uses a series of catalytic adiabatic reactor beds

So, one is shift and another is reactions of carbon oxides with hydrogen. So, both endothermic and exothermic reactions are going on and over all reaction each exothermic reaction. So, high temperature will not favor it. So, low temperature will favor this reaction.

Very interesting thing is that although these three major reactions are responsible and CO and H22 is to one ratio, it is described in many literatures that methanol will be produced from CO and H2 when the H2 and CO ratio is 2 is to 1, but it has been shown that presence of carbon dioxide is essential at the initial stage to initiate the reaction. So, 5 to 8 percent CO2 is essential that is why H2 by CO ratio is equal to 2 to 2.2, this is replaced by another factor that is R factor.

So, R factor is equal to H2 minus CO2 divided by H2 minus CO2 divided by CO plus CO2. So, this factor is almost equal to 2 it is near to 2. So, this is the favorable condition for the methanol synthesis in the methanol reactor and the temperature is also lower normally 220 to 250 degree centigrade and 50 to 80 bar per pressure it is required for the synthesis of the methanol through this route some other reactions also take place here some other reactions also take place.

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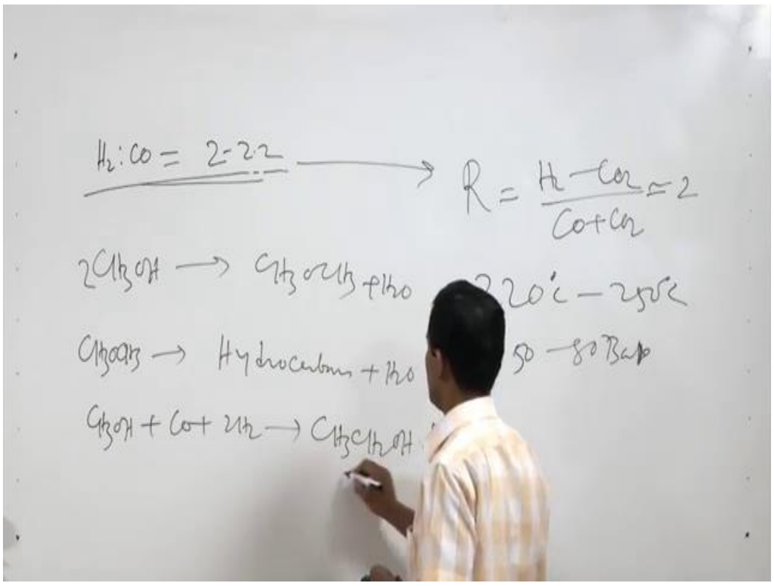

Here in the methanol reactor those are higher alcohol production d m e production CH 3 OH that will give us S 3 O, CH 3; 2 CH 3 OH plus H2O CH 3 OCH 3 can give us hydro carbons plus H2O or CH 3 OH can react with CO plus H 2 and this can give us CH 3 CH 2 OH higher alcohol. So, higher alcohol one hydro carbon and DME, these are the byproducts which are produced in the methanol reactor.

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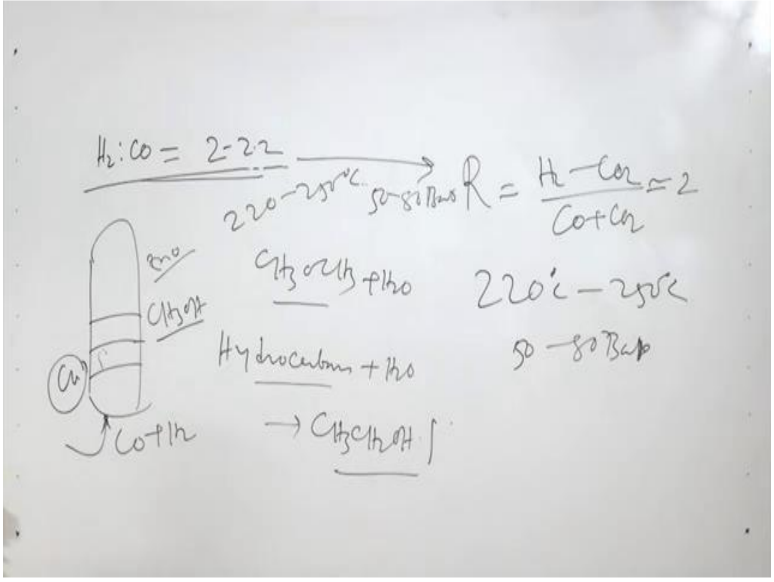

In this type of reactor, catalyst play a role and copper catalyst is basically used C u Z n O catalyst is used in this case which utilizes the temperature of 220 to 250 degree centigrade and 50 to 80 bar pressure some other catalyst are also available which can con convert Syngas to methanol, but the temperature and pressure requirement is different.

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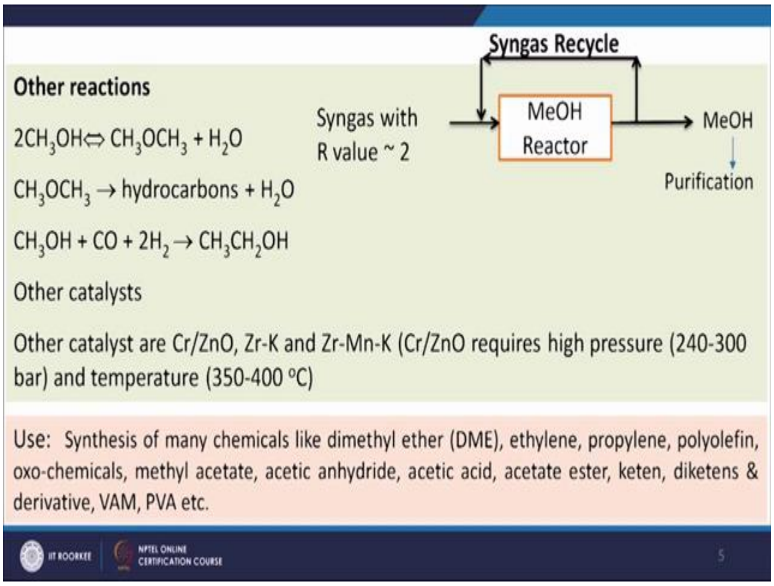

Other reactions

$2CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O$

$CH_3OCH_3 \rightarrow \text{hydrocarbons} + H_2O$

$CH_3OH + CO + 2H_2 \rightarrow CH_3CH_2OH$

Other catalysts

Other catalyst are Cr/ZnO, Zr-K and Zr-Mn-K (Cr/ZnO requires high pressure (240-300 bar) and temperature (350-400 °C)

Use: Synthesis of many chemicals like dimethyl ether (DME), ethylene, propylene, polyolefin, oxo-chemicals, methyl acetate, acetic anhydride, acetic acid, acetate ester, keten, diketens & derivative, VAM, PVA etc.

Here some catalysts are mentioned Cr ZnO Zr-K and Zr-MnK. So, Cr ZnO, this requires high pressure 240 to 300 bar and temperature 350 to 400 degree centigrade. So, this process is not boot because high pressure is required here and this CO ZnO in commercial plans used in solid and gas phased reactions this uses solid and gas phased reaction. So, in the reactor catalyst are loaded and CO H 2 is passed through it and CH 3 OH is formed. So, the mechanistic way CO and H 2 enters into the pores of the catalyst and on the active sides basically the copper is responsible to provide active sides and ZnO provides supports. So, these active sides the reactions take place and CH 3 OH forms that are why there is good possibility of heat losses.

So, to avoid this disadvantage people are trying to use low temperature and low pressure methanol synthesis in homogeneous phase reaction the gas absorption on the catalyst requires high pressure of the reactor, but if the catalyst are taken in to a solvent then gas is passed into the solvent then the pressure requirement is less.

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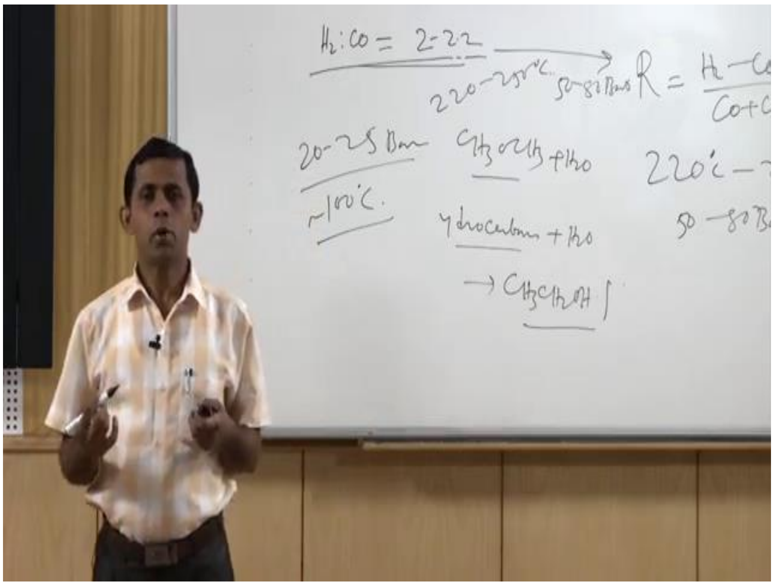

That is why, within 22 to 25 bar pressure and around 100 degree centigrade temperature the methanol synthesis is possible in homogeneous reactor and people have walked on it and some catalyst have been developed that is nickel catalyst and another is your chopper base oxide and alkoxide these 2 types of catalyst have been used in 2 different processes for the homogeneous phase and low temperature low pressure methanol synthesis.

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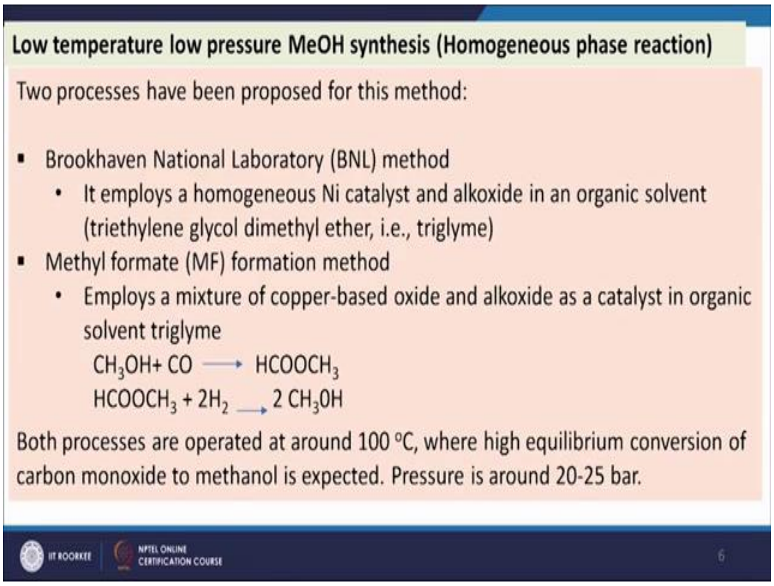

Low temperature low pressure MeOH synthesis (Homogeneous phase reaction)

Two processes have been proposed for this method:

- Brookhaven National Laboratory (BNL) method
  - It employs a homogeneous Ni catalyst and alkoxide in an organic solvent (triethylene glycol dimethyl ether, i.e., triglyme)
- Methyl formate (MF) formation method
  - Employs a mixture of copper-based oxide and alkoxide as a catalyst in organic solvent triglyme

$CH_3OH + CO \longrightarrow HCOOCH_3$

$HCOOCH_3 + 2H_2 \longrightarrow 2\,CH_3OH$

Both processes are operated at around 100 °C, where high equilibrium conversion of carbon monoxide to methanol is expected. Pressure is around 20-25 bar.

So, one method that is BNL method; Brookhaven National Laboratory method uses the nickel catalyst in the solvent that is triglyme and another method is methyl format formation method in this case copper base oxide and alkoxides are used in the solvent and the reaction is CH 3 OH reacts its CO to form H CO OC H 3 methyl format and then methyl format further reacts with hydrogen and it gives methanol. So, these although these processes require less temperature and less pressure, but these are not commercially used.

Now, we have 2 systems one is heterogeneous catalyst reaction another is homogeneous catalyst reactions then what will be their reactor type for the methanol synthesis; obviously, as a 2 different systems we are handling. So, different reactors will be used preferably in these 2 cases.

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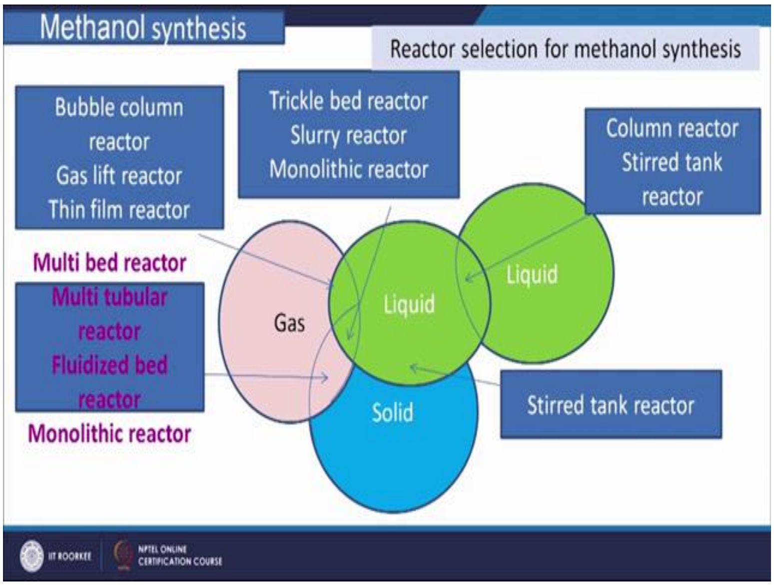

Methanol synthesis

Reactor selection for methanol synthesis

Bubble column reactor
Gas lift reactor
Thin film reactor

Trickle bed reactor
Slurry reactor
Monolithic reactor

Column reactor
Stirred tank reactor

Multi bed reactor
Multi tubular reactor
Fluidized bed reactor
Monolithic reactor

Stirred tank reactor

In the first case when the heterogeneous catalyst is used in that case solid and gas phase reactions solid and gas phase reactions. So, suitable reactors are multi bed reactor multi tubular reactor fluidized bed reactor and monolithic reactor high, whereas in the second case the solid liquid and gas phase reaction in this case trickle bed reactor slurry bed and monolithic reactors are preferable, but as in industry heterogeneous methanol is validly used. So, the most of the industrial methanol synthesis contain multi tubular reactor.

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So, this multi tubular reactor the catalyst time is around 2 years; and this catalyst can be deactivated if the temperature increases above 300 degree centigrade. So, these are the features of the heterogeneous reactors for the methanol synthesis which are used in commercial scale now what is the mechanism how the methanol is formed in the heterogeneous catalyst reactors that has been proposed by froment.

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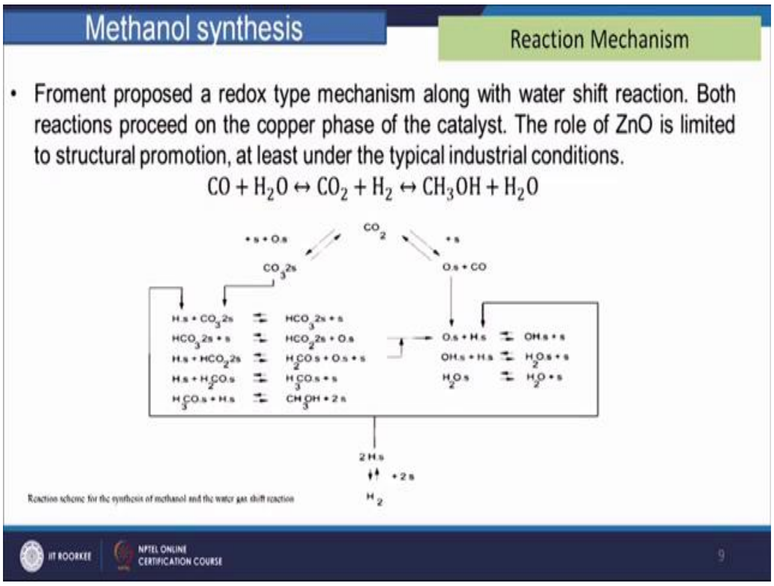

Methanol synthesis

Reaction Mechanism

- Froment proposed a redox type mechanism along with water shift reaction. Both reactions proceed on the copper phase of the catalyst. The role of ZnO is limited to structural promotion, at least under the typical industrial conditions.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \leftrightarrow CH_3OH + H_2O$$

Reaction scheme for the synthesis of methanol and the water gas shift reaction

And froment; it is proposed that CO and H 2 O reacts with and then it converts to CO 2 and H 2 then CO 2 and H 2 reacts to form say CH 3 OH and the they have proposed that the gas initially adsorbed on the catalyst surface solid surface and then reaches to the active sides and then reaches to the active sides and then in active sides some redox reduction is going on.

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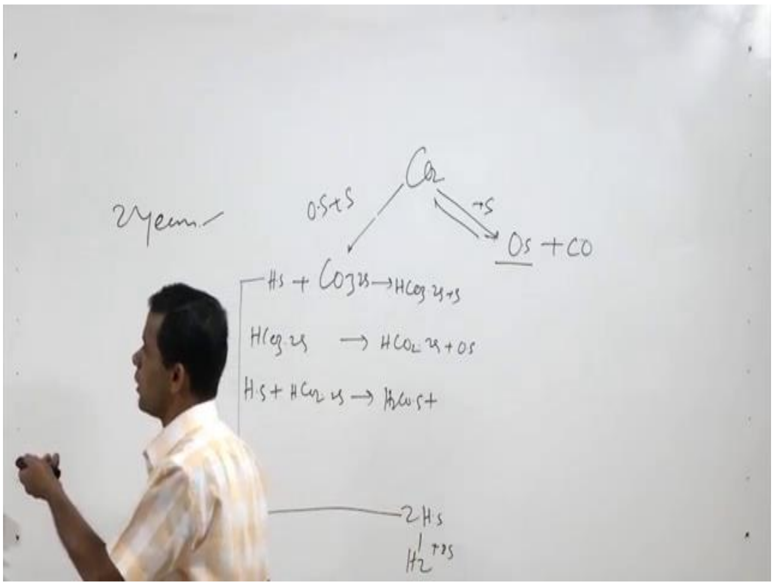

So, when the carbon oxide is formed then carbon dioxide can be reduced to CO and O that is S in the sides S. So, one side is required that is this reduction is going on another CO 2 can be converted to CO 3 to S CO 3 to S. So, this OS which is produced here this OS plus another S.

So, that will give us CH 3 OS and do you have here H 2 that H 2 will be converted to 2 HS. So, plus 2 S; so that will give 2 HS. So, these 2 HS that will come and will react with here this one CH 3 2 S and it will give us H CO 3 2 S plus S. So, S CO 3 will further react with H CO 3 2 S will gives H CO 2 2 H plus OS this H CO 2 will further reactor HSH CO 2. So, this will give us that H 2 CO S plus that is OS plus S, similarly this HS will again react with H 2 CO S and it will give H 3 CO S and H 3 CO S again it will react with H S and it will give us H CH 3 O h. So, methanol is produce by these reactions

Similarly, that OS which is generated here when H S is coming here So that will be reacting with OS and OH will form. So, O H plus H S is H 2 O S and S 2 H 2 H 2 plus sites. So, we are getting now H2O and we are getting CH 3 OH. So, this is the mechanism for the synthesis of this methanol in the heterogeneous way catalytic reactor.

Now, we are going for discussion on DME. So, dimethyl ether that can be produced from methanol dehydration using some catalyst or this can be used from the Syngas through single step using bimetallic or bi functional catalyst.

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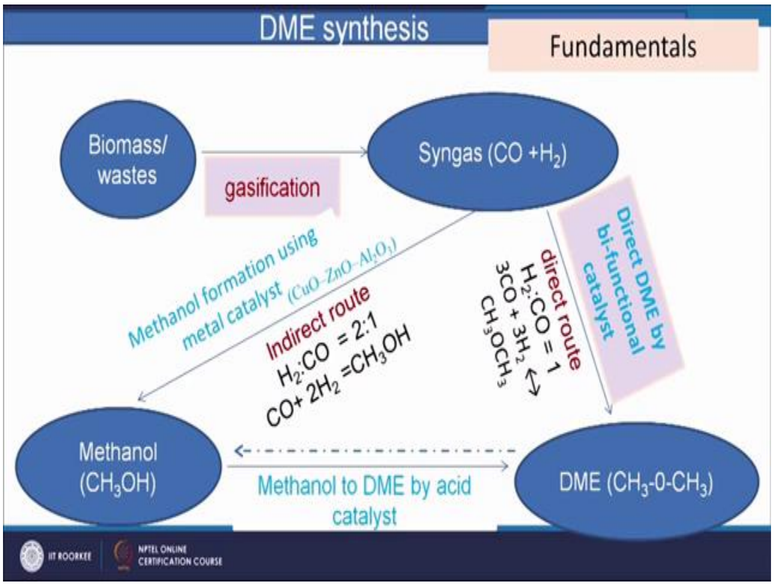

DME synthesis

Fundamentals

Biomass/ wastes

gasification

Syngas (CO +H_2)

Methanol formation using metal catalyst (CuO-ZnO-Al_2O_3)

Indirect route

H_2:CO = 2:1

CO+ $2H_2$ =CH_3OH

direct route

H_2:CO = 1

3CO + $3H_2$ ↔ CH_3OCH_3

Direct DME by bi-functional catalyst

Methanol (CH_3OH)

Methanol to DME by acid catalyst

DME (CH_3-0-CH_3)

So, in the first case, methanol synthesis you know S 2 is to CO ratio is 2 is to 1 then methanol dehydration in the second case H 2 is to CO ratio should be 1. So, this is the schematics for DME synthesis.

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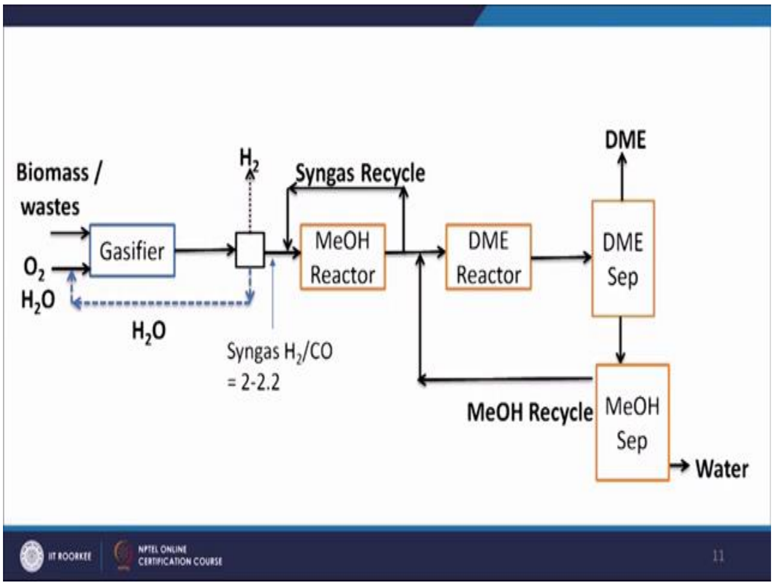

So, in this case, we see that from the Syngas we will get methanol then methanol can be converted to DME. So, when DME is produced there will not be complete conversion of methanol. So, some methanol will also be remaining. So, DME separation will take place and it will give pure DME and methanol separation will take place to remove water from methanol and that methanol can be recycled. So, this is the flow diagram for the production of DME from the Syngas through methanol route.

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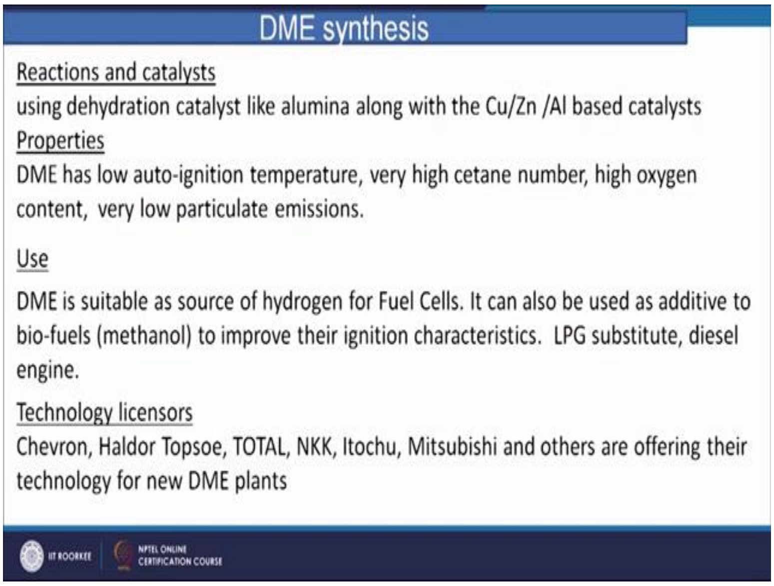

DME synthesis

Reactions and catalysts

using dehydration catalyst like alumina along with the Cu/Zn /Al based catalysts

Properties

DME has low auto-ignition temperature, very high cetane number, high oxygen content, very low particulate emissions.

Use

DME is suitable as source of hydrogen for Fuel Cells. It can also be used as additive to bio-fuels (methanol) to improve their ignition characteristics. LPG substitute, diesel engine.

Technology licensors

Chevron, Haldor Topsoe, TOTAL, NKK, Itochu, Mitsubishi and others are offering their technology for new DME plants

So, the catalyst which is used that is alumina along with C u Z n and alumina based catalyst and this DME has some good properties fuel properties and it can be used for LPG substitute or can be used as a in diesel engine.

So, and also it has less environmental pollution there are number of technologies or licenses for DME some are mentioned earlier like chevron, Haldor, Topsoe, TOTAL NKK, Mitsubishi, etcetera.

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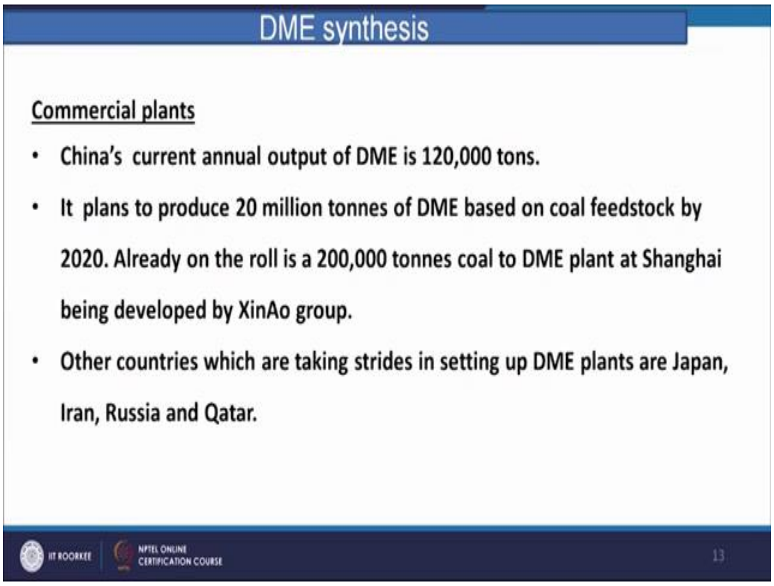

DME synthesis

Commercial plants

- China's current annual output of DME is 120,000 tons.
- It plans to produce 20 million tonnes of DME based on coal feedstock by 2020. Already on the roll is a 200,000 tonnes coal to DME plant at Shanghai being developed by XinAo group.
- Other countries which are taking strides in setting up DME plants are Japan, Iran, Russia and Qatar.

Now, let Us see the production of DME among the world. So, china has a present capacity of DME of 120,000 tons and it is planning to produce 20 million tons of DME based on coal feedstock by 2020, many other countries like Japan, Iran, Russia and Qatar, they are also planning to produce DME.

But DME and methanol we can produce from Syngas, but the difficulty is that as per the present technology available we cannot used the Syngas produced from biomass and waste for the methanol and DME synthesis because of the economics of the process for the use of the DME and methanol as a fuel it has to compete with the diesel and petrol. So, the price of crude oil will influence the importance of the processes.

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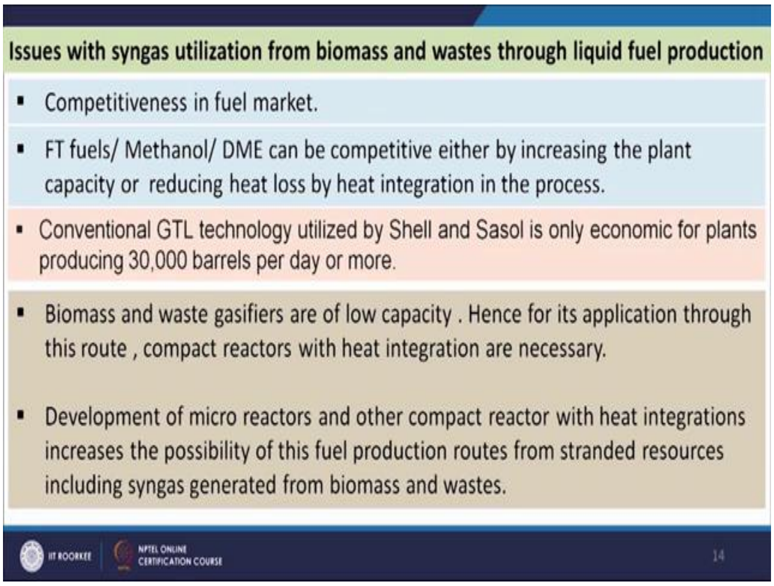

Issues with syngas utilization from biomass and wastes through liquid fuel production

- Competitiveness in fuel market.
- FT fuels/ Methanol/ DME can be competitive either by increasing the plant capacity or reducing heat loss by heat integration in the process.
- Conventional GTL technology utilized by Shell and Sasol is only economic for plants producing 30,000 barrels per day or more.
- Biomass and waste gasifiers are of low capacity . Hence for its application through this route , compact reactors with heat integration are necessary.
- Development of micro reactors and other compact reactor with heat integrations increases the possibility of this fuel production routes from stranded resources including syngas generated from biomass and wastes.

And efforts on to improve the economy of the process for the production of the methanol and DME and they are 2 approach top up and top down to increase the capacity of the plant. So, that economy will increase another is to use small scale reactor with more heat integration. So, heat loss in will be reduced so that the process can be effective. So, this is the trend and when the second option will be more developed when we will get smalls scale reactors with more heat integration then the utilization of Syngas generated from biomass and waste through these fuel woods will be economic and suitable there are some good news that recently the small scale gas to liquid plants have been developed one example is Velosis. So, Velosis has developed a small scale plant which can produce 1500 barrel per day to 15000 barrel per day f t fuels.

Whereas for large scale production of f t synthesis or f t fuels 30000 barrels per day is required. So, the new invention of this new reactor that is micro channel reactor that will increase the possibility of the utilization of the Syngas produced from the biomass in waste for this f t synthesis one example the Velosis first commercial plant is under constructions in Oklahoma city and this is a joint venture with in Velosis waste management incorporation energy and Vantec engineers see in 2016 the plant is expected to run.

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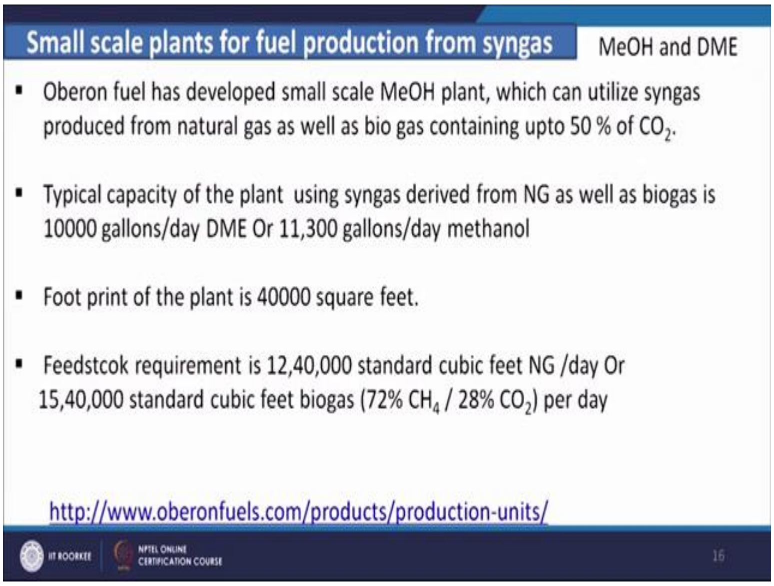

Small scale plants for fuel production from syngas

MeOH and DME

- Oberon fuel has developed small scale MeOH plant, which can utilize syngas produced from natural gas as well as bio gas containing upto 50 % of CO_2.
- Typical capacity of the plant using syngas derived from NG as well as biogas is 10000 gallons/day DME Or 11,300 gallons/day methanol
- Foot print of the plant is 40000 square feet.
- Feedstcok requirement is 12,40,000 standard cubic feet NG /day Or 15,40,000 standard cubic feet biogas (72% CH_4 / 28% CO_2) per day

http://www.oberonfuels.com/products/production-units/

Another is your in planning stage that is Astaguna Ohio near lake Erie and it is 2,800 barrel per day productions is expected, similarly in small scale reactor for methanol synthesis have also been developed Oberon fuel has developed small scale methanol plant which can utilize Syngas produced from natural gas as well as biomass the capacity is at ten thousand gallons per day DME or eleven 1,300 gallons per day methanol and foot print is also less that is 40,000 square feet and feets of requirement is 1,240,000 stand cubic feet natural gas feet natural gas or 1,540,000 standard cubic feet biogas containing 72 percent methane 20 percent CO 2 per day.

Next we will coming to higher alcohol synthesis. So, higher alcohol is synthesized during the methanol synthesis just you have discussed. So, if in presence of C u and z n O catalyst, other catalyst are also suitable for these reactions and here some catalyst like C u C o C r rhodium and other group eight metals have been mentioned here.

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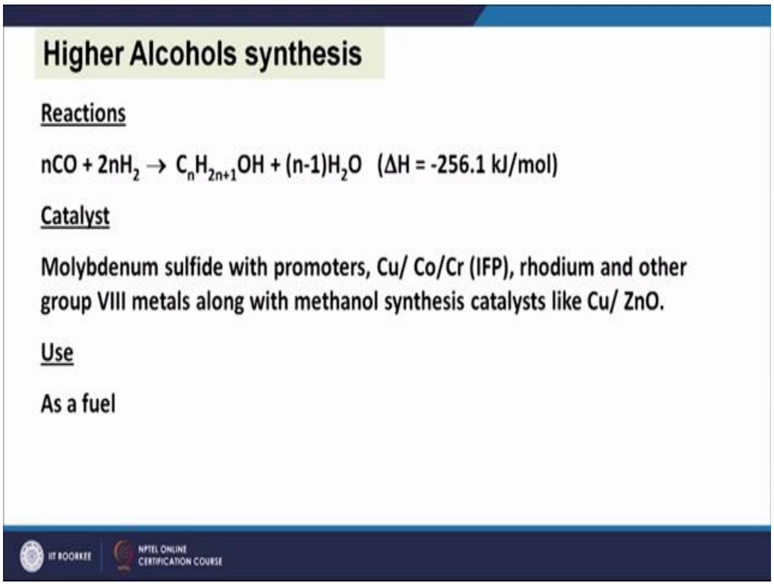

Higher Alcohols synthesis

Reactions

$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \quad (\Delta H = -256.1\ kJ/mol)$

Catalyst

Molybdenum sulfide with promoters, Cu/ Co/Cr (IFP), rhodium and other group VIII metals along with methanol synthesis catalysts like Cu/ ZnO.

Use

As a fuel

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But there is no commercial plant for the higher methanol synthesis, but biological routes are also being developed and bio engineering resource incorporation has developed a bio based process for the production of higher alcohols that is ethanol and it is 3 percent concentration is possible they have developed constraint which can resist sulphur and can overcome 28 to 40 degree centigrade with Co rich gas.

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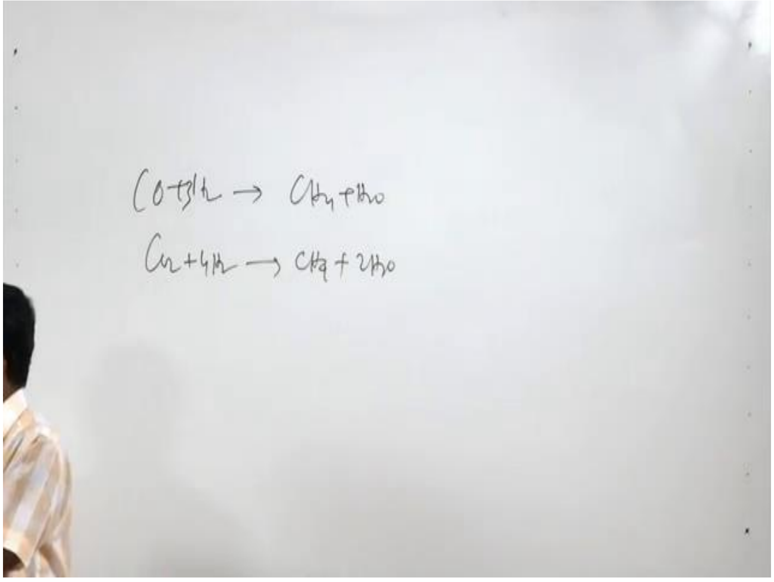

$CO + 3H_2 \rightarrow CH_4 + H_2O$

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Next will come to synthetic natural gas SNG, natural we know CH4. So, CH 4 can be produced from CO plus H 2. So, CO plus H 2 3 S 2 that can give us CH 4 plus H2O and

CO 2 plus 4 H 2 can give us CH 4 plus 2 H2O. So, with the help of suitable catalyst the CO and H 2 that Syngas can be converted to methane that is called synthetic natural gas and number of catalyst has been mentioned here and their superiority has also been given in this preference list.

Next will discuss on the hydrogen production, so hydrogen production we have discussed in the previous module that water gas shift reaction is responsible to increase the hydrogen content in the Syngas.

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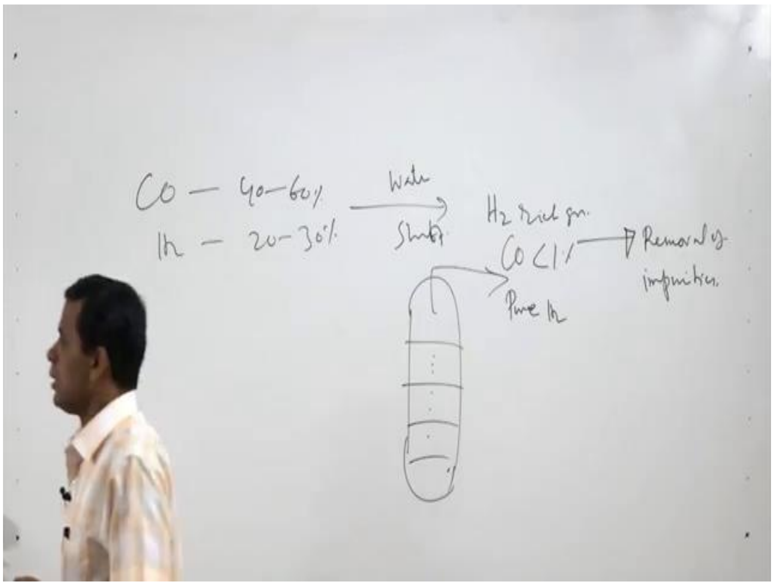

In the Syngas, CO is around say 40 to 60 percent and hydrogen is around your 20 to 40 percent. So, by water shift reaction, we can produce here hydrogen these gas that is CO is less than 1 percent; CO is less than 1 percent, but that 1 percent contain some impurities. So, that has to be removed. So, removal of impurities is very important.

So, what can be available as impurities higher alcohol hydrocarbon moisture? So, these are the major impurities which are available with this hydrogen. So, number of adsorbents are used number of adsorbents are used specific to remove different components.

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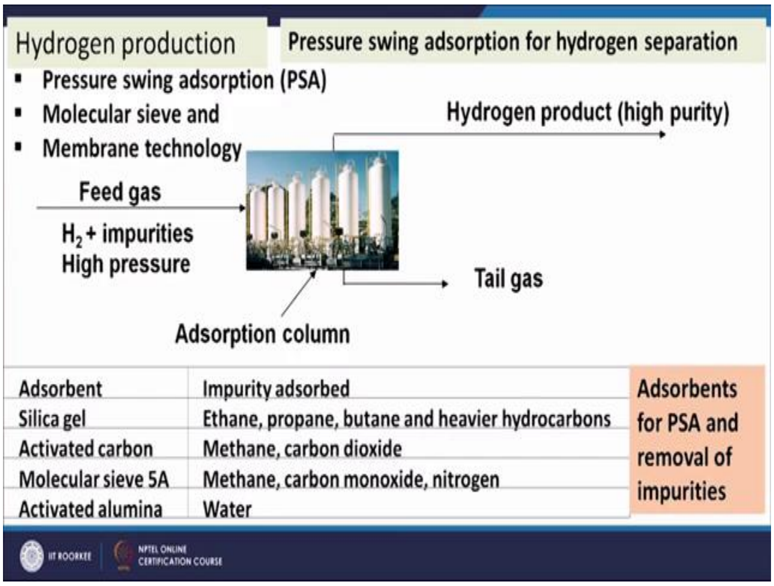

Hydrogen production

Pressure swing adsorption for hydrogen separation

- Pressure swing adsorption (PSA)
- Molecular sieve and
- Membrane technology

Feed gas

H_2 + impurities
High pressure

Hydrogen product (high purity)

Tail gas

Adsorption column

Adsorbent	Impurity adsorbed
Silica gel	Ethane, propane, butane and heavier hydrocarbons
Activated carbon	Methane, carbon dioxide
Molecular sieve 5A	Methane, carbon monoxide, nitrogen
Activated alumina	Water

Adsorbents for PSA and removal of impurities

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Present in the Syngas some examples of absorption are here that is silica gel activated carbon molecular sieve activated alumina. So, silica gel is used to remove ethane propane butane and heavier hydrocarbons activated carbon is used remove methane carbon dioxide molecular sieve is used methane to remove methane carbon dioxide nitrogen and activated alumina is used to remove water.

So, this is the method based on adsorption process through which hydrogen will not be adsorbed in the base, but other impurities will be adsorbed in the base in the bed adsorbed in the bed and pure hydrogen we can collect from the top of this absorption column apart from this some other methods that is molecular sieve and membrane technology are also available for the separation of hydrogen. So, membrane technology; obviously, walks on the size exclusion. So, hydrogen having the lowest size that will be passed through the pores of the membrane, but other molecules will not be able to pass through the membrane.

So, this is the mechanism for the membrane technology for separation of hydrogen from the impurities in the Syngas and for absorption method there are some commercial processes that is pressure swing and temperature swing absorption methods.

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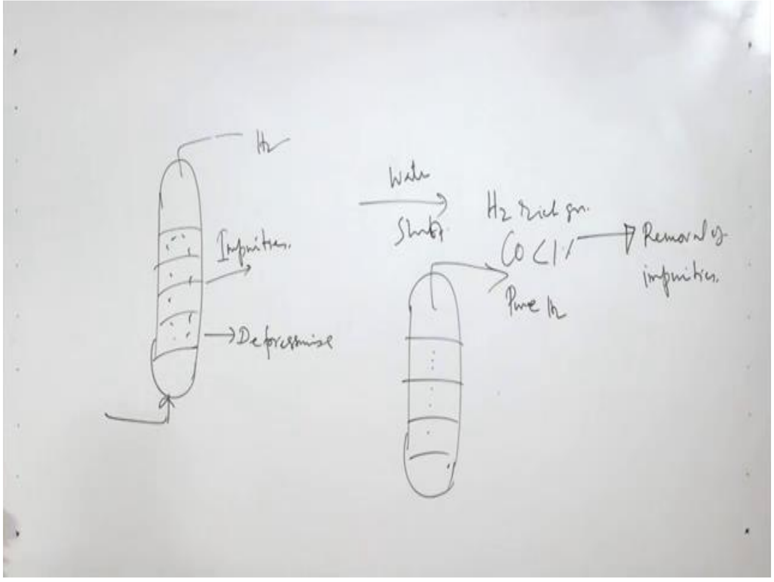

So, in this case at first the column is pressurized. So, when the pressurized more gas molecules will be adsorbed in the absorbance bed and we will get pure hydrogen with time this bed will be exhausted then we need to regenerate it. So, we have to depressurize it depressurize. So, this is a physical absorption physical phenomenon. So, with reduction of the pressured the adsorbed gases will also be coming out from the absorbance.

So, ones the bed exhausted we will stop collecting hydrogen and will reduce the pressure will get the impurities then we will send some purge. So, we are purging. So, purging will help to remove all the impurities present inside then the bed will be ready for further process and this bed will be further pressurized.

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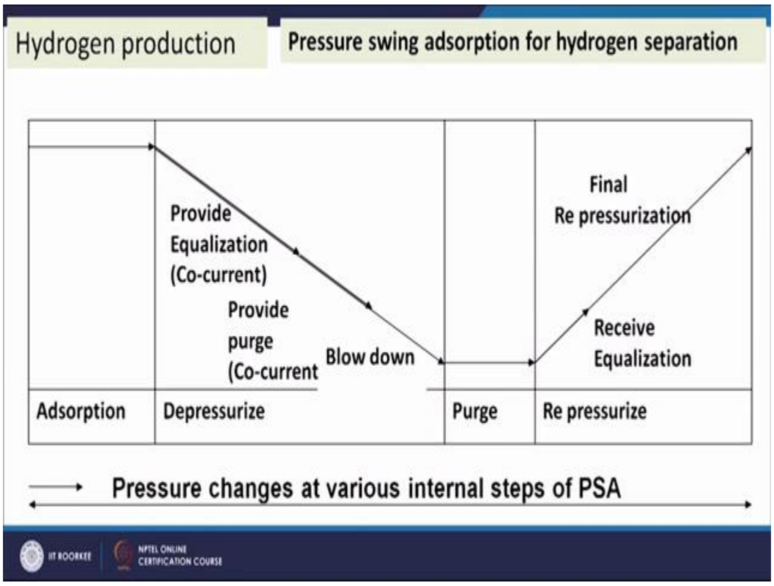

Hydrogen production

Pressure swing adsorption for hydrogen separation

Provide Equalization (Co-current)

Provide purge (Co-current

Blow down

Final Re pressurization

Receive Equalization

Adsorption	Depressurize	Purge	Re pressurize

Pressure changes at various internal steps of PSA

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So, this is the pressure swing absorption process. So, through this we can get pure hydrogen from the Syngas, up to this in this module and thank you very much for your patience.