Inorganic Chemical Technology

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Lecture - 07
Synthesis gas

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Synthesis gas. So, before going into the details of today's lecture what we will be doing? We will be doing a kind of recapitulation of what we have studied in last two classes.

In last two classes we have seen a few basics of fuel and industrial gases and then what is the requirement that why should we start studying about fuel gas and an industrial gases ahead of you know manufacturing processes of any of inorganic chemicals which is the main content of the course. The such kind of reasons we have seen because we understand this fuel gases and industrial gases almost all used in most of the inorganic and chemical industries one way or other way.

So, that is the reason we should have a kind of information about this fuel and industrial gases as well.

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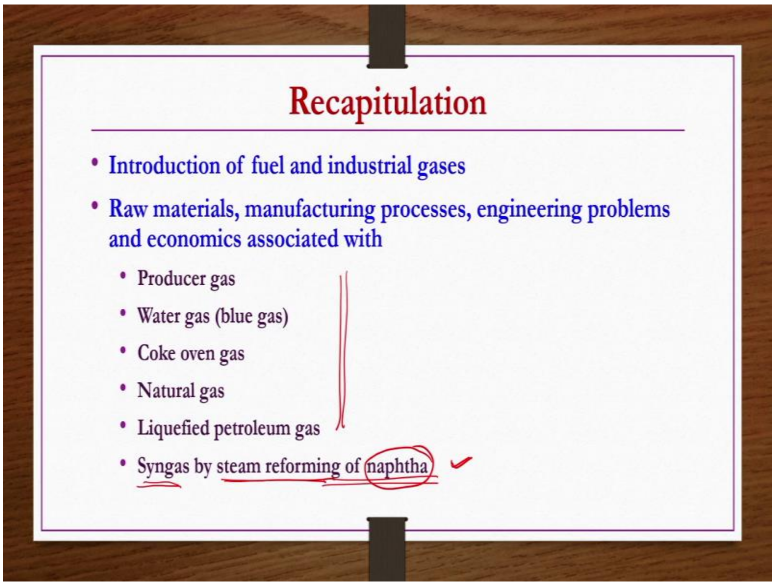

Recapitulation

- Introduction of fuel and industrial gases
- Raw materials, manufacturing processes, engineering problems and economics associated with
  - Producer gas
  - Water gas (blue gas)
  - Coke oven gas
  - Natural gas
  - Liquefied petroleum gas
  - Syngas by steam reforming of naphtha

So, that is what we have seen a few basics of fuel and industrial gases then what we have done? We have categorized the different types of fuel gases and then we start discussing manufacturing process of different types of industrial gases that is raw materials manufacturing processes engineering problems and economics associated with producer gas, water gas or blue gas, coke oven gas, natural gas, liquefied petroleum gas this is what we have studied in detail completely.

And then about the synthesis gas also we started in the previous lecture where we have studied a few basics of synthesis gas and then how many methods of production of synthesis gas available in the different types of chemical plants. Nowadays those things we have seen out of which we have discussed steam reforming of naphtha process to get the synthesis gas and then different routes based on the different products that are that you are willing to have.

Whether you want to have CO plus H 2 synthesis gas or H 2 hydrogen synthesis gas or ammonia synthesis gas based on that one three different approaches three different alternatives we have seen in steam gas production by steam reforming of naphtha. We have also seen what is naphtha and then you know different types of you know aliphatic and aromatic naphtha etcetera those details also we have seen in the previous lecture right.

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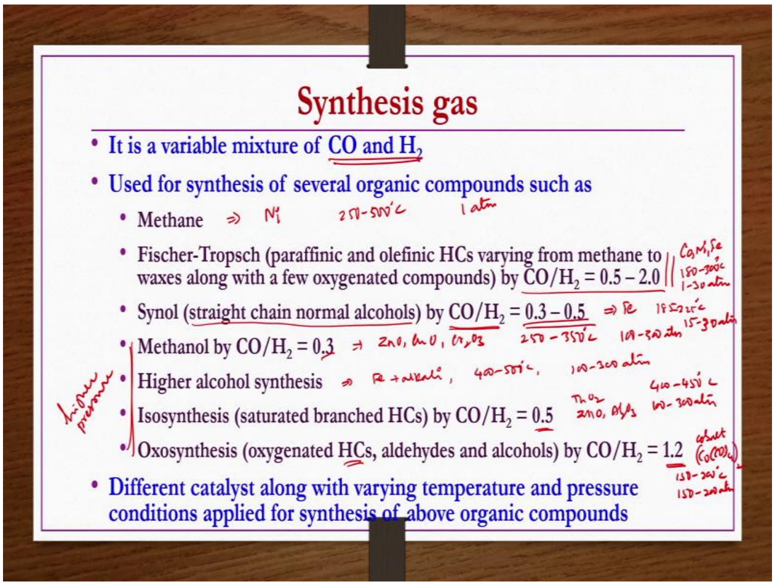

Synthesis gas

- It is a variable mixture of CO and H_2
- Used for synthesis of several organic compounds such as
  - Methane ⇒ Ni 250-500°C 1 atm
  - Fischer-Tropsch (paraffinic and olefinic HCs varying from methane to waxes along with a few oxygenated compounds) by $CO/H_2 = 0.5 - 2.0$ Co, Ni, Fe 150-300°C 1-30 atm
  - Synol (straight chain normal alcohols) by $CO/H_2 = 0.3 - 0.5$ ⇒ Fe 185-225°C 15-30 atm
  - Methanol by $CO/H_2 = 0.3$ ⇒ ZnO, CuO, Cr_2O_3 250-350°C 100-300 atm
  - Higher alcohol synthesis ⇒ Fe + alkali, 400-500°C, 100-300 atm
  - Isosynthesis (saturated branched HCs) by $CO/H_2 = 0.5$ ThO_2 ZnO, Al_2O_3 400-450°C 100-300 atm
  - Oxosynthesis (oxygenated HCs, aldehydes and alcohols) by $CO/H_2 = 1.2$ cobalt ($Co(CO)_4$) 150-200°C 150-200 atm
- Different catalyst along with varying temperature and pressure conditions applied for synthesis of above organic compounds

higher pressure

However, this lecture is also based on synthesis gas. So, then we have a kind of a introductory information once again about the synthesis gas that is it is a variable mixture of CO plus H 2 and then it is useful for synthesis of several organic components such as methane, then paraffinic and olefinic hydrocarbons varying from methane to waxes along with few oxygenated compounds using Fischer-Tropsch method by varying CO 2 H 2 ratio between 0.5 to 2.

And then synols which is a common terminology for straight chain normal alcohols this can be obtained by CO 2 CO carbon monoxide to H 2 ratio between 0.3 to 0.5 whereas, methanol by having this ratio to 0.3 and then higher alcohols up to c n alcohol synthesis etcetera can also be done by using synthesis gas we can also produce saturated branched hydrocarbons by iso synthesis by having this ratio of CO and H 2 0.5.

Then oxosynthesis that is oxygenated hydrocarbon something like aldehydes alcohols etcetera can also be produced by maintaining CO divided by H 2 ratio of 1.2 value. And then; obviously, these are a kind of simplification simple information that we are giving if we go in specific about each of these processes the temperature pressure and the catalyst would be there they would be varying from one to other ok.

Now, what we will be doing? We will be having a kind of different types of catalyst that are used to get such kind of organics as shown above and then what are the temperature and pressure conditions let us say if you wanted to produce methane, you need to have a nickel catalyst temperature may be 250 to 500 degree centigrades and then pressure may be 1 atmospheric pressure is sufficient.

But if you wanted to apply Fischer Tropsch approach to get different types of chemicals, you need to have a catalyst like a cobalt, nickel, iron at temperature 180 to 300 degree centigrades or this is the process temperature and then pressure may be 1 to 30 atmospheres whereas, in order to produce synols then you may need to have a catalyst like iron catalyst temperature between 185 to 225 degree centigrades.

And then pressure may be between 15 to 30 atmosphere for methanol production you need to have a catalyst ZnO zinc oxide, copper oxide or chromium oxide these catalyst are required temperature may be between 250 to 350 degree centigrades whereas, the pressure is very high pressure required that is 100 to 300 atmospheres right.

If you wanted to produce higher alcohols from the synthesis then iron plus alkali catalyst may be required. Temperature may not be temperature is in the range of 400 to 500 degree centigrades and then pressure is again between 100 to 300 atmospheric pressures for iso synthesis the catalyst are provided like ZnO Al 2 O 3 alumina etcetera the temperature may be between 400 to 450 degree centigrades and then pressure is 100 to 300 atmospheres.

Whereas, oxosynthesis you need to have a cobalt carbonate catalyst right temperature is not that high that is 150 to 200 degree centigrade is sufficient, but the pressure is very high that is two 150 to 200 atmospheric. So, what you can see here from for producing methanol or higher alcohols isosynthesis oxosynthesis components, you need to have higher pressure conditions ok if you wanted to produce them from the synthesis gas fine.

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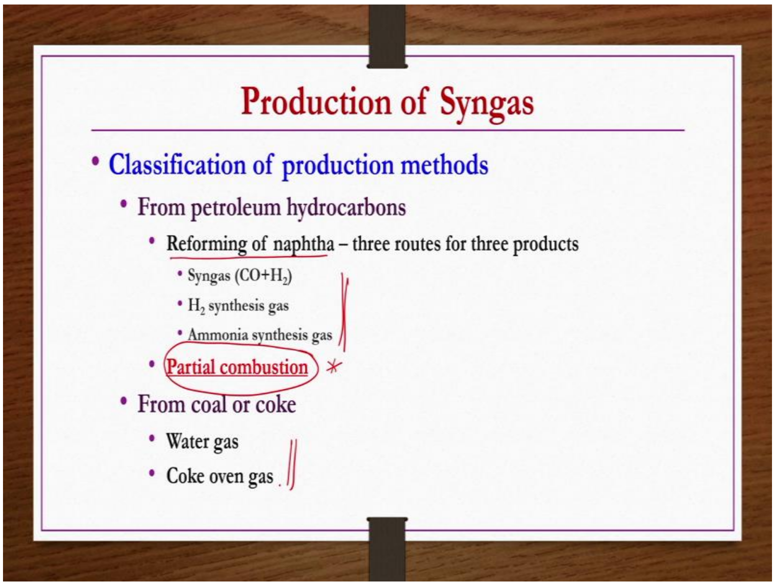

Production of Syngas

- Classification of production methods
  - From petroleum hydrocarbons
    - Reforming of naphtha – three routes for three products
      - Syngas ($CO+H_2$)
      - H_2 synthesis gas
      - Ammonia synthesis gas
    - Partial combustion *
  - From coal or coke
    - Water gas
    - Coke oven gas

So, now, what are the different types of production methods we have seen? There are two major methods one is from petroleum hydrocarbons if you are using petroleum hydrocarbons or natural resources or something like a natural gas etcetera then we have two methods if you are producing this from coal or coke, then we have a two methods.

From petroleum hydrocarbons one method is reforming steam reforming of naphtha there are three routes for three products alternative that is three alternatives that are there that we have already seen that is syngas if you wanted to have CO plus H 2.

If you have if you need to produce H 2 synthesis gas, if you need to produce ammonia synthesis gas then three different alternatives are there from the same process depending on your requirement, you can choose the set of you know the flow sheet that we have discussed in the previous class this is we have already discussed in the previous class.

Today we are going to discuss how to produce synthesis gas by partial combustion method. So, what are the raw materials? What are the reactions? What are the quantitative requirements process flow sheet and then process economics etcetera these things we are going to see in today’s lecture right.

Previously we have also seen from coal or coke we can produce water gas or water gas and coke oven gas as well ok.

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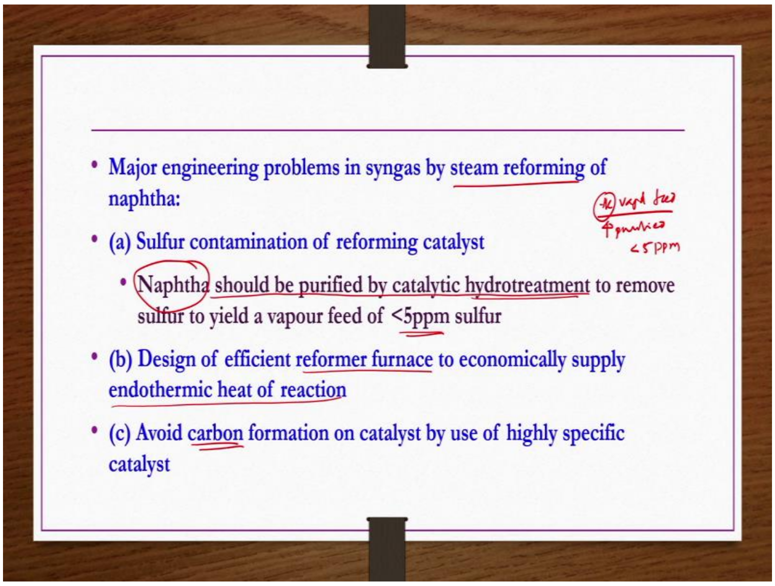

- Major engineering problems in syngas by steam reforming of naphtha:
- (a) Sulfur contamination of reforming catalyst
  - Naphtha should be purified by catalytic hydrotreatment to remove sulfur to yield a vapour feed of <5ppm sulfur
- (b) Design of efficient reformer furnace to economically supply endothermic heat of reaction
- (c) Avoid carbon formation on catalyst by use of highly specific catalyst

HC vapd feed
purified
<5ppm

So, before going into the details of production of synthesis gas by partial combustion of naphtha or natural gas and what we do? We will be having a kind of a discussion about major engineering problems in production of syngas by steam reforming of naphtha that we have seen yesterday.

What we have seen in yesterday? There is a reformer which is provided with steel tubes we have a nickel catalyst right and then this reactor is maintained at high temperature. So, preheated naphtha enters this reactor and then when they enter into the reactor reforming reactions take place and then CO, H 2, CO 2 etcetera are produced that is what we have seen.

So, then sulfur may be present in the feed what is the feed that we have taken? We have taken hydrocarbon vapour feed that is what the feed that we have taken for this steam reforming of naphtha. So, these hydrocarbons should be purified they should be purified if there is a sulfur at all in general in most of the petroleum crude sulfur is present.

So, if it is present in the crude. So, then during the subsequent operations in the products sulfide hydrogen sulfide and other sulfides are going to be present. So, that one has to make sure. So, if sulfur is present in the feed material itself. So, that is going to hamper the process dearly in the case of a synthesis gas production by steam drafting by steam reforming that is the reason one has to make sure that in the feed hydrocarbon vapour feed whatever we are taking there should not be sulfur more than 5 ppm.

So, that is the reason naphtha should be purified by catalytic hydro treatment prior to the steam reforming so, that to avoid this sulfur presence of sulfur in the feed ok. It should not be more than 5 ppm in the feed ok. So, naphtha feed whatever is there before using it for the steam reforming to get synthesis gas that has to be properly hydro treated that catalytic hydro treatment has to be done that is reacting of naphtha using hydrogen in the presence of catalyst.

So, that hydrogen reacts with the sulfur present in the this naphtha and then it produces H 2 S or other sulfide gases which can be removed easily right. Then after that the naphtha or purified hydrocarbons vapour whatever is there you have to check whether the higher sulfur is how much it is there?

If it is less than 5 ppm then you can take it to the steam reforming reaction to produce the synthesis gas. Second one is the design of efficient reformer furnace to economically supply endothermic heat of reaction. Previous class we have seen different types of reactions in the steam reforming of naphtha case to produce synthesis gas right. So, there are two endothermic reactions are there.

So, that the heat should be supplied to the reaction so, that to take those two reactions because those are endothermic reactions, but we have seen that lot of heat is evolved in the process. So, that should be properly designed I mean plant has to be designed properly so, that to; so, that to take or consider you know collect that heat properly and then supply it to the endothermic reactions.

So, such a way one has to do efficient design of reformer furnace. Then anywhere any of the reactions that you take with naphtha, naphtha you take or any hydrocarbons you take and then you do the reactions at high temperature there is a possibility of carbon formation mostly there is a possibility of carbon formation.

What is the problem if it forms? It when the carbon forms it deposit it get deposited on the surface of the catalyst and then catalyst get deactivated and then subsequent reaction or the primary reactant slows down that is the major concern. So, you should select such a catalyst so, that the carbon formation is negligible almost negligible or it is 0 such a catalyst you have to choose for the process right.

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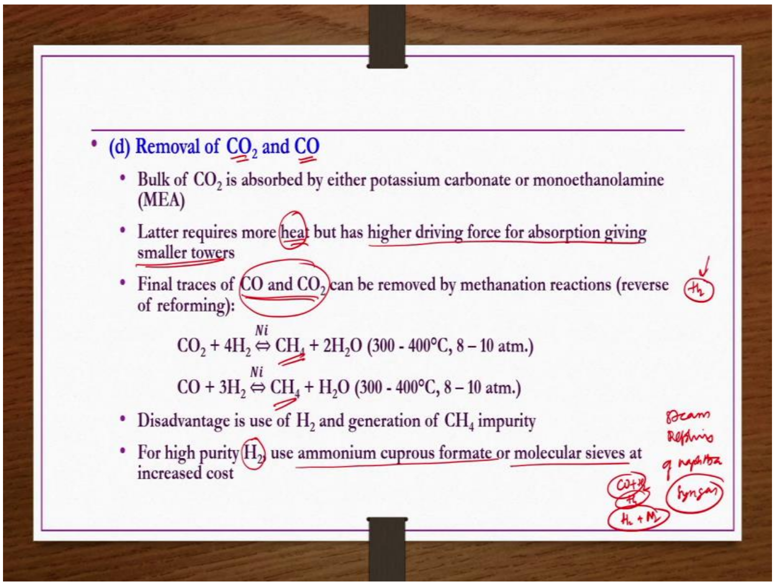

- (d) Removal of CO_2 and CO
  - Bulk of CO_2 is absorbed by either potassium carbonate or monoethanolamine (MEA)
  - Latter requires more heat but has higher driving force for absorption giving smaller towers
  - Final traces of CO and CO_2 can be removed by methanation reactions (reverse of reforming):

$$CO_2 + 4H_2 \overset{Ni}{\Leftrightarrow} CH_4 + 2H_2O \ (300 - 400°C, 8 – 10 \text{ atm.})$$

$$CO + 3H_2 \overset{Ni}{\Leftrightarrow} CH_4 + H_2O \ (300 - 400°C, 8 – 10 \text{ atm.})$$

  - Disadvantage is use of H_2 and generation of CH_4 impurity
  - For high purity H_2 use ammonium cuprous formate or molecular sieves at increased cost

H_2 ✓

Steam Reforming

q naphtha

Syngas

$CO+H_2$

H_2

$H_2 + N_2$

Then removal of CO 2 and then CO. Because we know that process if you are required to do the synthesis gas production this plant if you wanted to operate in order to produce high concentrate or highly purified hydrogen then this CO 2 and CO has to be removed. So, then how efficiently are you removing that is going to be very essential ok.

So, bulk of CO 2 is absorbed by either potassium carbonate or mono ethanol amine solutions ok that is what we have seen ethanol amine solutions we have seen in the previous class ok they are used for absorbing the CO_2 that is present in the effluent gas of the furnace ok.

So, but this solution requires more heat, but has higher driving force for absorption giving smaller towers that is you can use smaller towers and then you can have a kind of higher driving force for the absorption so, that more absorption can takes place, but it requires more heat. So, then one has to make a trade off right. If you are if in the process itself there are several streams may be there where heat may be evolving.

So, if you can effectively collect and then supply wherever it is required for such kind of absorption then it is fine otherwise you have to make a tradeoff between should you go for this MEA solution or potassium carbonate or any other solution like that is another issue.

And then final traces of CO, CO_2 can be removed by methanation reaction. The reverse of steam reforming reaction is taking place. So, what is the problem right? The first of all after CO conversion in CO by shift conversion by shift converter CO has been converted to CO_2 and then, but still there are some traces of CO would be there along with the CO_2 and then when you remove the CO_2 using the solution CO_2 most of it is removed.

But still after that also some traces of CO and CO_2 would be present along with the H_2 right. If you are if you wanted to produce high purity H_2 then they should not be there even in traces then methanation is one of the best possibility, but you know here using we actually you are producing this you wanted to remove these traces because you wanted to produce high purity H_2.

But again you are using the same high purity H_2 to remove this traces only traces of CO and CO_2 that is one limitation right. Another limitation is that it is forming methane. Though methane is not going to be you know disadvantageous, but if you wanted to have a pure hydrogen. So, then; obviously, it is going to be a treated as a impurity ok. So, that is another limitation of this method ok.

For high purity H_2 sometimes you may need to use ammonium cuprous formate or molecular sieves which again increases the cost of production ok. So, these are the some major engineering problems associated with the steam reforming of naphtha to produce syngas. Syngas either CO plus H 2 or only H 2 or H 2 plus N 2 syngas ammonia synthesis gas whatever you want to produce right.

So, these are the issues one has to handle carefully even if it is the beginning of the plant designing and installation or even during the operation of a existing plant one has to be careful about such kind of problems ok. There may be more number of problems associated with any plant, but in general whatever the problems that we are discussing in the course at the end of each chemical production you know they are major engineering problems.

So, they may be common for almost all plant. So, then one has to be aware of such kind of engineering problems ok.

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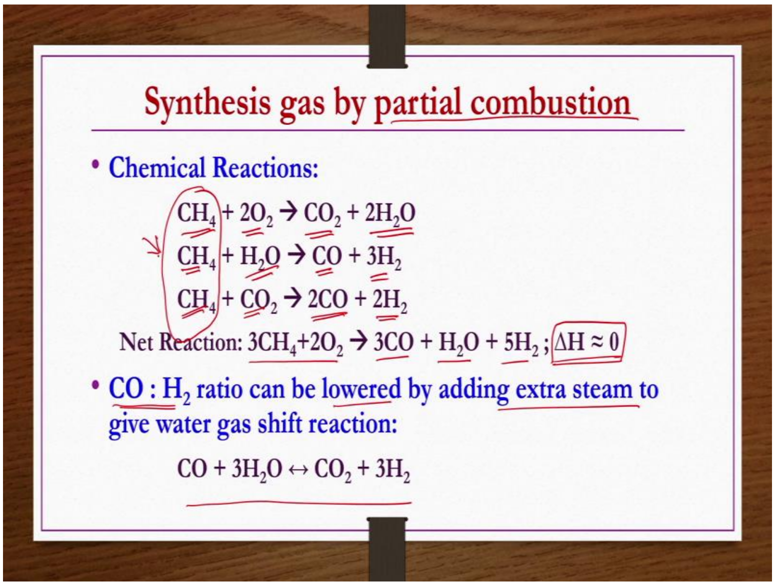

Synthesis gas by partial combustion

- Chemical Reactions:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$CH_4 + H_2O \rightarrow CO + 3H_2$

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$

Net Reaction: $3CH_4 + 2O_2 \rightarrow 3CO + H_2O + 5H_2$; $\boxed{\Delta H \approx 0}$

- $CO : H_2$ ratio can be lowered by adding extra steam to give water gas shift reaction:

$CO + 3H_2O \leftrightarrow CO_2 + 3H_2$

So, now we see synthesis gas production by partial combustion ok. Now first we see chemical reactions CH 4 reacts with O 2 to give CO 2 and 2 H 2 O, 2 moles of oxygen we are utilizing. And then CH 4 reacting with water giving rise to CO plus 3 H 2 and then another possible reaction is CH 4 reacting with already produce CO 2 giving rise 2 CO and 2 H 2 right.

So, these are the reactions possible in the gas generator reactor that we are going to see which is often used for the partial combustion of a natural gas partial combustion of natural gas or hydrocarbons you know sometimes other hydrocarbons also used. So, if you are using them in the gas generator reactor.

So, then these kind of reactions are possible the net reaction is that three CH 4 plus 2 O 2 giving rise to three CO H 2 O plus 5H 2 and then steam may be adjusted or provided such a way that delta H of the reaction is approximately 0 right. This ratio CO 2 H 2 can also be lowered by adding extra steam to give water gas shift reaction and then that reaction is reversible it is known to everyone right.

So, these are the possible reaction that occur in the gas generator reactor chamber ok where partial combustion of a feed material is taking place. So, what is the feed that we are taking? From as per these reactions we are taking natural gas.

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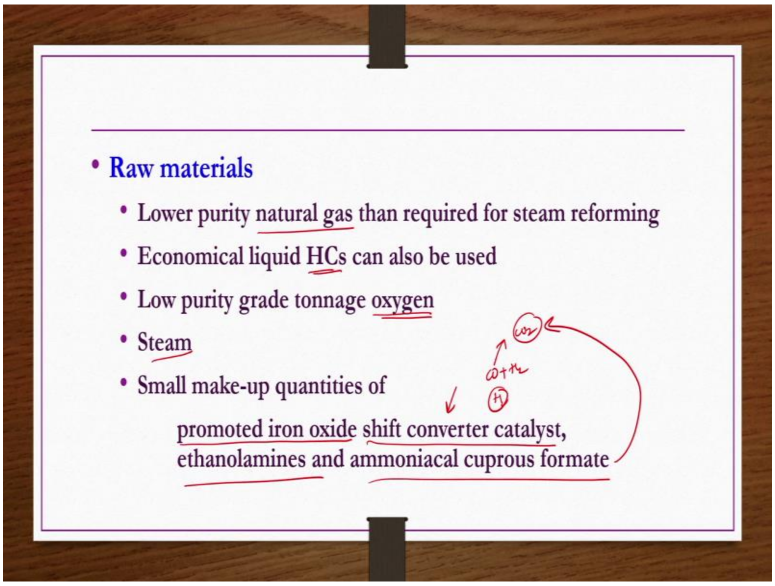

- Raw materials
  - Lower purity natural gas than required for steam reforming
  - Economical liquid HCs can also be used
  - Low purity grade tonnage oxygen
  - Steam
  - Small make-up quantities of

    promoted iron oxide shift converter catalyst, ethanolamines and ammoniacal cuprous formate

So, based on the reactions what we can understand? One of the important raw material is lower purity natural gas. You don’t need to have high purity natural gas lower purity natural gas is sufficient for you to produce synthesis gas. Then economical liquid hydrocarbons can also be used.

A hydrocarbons which are not very expensive they can also be used in the partial combustion method to produce this synthesis gas ok. Low purity grade tonnage oxygen is required then steam is required small makeup quantities of obviously, catalyst and solutions are required for absorption reaction and absorption respectively.

So, promoted iron oxide shift converter catalyst is required, ethanolamines and an ammoniacal cuprous formate solutions are required for the absorption. The shift converter is required let us say rather having CO plus H 2 if you wanted to have more H 2 then what you do? You do the water gas shift reaction and then the CO converts to CO 2 and then the CO 2 gets absorbed by ethanolamine solutions or ammoniacal cuprous formate.

That is after that you know partial combustion reaction chamber most of the methods or the you know separation purification methods are more or less similar to what we have seen in the previous method of steam reforming.

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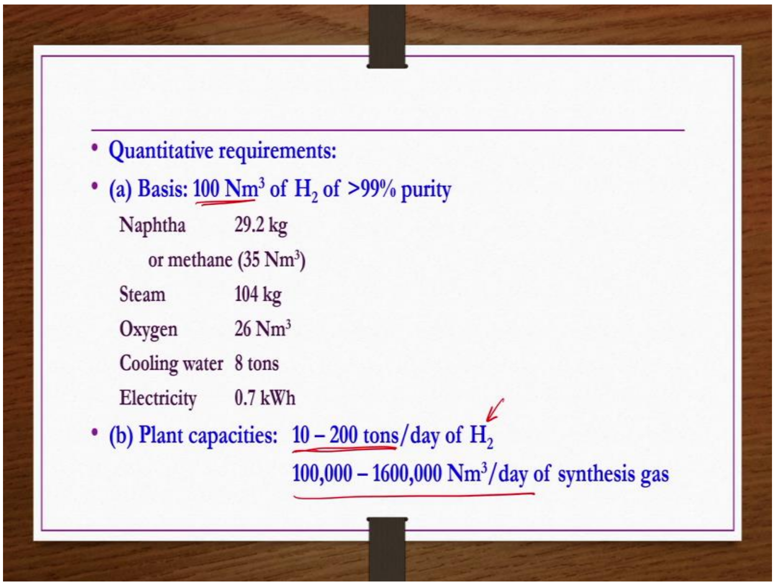

- Quantitative requirements:
- (a) Basis: 100 Nm^3 of H_2 of >99% purity

Naphtha	29.2 kg
or methane (35 Nm^3)	
Steam	104 kg
Oxygen	26 Nm^3
Cooling water	8 tons
Electricity	0.7 kWh

- (b) Plant capacities: 10 – 200 tons/day of H_2
  100,000 – 1600,000 Nm^3/day of synthesis gas

Quantitative requirements this is very essential. Let us say if you wanted to produce 99 percent or more than 99 percent pure hydrogen and then if you wanted to produce 100 normal cubic meters of such hydrogen then how much naphtha is required? Around 29.2 kgs. If you are using natural gas then how much it is required? Methane 35 normal cubic meters required steam 104 kgs, oxygen 26 normal cubic meters, cooling water 8 tons, electricity 0.7 kilowatt hour required.

And then plant capacity is little less 10 to 200 tons per day if you are intended to have hydrogen only not CO plus H 2, but only H 2. But if you wanted to have CO plus H 2 then capacity is quite high that is 100000 to 1600000 normal cubic meters per day of synthesis gas ok.

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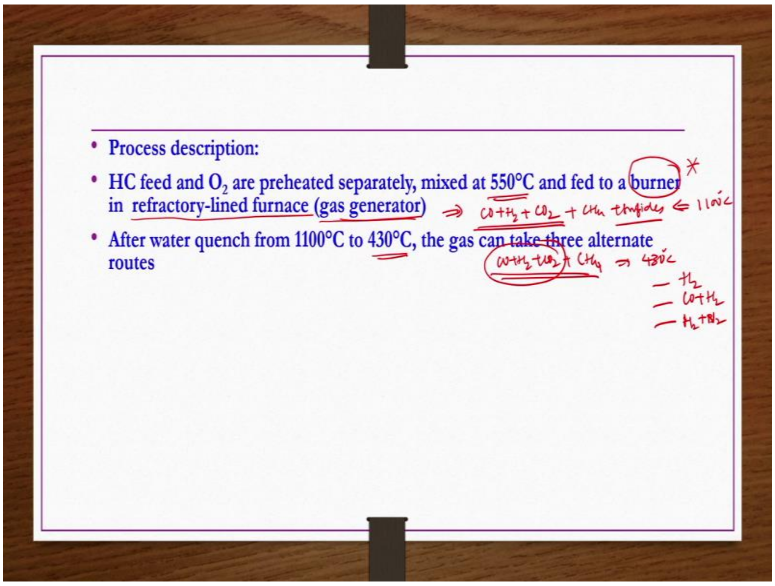

- Process description:
- HC feed and O_2 are preheated separately, mixed at 550°C and fed to a burner in refractory-lined furnace (gas generator)
- After water quench from 1100°C to 430°C, the gas can take three alternate routes

*

$\Rightarrow CO + H_2 + CO_2 + CH_4$ + sulfides $\Leftarrow$ 1100°C

$CO + H_2 + CO_2 + CH_4 \Rightarrow$ 430°C

— H_2

— $CO + H_2$

— $H_2 + N_2$

Now, first we see the process description because as I mentioned process description after the partial combustion reaction taking place in a gas generator reactor, the separation sections are more or less same as what we have seen in the previous class where steam reforming of naphtha has been studied discussed in order to get synthesis gas ok.

So, that is the reason we are first seeing the process first we see process description. The feed material hydrocarbon or methane whatever you are taking as a feed and then oxygen which you are taking low grade oxygen that is as described in raw material separately individually you take and then heat them and then mix at 550 degree centigrade and feed to a burner in a refractory lined furnace which we call gas generator.

So, now here this burner design is going to be very essential you need to have a very stable burner because this when the feed and oxygen are coming so; obviously, that burn whatever the flame produced by the burner is not going to be stable. So, you have to design such a way that you know it has to be stable ok.

And then after the reaction whatever the components that are produced are CO H 2 and CO 2 primarily or whatever the effluent gas after the gas generator that you get primarily CO H 2 and CO 2 there may be some traces of CH 4 and then sulfides etcetera also may be there depending on the feed that you have taken how pure it is right.

So, these gases would be at very high temperature at 1100 degree centigrade something like that. So, such gases at such these gases at such high temperatures are very dangerous. So, then what you have to do? You have to quench them immediately after the reactor when they come out as effluent you quench them to lower temperature 430 degree centigrade using the water quenching process right.

And then once the gases they are still the same gases after this step also same gases are there, but now they are at lower temperature at 430 degree centigrades right. Then these gases now these are the you know product gases let us say primarily these things are you know making up to almost like more than 90 percent of gas effluents are having CO H 2 and CO 2.

Now, whether you need H 2 or you need CO plus H 2 or you wanted to take it to the ammonia synthesis plant so, that to have N 2 plus 3 H 2 these kind of things depending on your requirement you know different steps are there, but now we there is another alternative is also there because once hydrogen is produced so, then you can use it in ammonium synthesis anyway.

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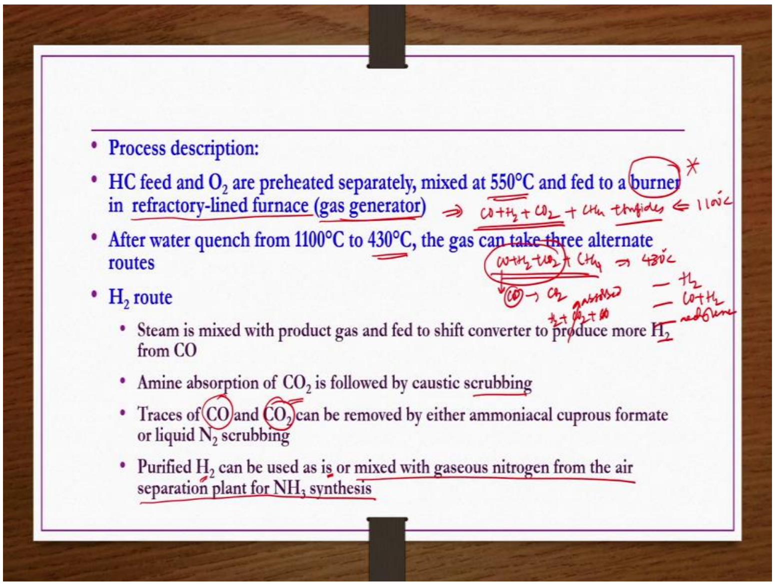

- Process description:
- HC feed and O_2 are preheated separately, mixed at 550°C and fed to a burner in refractory-lined furnace (gas generator)
- After water quench from 1100°C to 430°C, the gas can ~~take three~~ three alternate routes
- H_2 route
    - Steam is mixed with product gas and fed to shift converter to produce more H_2 from CO
    - Amine absorption of CO_2 is followed by caustic scrubbing
    - Traces of CO and CO_2 can be removed by either ammoniacal cuprous formate or liquid N_2 scrubbing
    - Purified H_2 can be used as is or mixed with gaseous nitrogen from the air separation plant for NH_3 synthesis

So, but here acetylene production is the another possibility like compared to the previous steam reforming method that we have seen. In the steam reforming method we have option only for H 2 CO plus H 2 and then N 2 plus 3 H 2 these three gases combination is only possible now here acetylene production is also possible right depending on what is your aim. So, you the process steps would change right.

If you wanted to have H 2 route or; that means, if you wanted to produce more H 2 then what you have to do? Out of these three components this CO whatever is there that you convert to the CO 2 by water gas shift reactor by passing through a shift converter. So, that you know primarily then you will be having H 2 plus CO 2 plus some traces of CO should be there, but negligible ok.

Then this CO 2 if you absorb in some solution then pure H 2 you will be having. So, that is the step that we are going to follow that is steam is mixed with product gas and fed to shift converter to produce more H 2 from CO right amine absorption of CO 2 is followed by caustic scrubbing to remove whatever the CO 2 is there in the mixture of H 2 plus CO 2 right.

And then whatever the traces of CO and then CO 2 are there they can be removed by either ammoniacal cuprous formate or liquid nitrogen scrubbing approaches. Purified H 2 can be used as it is or mixed with gaseous nitrogen from the air separation plant for ammonia synthesis right.

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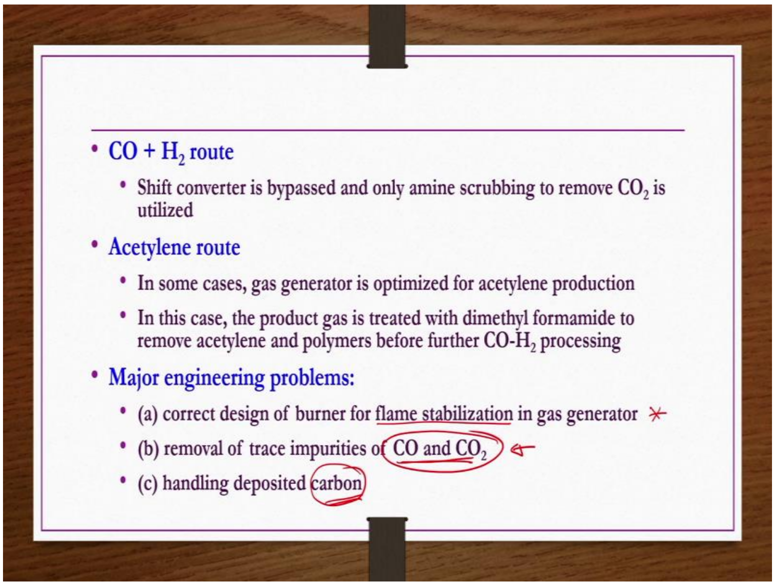

- $CO + H_2$ route
  - Shift converter is bypassed and only amine scrubbing to remove CO_2 is utilized
- Acetylene route
  - In some cases, gas generator is optimized for acetylene production
  - In this case, the product gas is treated with dimethyl formamide to remove acetylene and polymers before further $CO\text{-}H_2$ processing
- Major engineering problems:
  - (a) correct design of burner for flame stabilization in gas generator
  - (b) removal of trace impurities of CO and CO_2
  - (c) handling deposited carbon

If you wanted to have CO plus H 2 route so, that to get synthesis gas with the various you know ratio of CO plus H 2 only without any CO 2. Then what you have to do? You just bypass that water gas shift converter and then remove CO 2 by absorption that is it.

Shift converter is bypassed only amine scrubbing to remove CO 2 is utilized then acetylene route in some cases gas generator is optimized for acetylene production in this case the product gas is treated with dimethyl formamide to remove acetylene and polymers before further CO H 2 processing is to be done.

And then what are the engineering problems? Here as I mentioned correct design of burner for flame stabilization in gas generator is very very essential based on the stability of the flame the product composition of CO 2 CO and H 2 is going to change that is present in the effluent gas of the from the gas generator that is coming from the gas generator ok.

So, it is very much essential other two problems are similar like similar compared to the previous method of steam reforming method what are the removal of traces of impurities like CO CO 2 right and then handling of deposited carbon right. So, you removal for this removal you may be using expensive solutions or solvents and then or molecular sieves etcetera so, that makes process expensive.

Even if you are doing methanation reaction to convert them into methane or something like that then that methane is going to be present as impurities such kind of problems are there in the previous method and this method also there. And then as I mentioned the carbon formation if the reaction is occurring is at high temperature then is a common problem any of the organic synthesis that you do for if you are doing at high temperatures and high pressures.

So, then that carbon if it get deposited on the catalyst surface catalysts will deactivated and then reaction progress may not be there. So, then for that reason what you have to do? You have to choose a catalyst such a way that in a given particular process the carbon formation would be negligible.

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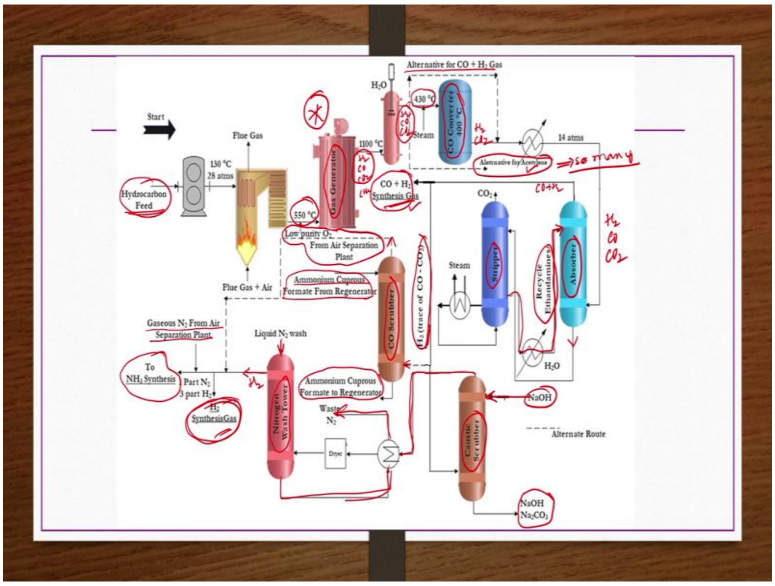

Now, same thing whatever we describe the process we can discuss through flow sheet here ok. So, the process description is given there and now we are going to see the same thing by flow sheet ok. So, we take hydrocarbon feed and then heat it to certain temperature at certain pressure conditions as per the requirement.

How do we do? We pass it through a chamber by through which flue gas and then airs are flowing at certain as per the required temperature right and then what you do separately you take low purity oxygen from air separation plant and then you heat it preheat right.

So, the hydrocarbons and then oxygen separated from air separation plant are individually preheated to certain high temperature and mixed at 550 degree centigrade before feeding to the gas generator reactor. So, gas generator is the chamber in which the partial combustion of feed is taking place right.

When this partial combustion is taking place we will be getting H 2 CO and CO 2 along with some impurities like methane and sulfates etcetera. So, primarily H 2 CO and CO 2 would be there right. So, these would be at high temperature like you know 1100 degree centigrade or something like that these gases at certain such high temperatures are going to be very dangerous.

So, then immediately you do you what you do? You quench them. So, you take a tower pass these gases from the bottom of the tower and from the top you spray the water cool water. So, that the temperature immediately fall down to 430 degree centigrades right. So, but the composition is still same primarily H 2 CO and then CO 2. So, these gases if you wanted to produce acetylene.

So, then there is a separate route right so, many approaches are there, so many we have already seen in week 1 lecture. So, alternative approaches. So, there we have seen for acetylene. So, many methods are there. So, we are not going to discuss how to produce acetylene from this combination of a effluent gas right.

So, that is not required as per the you know this week's lecture that is required in organic chemical technology separate course ok. Other thing is that let us say if you wanted to have CO and H 2 only then what you do? You take this gases H 2 CO CO 2 gases through this approach bypass the reactor right.

And then you do the scrubbing using in absorption column you scrub the H 2 CO CO 2 whatever are there those gases at 430 degree centigrades and 14 atmosphere you pass through absorption column where ethanol amine solutions are produced where ethanol amine solutions are provided so, that to absorption of CO 2 can be taken place or CO 2 may be absorbed into those solutions right.

So, once CO 2 is absorbed. So, then you may be having only CO and then H 2 almost 99 percent. So, this CO and H 2 you can collect it as synthesis gas right. So, the solution is you know you cannot have you know tons per day of solution for the simple absorption.

So, what you do? You have to recycle it whatever the spin solution or diluted solution where CO 2 is being absorbed so, that you take it to the stripper section right in the stripper section you remove the CO 2 from the you know solution right absorption and stripper are opposite absorption is absorbing the gas into the liquid stripping is you know removing the gas from the liquid.

So, once you remove the CO 2 from the liquid that liquid you can take back to the absorber. So, that this recycling of solution takes place and then you don't need large quantities of a you know solution for this absorption alone ok. So, two alternatives we have seen acetylene production alternative and then synthesis gas CO plus H 2 production we have seen.

Let us say if you wanted to have pure hydrogen synthesis gas then what you have to do after this scrubbing section? What you do? This effluent gas at 430 degree centigrade that effluent gas is having H 2 CO and CO 2 that you take to CO converter which is at 400 degree centigrade.

And then iron catalysts is present here what happens? In this converter CO would be converted to the CO 2 CO would be converted to the CO 2. So, primarily output or effluent gases of the CO converters are H 2 and then CO 2 only. Traces of CO N a O they may be there. So, then after this converter then process is same you take it to the CO 2 absorber and then once from the CO 2 absorber CO 2 is removed. So, then pure H 2 would be there.

So, then the pure H 2 with only traces of CO 2 you know you can get and then that you can subsequently take to the caustic scrubbing or CO scrubber using the cuprous ammonium cuprous formate solution separately to further purify the hydrogen ok. So, let us say if you take it to the caustic scrubber. So, here you are using a new NaOH solution and then this hydrogen gas with traces of CO CO 2 are pass are allowed to pass through this scrubber from the bottom and from the top you are taking NaOH solution.

So, in this solution what happens? Whatever the traces of CO CO 2 are there they will be absorbed within NaOH and then NaOH along with the sodium carbonate some type some kind of reaction with the NaOH and then CO 2 may takes place and then sodium carbonate may form right.

So, those things are collected from the bottom from the top after removing the CO CO 2 they are collected and then dried and then sent to a nitrogen wash tower even if further some CO CO 2 etcetera are still present even after caustic scrubber then you can pass it through a nitrogen wash tower where liquid nitrogen is provided from the top to remove the CO.

And then almost like pure 99 percent or more than 99 percent H 2 you get as a synthesis gas that you can collect right. So, here whatever the liquid nitrogen used for the absorption of traces of CO CO 2 that will be again diluted. So, then what you have to do? You have to pass through your steam chamber and then recover the waste N 2.

Whatever the gases are there let us say they should be taken on to the dryer and then fed back to the nitrogen wash tower further for the further purification of those gases ok. Let us say you take alternative approach of purifying H 2 through CO scrubber. So, here this is the alternative approach. So, here what you do? The effluent H 2 we traces of CO CO 2 are taken to the CO scrubber where ammonium cuprous formate solution is provided from the top.

And then these gases are provided are allowed to pass through this scrubber from the bottom. So, in the counter current way they interact and then the CO is being absorbed into the solution. So, then spent solution whatever is there that is collected from the bottom and then sent to the regenerator and then from the regenerator that is again you know provided to the scrubber from the top again.

So, the same solution is recycled here also ok. So, after this step again almost like 99 percent pure H 2 you will be having that H 2 is again collected as a H 2 synthesis gas which is having more than 99 percent purity. So, this H 2 may be combined with the gases into which is obtained from air suppression unit and then one part of N 2 and three parts of H 2 are mixed to get ammonia synthesis gas that is separate ok.

So, now see only after this reactor or gas generator after this step so, many alternatives are there depending on your requirement. It is not like that each synthesis gas plant which is based on the partial oxidation is having all of them. If your aim is to get hydrogen only. So, then you avoid other things.

If your aim is only to get CO H 2 why to waste your money on the installation and operation of so, many other unit operations which are required to remove you know used to remove for CO CO 2 etcetera ok. So, based on your requirement you have to decide what should be there what should not be there in the plant ok.

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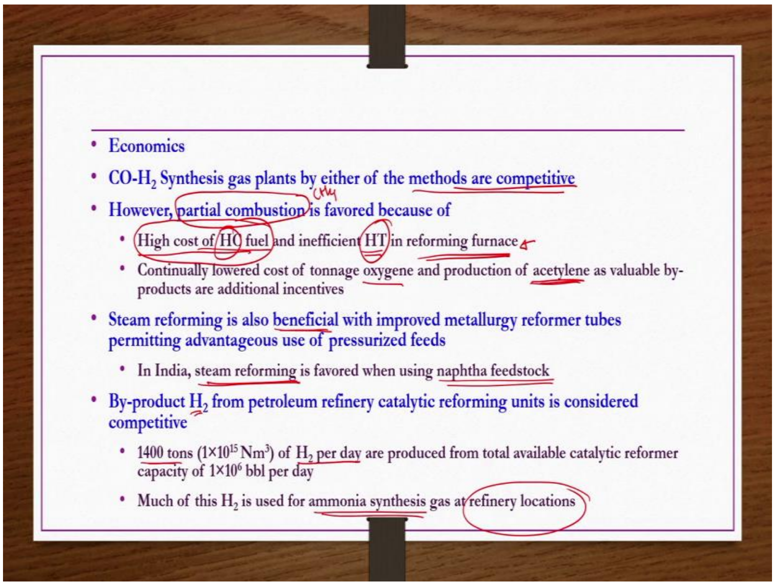

- Economics
- CO-H_2 Synthesis gas plants by either of the methods are competitive

CH_4

- However, partial combustion is favored because of
  - High cost of HC fuel and inefficient HT in reforming furnace
  - Continually lowered cost of tonnage oxygene and production of acetylene as valuable by-products are additional incentives
- Steam reforming is also beneficial with improved metallurgy reformer tubes permitting advantageous use of pressurized feeds
  - In India, steam reforming is favored when using naphtha feedstock
- By-product H_2 from petroleum refinery catalytic reforming units is considered competitive
  - 1400 tons (1×10^{15} Nm^3) of H_2 per day are produced from total available catalytic reformer capacity of 1×10^6 bbl per day
  - Much of this H_2 is used for ammonia synthesis gas at refinery locations

Coming to the economics of synthesis gas by both methods. CO H 2 synthesis gas plants by either of the methods are competitive. So, we cannot say which is good which is bad it depends on the feed and all that ok; however, partial combustion is favored because of high cost of hydrocarbon fuel.

In the partial combustion what we are using? We are using mostly methane natural gas because if you want to do the partial combustion of hydrocarbons to produce synthesis gas those hydrocarbons are you know expensive. So, you do not want. So, rather that one you are using methane in general in partial combustion method.

So, because of that reason and then another issue is that insufficient heat transfer in reforming furnace of a steam reforming method in the steam reforming method what happens? The insufficient heat transfer takes place within the furnace. So, that is another reason because of that reason partial combustion because of these two things right you know because if you wanted to do steam reforming approach then you need hydrocarbons which are expensive.

And then if you wanted to do the steam reforming then in the reforming furnace the heat transfer is not efficient. So, because of these two reasons people prefer for the partial combustion in general and then continually lowered cost of tonnage oxygen and production of acetylene as valuable byproducts or additional incentives in the partial combustion method you need to have a oxygen low grade oxygen is sufficient and then its decreasing cost is often in general decreases right with the time.

And then production of acetylene is the other possibility that is another valuable chemical that you are getting as a byproduct. So, this is the another advantage of partial combustion method to produce synthesis gas, but; however, steam reforming is also having certain advantages like steam reforming is also beneficial with improved metallurgy, reformer tubes permitting advantages use of pressurized feeds.

Actually steam reforming reactor whatever is there we have a steel tubes within the steel tubes we have these catalyst particles etcetera right nickel catalyst particles are inserted. So, you know these gases when come they react there is a possibility of a pressure rise usually whenever any reactor if the hydrogen is produced inside the reactor during the reaction then pressure shoots up in general its very common right. So, you need to have a you know certain kind of tubes which can sustain the high pressures as well.

So, nowadays there are furnaces you know which are providing such kind of advantage of using pressurized feeds. In India steam reforming is favored when using naphtha feedstock because we know that naphtha can also be used for the partial combustion right for the partial combustion method also naphtha hydrocarbons are used.

But; however, if you have a hydrocarbons or naphtha at lower cost you know economical cost or cheaper cost, then it is better to go for steam reforming rather going for the partial combustion right. You should not go to the steam reforming if your feedstock of naphtha is expensive otherwise you can go for the steam reforming.

Byproduct H 2 from petroleum refinery catalytic reforming units is considered competitive because around 1400 tons of H 2 per day are produced from total available catalytic reformer capacities of 1 into 10 power 6 barrels per day right and then most of this hydrogen is used for the ammonia synthesis purpose.

And that also at refinery location itself. So, because of this is the another advantage of having byproduct H 2 in the plant.

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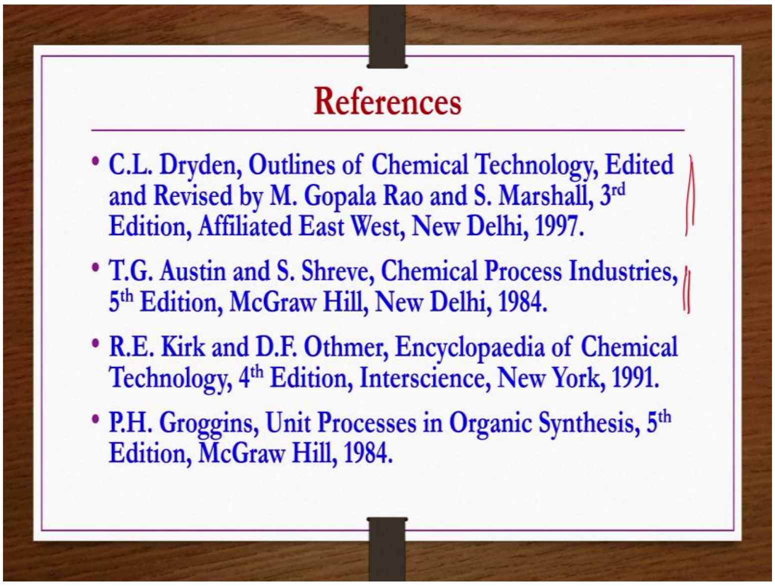

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The references for today's class are provided here you can find out these details any of these two books.

Thank you.