Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 04
Steam Methane Reforming Part - 1

In the earlier class we have seen, the methods for hydrogen production. And we have also seen that if we use steam reforming process then what are the process steps involved. We have seen the preliminary process which is the feedstock pretreatment process or preparing the feed. And then we have also seen that an optional unit, which could be a pre reformation unit is required if higher hydrocarbons are used for the reforming reaction.

When it is steam methane reforming pre reformer is not desired. Now, let us look at the main process which is steam reforming process. When feedstock used is methane it is known as Steam Methane Reforming else it is known as steam reforming reaction.

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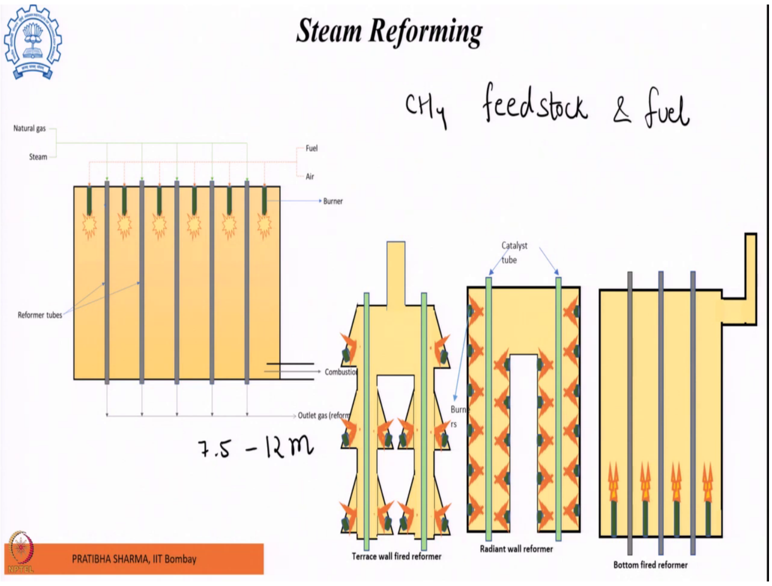

Steam Reforming

CH_4 feedstock & fuel

7.5 - 12m

Now, in this a preheated natural gas along with steam at a pressure of 2 to 2.5 MPa is passed into the reformer; wherein, there are catalyst filled tubes. The gray colored ones are the catalyst filled tubes. Here the reaction between methane and steam occurs so as to produce the required syn gas and we get the reformate gas. Now, if you look at the reformer geometry it consists of bundles of such tubes with length could be somewhere between 7.5 to 12 meters; thickness of about 1 to 2 centimeter.

And these tubes are filled with the catalyst along with support and promoters, what catalyst that we will see little later. Now, in these reformer tubes the reaction takes place, these reformer tubes are externally heated with various burners. So, it is a box or tubular furnace wherein there are many burners, which heat the reformer catalyst filled tubes and these burners could be arranged in various geometries.

So, either the furnace could be a top fired furnace wherein the burners are located at the top. It could be either the terrace fired reformer wherein from the sides the burner is heating the catalyst filled tubes it could be from the walls. These burners location could be on the walls so as to heat the catalyst filled tubes or it could be bottom fired reformer where the location of these burners is at the bottom.

However, irrespective of whatever is the geometry these tubes are carrying catalysts. The process is preheated natural gas along with steam passes through the reformer tubes, which are filled with catalyst thereby producing syn gas. In this process, if it is methane in the steam reformation process, methane acts as both feedstock as well as fuel. So, methane is both feedstock and it is also fuel. So, it is used for burning in the burners.

The fuel air mixture is passed through the burners; the fuel and air mixture combusts in different burners providing the required heat which is being utilized for the reaction to take place. Now, what is that reaction we will see further. One more thing to be mentioned here is the combustion product. So, here in methane burns to give the desired heat; however, it is not 100 percent heat required to the reactor filled tubes.

The combustion gases carry the remaining heat and these gases are still hot and have high grade heat that can be utilized in heat exchangers for either preheating the natural gas or for steam production. So, after that there could be a heat exchanger that can extract the heat which comes out with the combustion gases to either preheat the mixture or to generate steam. Now, let us look at the process of steam reformation.

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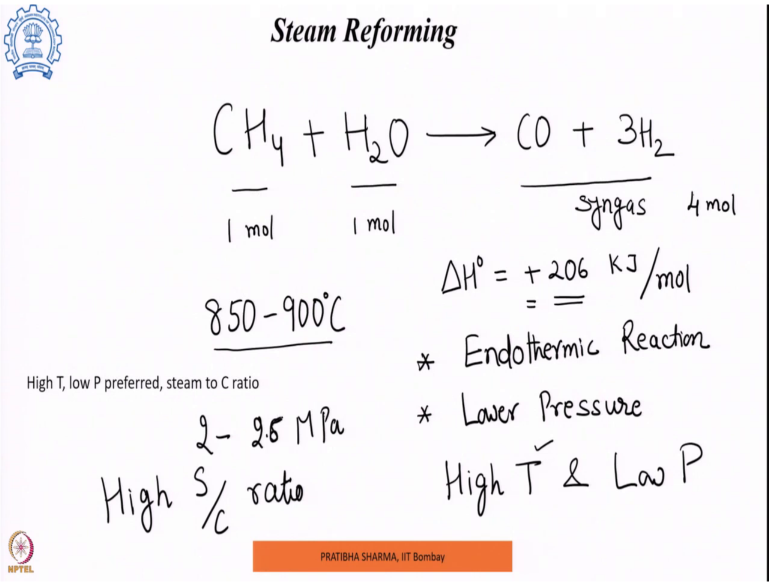

Steam Reforming

$$\underset{1\ mol}{\underline{CH_4}} + \underset{1\ mol}{\underline{H_2O}} \longrightarrow \underbrace{CO + 3H_2}_{syngas} \quad 4\ mol$$

$\Delta H^\circ = +206$ KJ/mol

850-900°C

High T, low P preferred, steam to C ratio

2- 2.5 MPa

High S/C ratio

* Endothermic Reaction

* Lower Pressure

High T & Low P

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If we look at the process of steam methane reformation, methane reacts with steam producing syn gas. So, very simple reaction methane which is feedstock reacting with the oxidant to produce syn gas. Now, couple of things to be considered here is, one is this sign. The process of steam methane reforming is an endothermic reaction, the value suggest that it is highly endothermic reaction.

At the same time, if we see 1 mole of methane reacts with 1 mole of steam to produce 4 moles of the product. So, as such by Le Chatelier's principle, there is an increase in volume. So, the reaction is favored at lower pressure. So, the desired conditions for operation of this reaction is high temperature and low pressure. Now, the reaction takes place at temperatures of 850 to 900 degree centigrade in the reformer tubes.

However, the pressure desired as per the thermodynamics reaction conditions is low, but most of the applications wherein the hydrogen will be used, they require hydrogen at a higher pressure. At the same time, if we increase the pressure the size of the reactor will be reduced and at the same time there will be a better throughput. So, as such these are operated at a higher pressure.

So, usually somewhere around 2 to 2.5 MPa is desired to operate reformers in this particular region. Now, this high temperature poses certain constraints; one is the metallurgical constraint for the reformer tubes. It should be stable under these high temperature and pressure conditions. So, these are to be made up of special material, but in actual practice, this reaction is operated under high steam to carbon ratio content.

So, the operation condition is to keep high steam to carbon ratio. The reason for keeping this high steam to carbon ratio is the coke which causes deactivation of the reforming catalyst. and this reaction is not favourable when we use high S by C ratio, the coke deposition which can lead to deactivation and several other challenges. The coke can deposit onto the surface of the catalyst reducing the active sites and can create hot spot because of that.

At the same time, the deactivation of catalyst can lead to higher tube wall temperature. The pores within the catalyst filled tube can get filled so the voids get filled. Thereby reducing the flow of the gases and increased tube wall temperature which can also lead to the tube failure.

So, in order to avoid all those a high steam to carbon ratio is preferred in this particular reaction. So, what is desired is a high temperature; although desired pressure is low, but usually these reforming reactors are operated under high pressure conditions somewhere around 2 to 2.6 mega pascal and a higher steam to carbon ratio.

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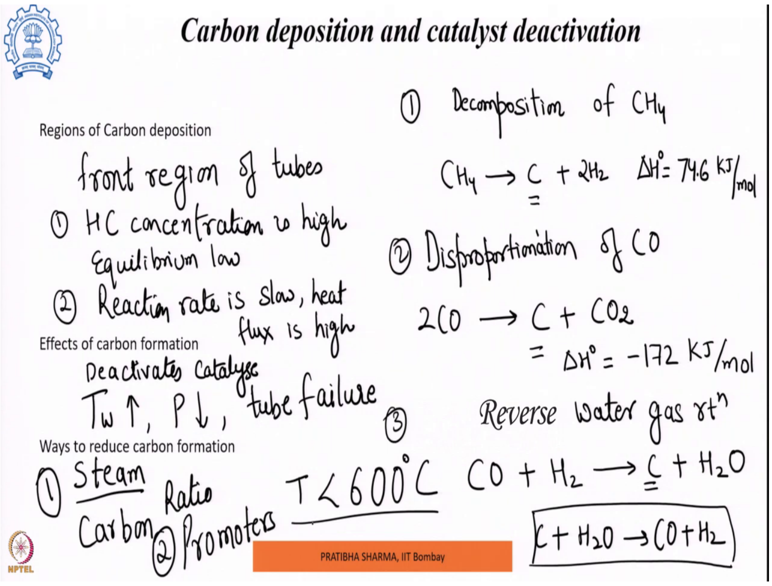

Carbon deposition and catalyst deactivation

Regions of Carbon deposition

front region of tubes

① HC concentration is high

Equilibrium low

② Reaction rate is slow, heat flux is high

Effects of carbon formation

Deactivates Catalyst

$T_w \uparrow$, $P \downarrow$, tube failure

Ways to reduce carbon formation

① $\frac{\text{Steam}}{\text{Carbon}}$ Ratio

② Promoters

$\underline{T < 600^\circ C}$

① Decomposition of CH_4

$CH_4 \rightarrow \underline{\underline{C}} + 2H_2 \quad \Delta H^\circ = 74.6\ KJ/mol$

② Disproportionation of CO

$2CO \rightarrow \underline{\underline{C}} + CO_2$

$\Delta H^\circ = -172\ KJ/mol$

③ Reverse water gas rt^n

$CO + H_2 \rightarrow \underline{\underline{C}} + H_2O$

$\boxed{C + H_2O \rightarrow CO + H_2}$

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Now, as we have seen that in the process of reformation there is a catalyst deactivation problem which could be seen and this occurs because of a wide number of reasons. So, the reasons for catalyst deactivation are several reactions like the decomposition of methane which can result into formation of coke. So, methane can decompose to give carbon and hydrogen, delta H for this process is 74.6 kilo joule per mole.

The another reaction which can lead to coke formation on the catalyst is disproportionation of carbon monoxide. The corresponding delta H for this reaction is -172 kilo joule per mole. This can also result into the coke formation. Now, if we see in the reformer tubes the major regions of coke formation is either it can occur on the inner tubes, inner wall of the tubes or it can occur at the top of the tubes on the front region.

The majority of the carbon occurs in the front region of the tubes and there are various reasons for it. If you see, the major reason for that is at the top of the tube the hydrogen hydrocarbon concentration is highest; however, the equilibrium is low at that region i.e, equilibrium conditions are not maintained. So, at the top of the region the reaction rate is slow; however, the heat flux is high.

So, there could be the carbon deposition that can occur onto the catalyst. Now, what this carbon being formed in the various reaction does? It deactivates the catalysts which can result in excessive tube wall temperature, it can lower the pressure, it can even lead to tube failures, it can block the porous medium which is there in the reformer tubes. Now, how can we take care of this carbon formation, one way as we have seen is to increase the steam to carbon ratio.

Now, if we look at the thermodynamics of the entire process we see that the carbon formation is preferred at temperatures less than 600 degree centigrade and that is why the reaction of steam methane reforming is usually a high temperature process and the reaction occurs at 850 to 900 degree centigrade under which the coke deposition is lower.

So, steam to carbon ratio is the best way to reduce this coke formation. One more method could be use of promoters. So, either different promoters could be used along with catalyst. So, we will see later that both catalyst support as well as the promoters play a dominating role in the reformation reaction.

These promoters provide the required basicity to the catalyst because acidic surfaces are more prone to the decomposition of methane. So, they provide the required basicity so that the carbon which is being formed undergoes the gasification reaction. This is a method by which we can remove the carbon formed.

In fact, there are two competing processes which are going on; the formations of carbon through any of these processes and the removal of carbon by means of carbon or coke gasification.However, at temperatures beyond 600 degree centigrade, the gasification will dominate or the carbon deposition will be lowered. Now, once after the steam methane reformation reaction, the next step which is being considered is the Water Gas Shift.

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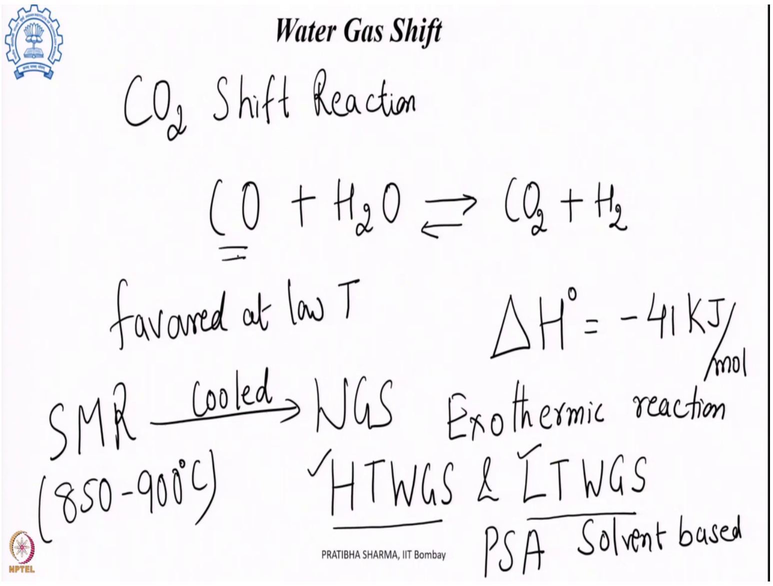

Water Gas Shift

CO_2 Shift Reaction

$$\underline{CO} + H_2O \rightleftharpoons CO_2 + H_2$$

favored at low T

$\Delta H^\circ = -41 \, KJ/mol$

$SMR \xrightarrow{\text{Cooled}} WGS$ Exothermic reaction

(850-900°C)

✓HTWGS & ✓LTWGS

PSA Solvent based

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Water gas shift reaction is carried out after the reformation reaction. This is done so as to increase the yield of hydrogen. In this process, the syn gas which is formed in the reforming step, the carbon monoxide component of it is being converted into carbon dioxide and at the same time we are getting more of hydrogen. However, the reaction is an exothermic reaction.

So, carbon monoxide in the presence of excess of steam gets converted into carbon dioxide and hydrogen. The reason of excess of steam is to reduce the deactivation of catalyst. So, from the value of delta H we can see that it is an exothermic reaction slightly exothermic reaction; that means, it is favored at low temperatures. Usually the kinetics of reactions are better at a higher temperature.

So, there is a trade off to keep higher temperature so in that case it could be favor of backward reaction if we keep higher temperature; at the same time if the temperature is lower down then the reaction kinetics will get slower. So, this is a trade off that we need to be looked at, although it is being favored at a lower temperature.

Now, in this particular process since the temperature required is lower after the steam methane reforming process wherein the exhaust gas comes at a higher temperature, which is roughly about the reaction occurs at 850 to 900 degree centigrade; around that the exit gas leaves the reformer unit it has to be cooled down in a intercooler before it enters into the water gas shift unit.

So, it has to be cooled down to the desired temperature now what is that desired temperature that depends whether this water gas shift reaction is being carried in one unit. High temperature water gas shift alone is being considered or both high temperature and low temperature water gas shift reactions are to be carried out. Now, what will decide whether it is only one step we have to do after the reformation or two steps that is determined by the purification step.

So, the purification step will tell for example, if it is the purification is done using pressure swing adsorption method, then only high temperature water gas shift is good enough; however, if it is solvent based removal method purification method then both high temperature as well as low temperature water gas shift are required to reduce the carbon monoxide levels in the outlet stream from the reforming unit.

So, depending upon the final purification step whether it will be high temperature water gas shift alone with pressure swing adsorption unit or whether it will be high temperature and low temperature water gas shift both, if it is solvent based cleaning removal of carbon dioxide followed by methanator to get pure hydrogen, the water gas shift set up will be different.

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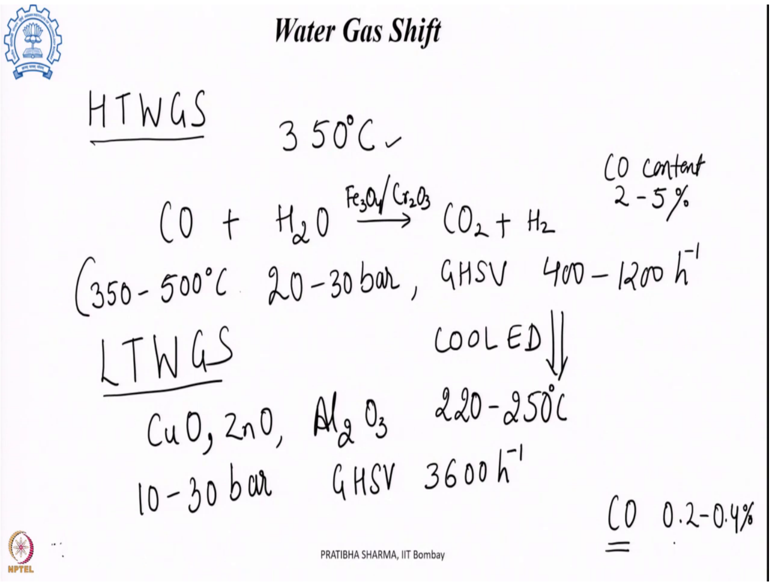

Water Gas Shift

HTWGS $350^\circ C$ ✓

CO content 2-5%

$$CO + H_2O \xrightarrow{Fe_3O_4/Cr_2O_3} CO_2 + H_2$$

($350-500^\circ C$ 20-30 bar, GHSV $400-1200\ h^{-1}$

LTWGS COOLED $\Downarrow$

CuO, ZnO, Al_2O_3 $220-250^\circ C$

10-30 bar GHSV $3600\ h^{-1}$

CO 0.2-0.4%

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In the high temperature water gas shift, the reformed gas which is obtained from steam methane reforming has to be cooled down to a temperature of 350 degree centigrade. So, the reformed gas was at 850 or 900 degree centigrade from reformer after the reformer has to be cooled down to 350 degree centigrade. And thereafter the carbon monoxide reacts with steam to give carbon dioxide and hydrogen.

The catalysts used are magnetite iron catalyst with chromium. And this reduces the carbon monoxide content to about 2 percent depending upon what is the feedstock. It is finally reduced to 2 to 5 percent after the first water gas shift reaction. Now, in this high temperature water gas shift reaction depending on the feed composition the temperature could be somewhere between 350 to 500 degree centigrade.

Conditions are: 350 to 500 degree centigrade, pressures of 20 to 30 bar, the gas hourly space velocity of 400 to 1200 per hour with a residence time of somewhere around 3 to 9 seconds. And finally, it could reduce the carbon mono oxide content to 3 to 5 percent. However, the low temperature water gas shift. The next step with solvent based removal method is the low temperature water gas shift this can further reduce down the carbon monoxide content to less than 1 volume percent.

So, carbon monoxide content is somewhat around 0.2 to 0.4 percent after this step. In the low temperature water gas shift reaction, the catalyst used are zinc oxide, copper oxide on alumina and the reaction takes place in the temperature range of 220 to 250 degree centigrade. So, after the high temperature water gas shift, further the gas needs to be cooled down for the low temperature water gas shift.

Under these conditions the carbon monoxide contents reduces to 0.2 to 4 percent, the pressure is around 10 to 30 bar, the gas hourly space velocities somewhere around 3600 per hour. Now, in the high temperature water gas shift, the benefit of foster kinetics at a slightly higher temperature is being taken care of. However, the low temperature water gas shift is used to further reduce the carbon monoxide content to less than 1 percent. Next, we will be looking at what are the different purification steps for getting pure hydrogen.

Thank you.