Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 05
Steam Methane Reforming Part - 2

In the last class we have seen the 3 steps involved in the steam reforming process. These were feedstock pretreatment process, the major steam methane reforming and the third one was water gas shift also known as carbon monoxide shift reaction.

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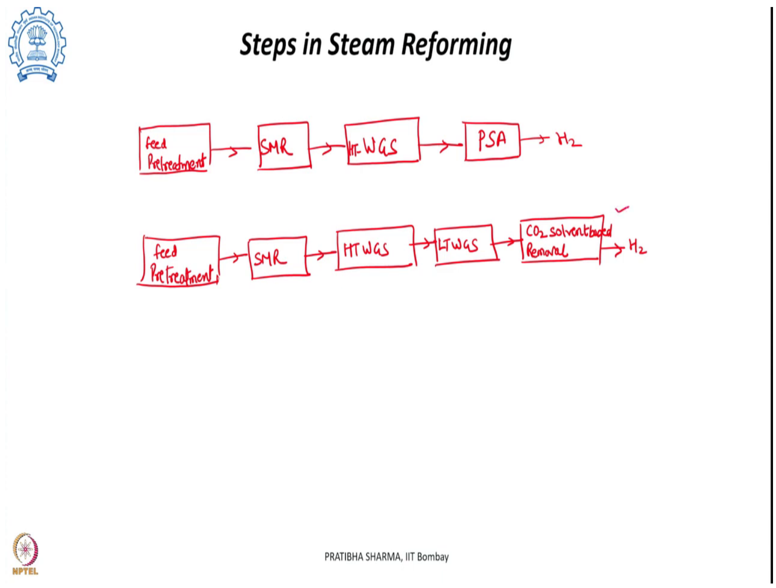

Now, today we will see the 4th step in the steam reforming . So, the last step which is the purification step that determines which water gas shift reaction reactor will be there. If it is pressure swing adsorption is the purification technique which is being utilized then only high temperature water gas shift reactor will be there.

However, if there is a change in the purification technique, a low temperature water gas shift will be followed if the final purification stage is carbon dioxide solvent based purification technique to get pure hydrogen.

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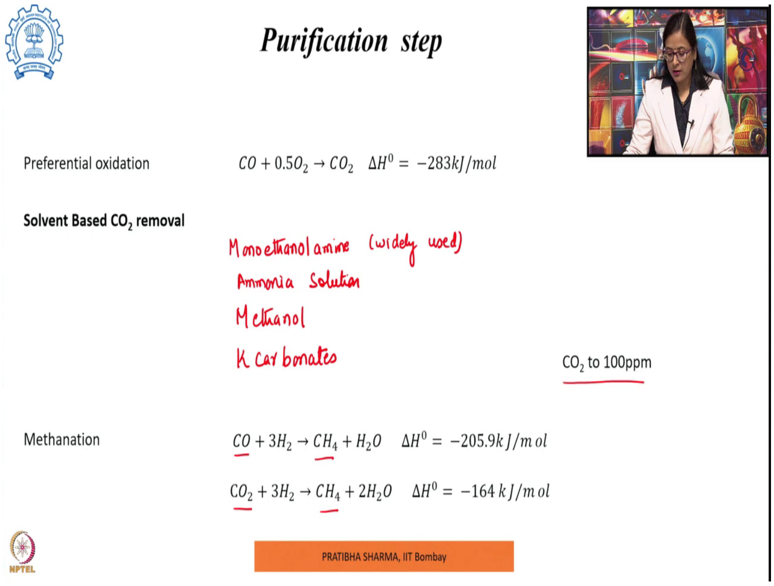

So, if solvent based carbon dioxide removal method is being used, in that case we know that from the low temperature water gas shift less than 1 percent of carbon monoxide is left and that can undergo preferential oxidation to convert into carbon dioxide.

Now, various solvents are being used to remove the carbon dioxide formed and the preferable ones are mono ethanol amine, this is the most widely being used. Ammonia solution, methanol, potassium carbonates, there are many solvents which are available, which absorb carbon dioxide to reduce the carbon dioxide content in the product to about 100 ppm. Now whatever is the left out carbon monoxide and carbon dioxide remaining in the product gas that can undergo methanation reaction in the methanator to finally, convert into methane. So, this is one type of purification.

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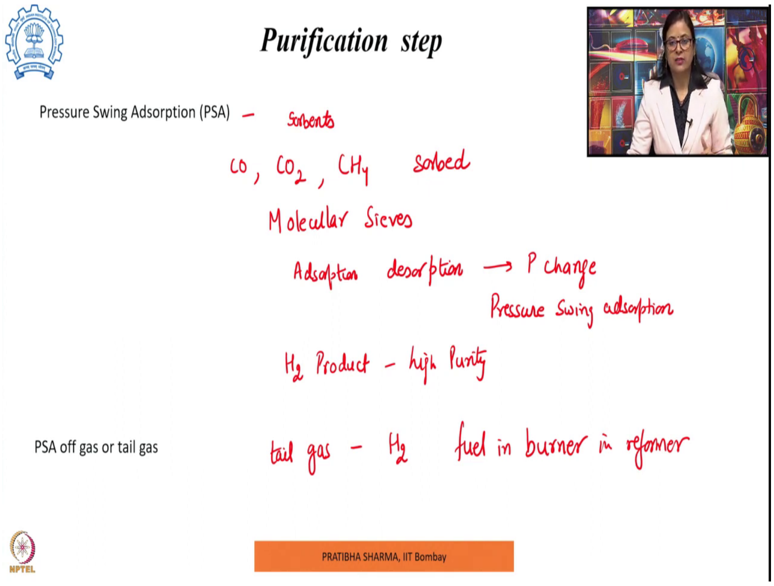

If however, pressure swing adsorption is used for purification in that case various adsorbents can be used. So, different sorbents can be used wherein on the surface of which the impurities like carbon monoxide, carbon dioxide, methane can get sorbed, so that we can remove all these impurities and we can get pure hydrogen as the product.

Now, primarily molecular sieves are being used for the separation of carbon dioxide or carbon based species and get pure hydrogen. Now, in these sorbents adsorption and desorption of the impurities occurs on the change of pressure that is why the name is pressure swing adsorption and we can get high purity hydrogen when all these impurities are selectively adsorbed on to the adsorbent surface.

After hydrogen is being obtained which is of high purity, the remaining off gas or tail gas itself has a certain amount of hydrogen and it has a calorific value; so that this off gas or tail gas from the pressure swing adsorption can be used as a fuel in burner in the reformer. So, this is about the purification step involved as the last step in the steam methane reforming. So, we have seen all the four steps separately.

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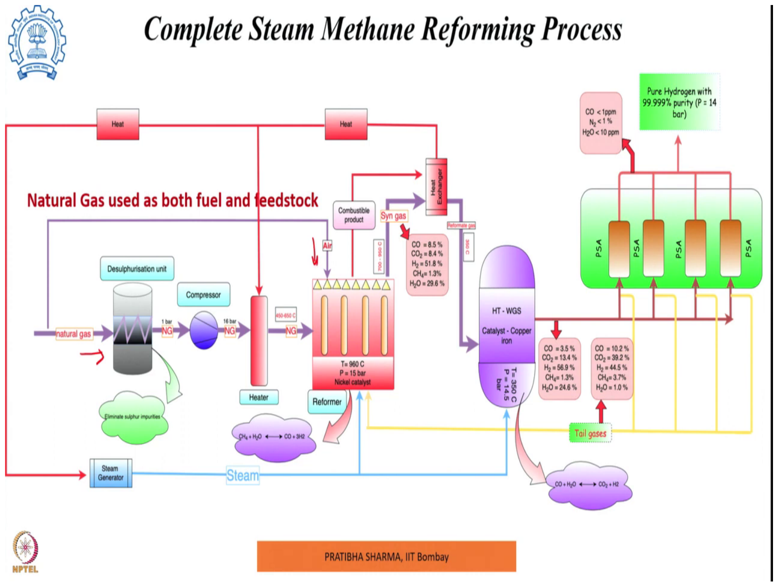

Now, let us see them together, so that we can know about the complete steam methane reforming process. Now, as we have seen natural gas acts as both fuel and feedstock in the steam methane reforming process. So, it acts as a feedstock entering into the desulphurisation unit and it acts as a fuel and supplies the required heat to the burners of the steam methane reformer.

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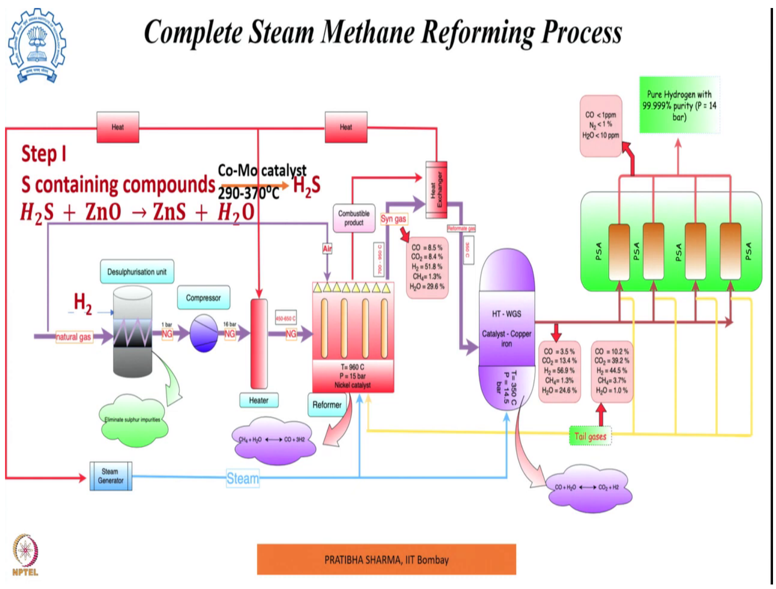

In the first step a small split steam of hydrogen from the product side is used for catalytic hydrogenation of sulphur containing compounds on a sulphur tolerant catalyst, which is cobalt molybdenum catalyst at a temperature of 290 to 370 degree centigrade and that forms H_2S. This H_2S which is formed is scrubbed on a zinc oxide bed to form ZnS and steam.

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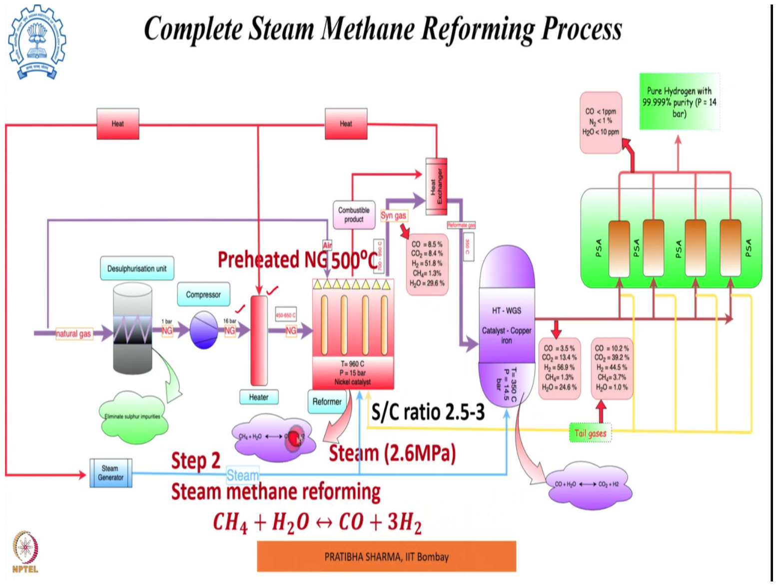

Now, once the sulphur containing impurities are removed in the desulphurisation unit, the treated natural gas goes to the second step which is the steam methane reforming process wherein methane is pretreated and the sulphur containing impurities are removed.

It is preheated and compressed along with steam at 2.6 MPa with a steam to carbon ratio of 2.5 to 3, an excess of steam to carbon ratio is required so as to reduce coke deposition. These are fed into the primary reformer or the main reformer unit which is the steam methane reformer.

Now, preheated natural gas along with steam enters into the reformer tubes, wherein it is a catalyst bed containing nickel on alumina and the reforming reaction takes place, methane reacting with steam to give syn gas.

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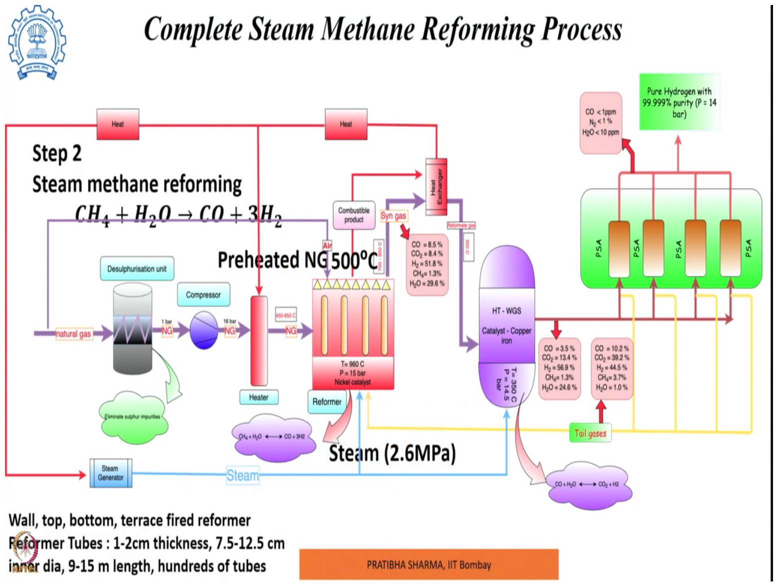

Now, these are tubular reformers tubular box type of furnace, wherein depending on where the burner is located these can be either top fired reformer, bottom fired reformer if the burners are on the bottom side, side fired reformer or terrace fired reformer.

In an industrial scale steam methane reformation plant there are hundreds of such tubes arranged in a reformer wherein the length of these tubes is somewhere around 9 to 15 meters. Its inner dia is around 7.5 to 12.5 centimeters with thickness of 1.2 centimeter.

Now, the heat which is required for the endothermic reaction that takes place in these reformer tubes is supplied by burning of the combustion of the fuel which is again natural gas along with air which is fed to the burners and on the combustion of it supplies the required heat.

Now, as we know that it is a very endothermic process, it requires lot of heat reaction takes place somewhere between 700 to 950 degree centigrade and because the reason for very high temperature both your feedstock as well as the oxidant are inert. So, a large amount of energy is required to make them active and react.

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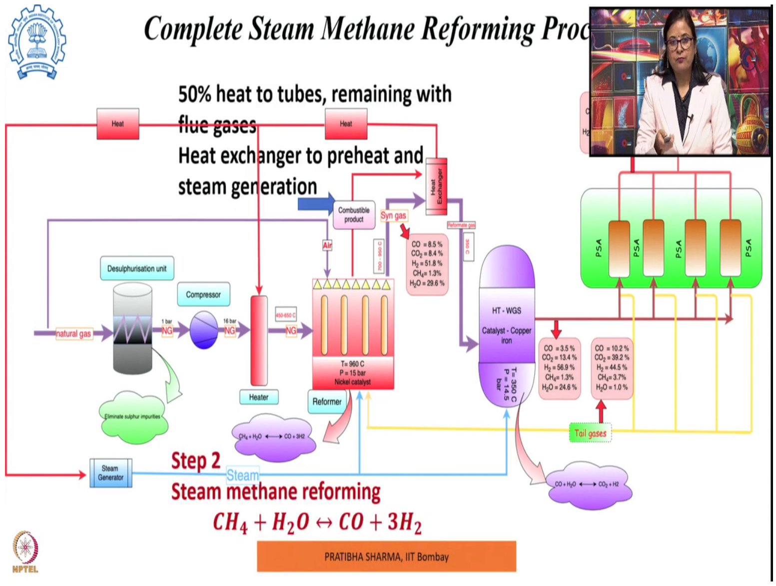

In this process of combustion which is taking place in the burner 50% of the heat which is being supplied is taken up for the reforming reaction in the tubes; however, the remaining heat which comes with the combustion gases or the flue gases that can also be utilized. So, the rest of the heat is recovered in a heat recovery section and that heat which is extracted from the reformer, from the combustion flue gases coming out from the reformer can be used either for steam generation or it can also be used for preheating the natural gas before it enters into the reformer.

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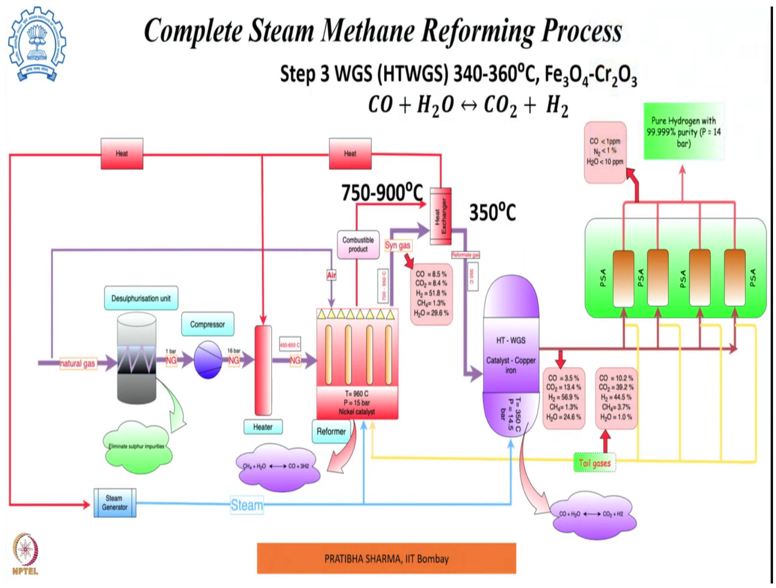

Now, the next step as we have seen is water gas shift reaction, wherein more hydrogen can be extracted. Carbon monoxide reacts with steam to produce carbon dioxide and one more mole of hydrogen. This reaction occurs at a temperature of 340 to 360 degree centigrade and this is slightly exothermic reaction; that means, it will be favored at lower temperature.

However, if we see the syn gas which is obtained from the steam methane reformer the temperature of it is around 750 to 900 degree centigrade and the required temperature for water gas shift reaction is approximately 350 degree centigrade. It has to be cool down from 750 to 900 to 350 degree centigrade and again that much of amount of heat is removed and can be utilized for steam generation.

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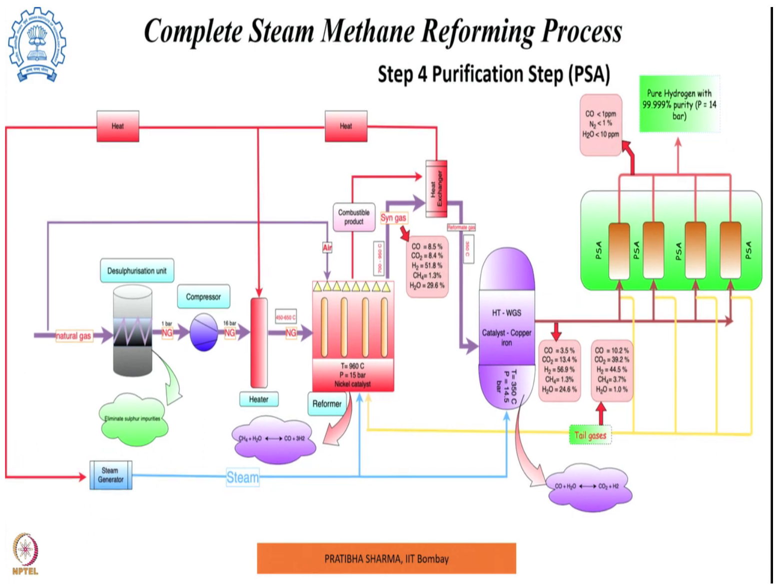

In the last step which we have seen today is purification step, finally, the product gas obtained after water gas shift goes to the pressure swing adsorption unit, wherein there is a batch process; however, using multiple adsorbent bends beds can made it continuous. And after PSA we get pure hydrogen with a purity of 99.999 percent pure at a pressure of approximately 14 bar.

However, there is still sufficient amount of hydrogen and other gases which have a certain calorific value are there in the tail gas or PSA off gas, that goes to the burner of the catalytic reformer steam reformer and can be used as a fuel for heating up and for the conduction of the endothermic steam methane reforming process.

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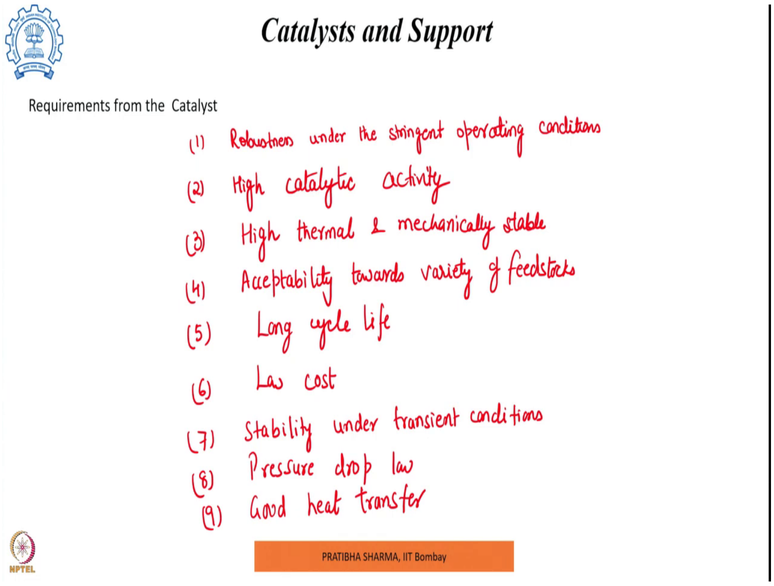

So, this is all about the reforming process; however, catalyst is an important part of the steam reforming reaction and we know that catalyst is actually a substance that increases a rate of the reaction, but it is not consumed in the reaction.

When it comes to steam methane reforming, there are several requirements that the catalyst need to meet out like, it should be robust under the stringent operating conditions; conditions like at the inlet of steam reformer temperature is about 450 to 650 degree centigrade. At the outlet it is 750 to 900 degree centigrade and the catalyst has to sustain under these temperature gradient temperature conditions.

It should have high catalytic activity. It should be thermally and mechanically stable. It should show acceptability towards certain change in the feedstock so, a variety of feedstocks. Definitely long cycle life is important. Cost, it should be less expensive, low in terms of cost. It should also show stability under transient conditions.

At the time of startup or shutdown, under those transient condition the catalyst should be stable enough. Pressure drop across the deformer should be lower in the catalyst bed and its heat transfer characteristic should be good.

So, these are the requirements in terms of the catalyst while selecting a catalyst it ideally should meet out these requirements.

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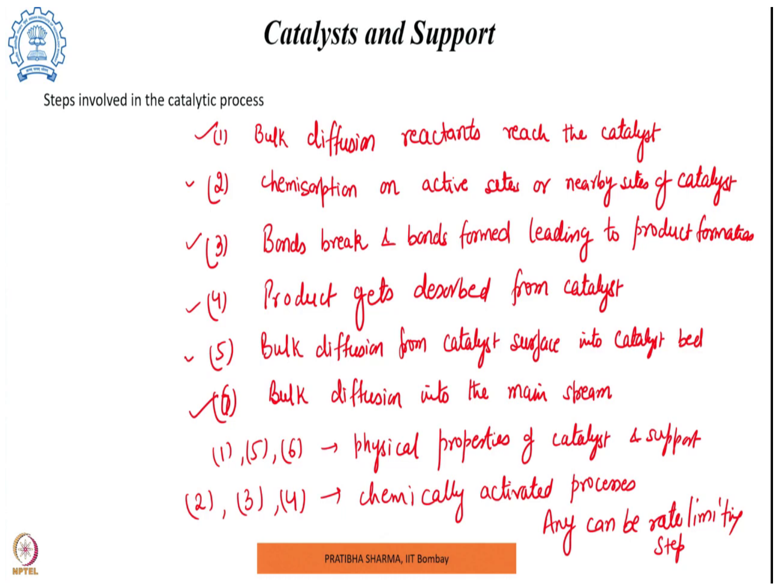

We know that when we are talking about a catalytic process, in the catalytic process on the surface of the catalyst the reactants adsorb, they undergo different reactions, bonds are formed, bonds are broken and finally, the product is formed and then catalyst returns back to its original initial state.

So, various steps which are involved in a catalytic process is first is the bulk diffusion wherein the reactants reach the catalyst surface. Thereafter the catalyst gets sorbed on the active sites of the reactants and get chemisorbed onto active sites or nearby sites of the catalyst.

In the third step, bonds break and bonds are formed leading to product formation. Once the product is formed thereafter the product has to desorbed from catalyst surface. Finally, it has to undergo the bulk diffusion from surface into the catalyst bed and finally diffuses into the mainstream: mainstream of the product gas

Now, if we see these processes process 1, process 5, and process 6, these are actually sort of physical processes wherein these depends upon the physical properties of catalyst, of active support and the media. However, if we see the process 2, process 3 and process 4 these are chemically activated process where reactants are consumed, conversion of reactants takes place, formation of product takes place, formation of various intermediates before the formation of product occurs.

So, the interaction between the catalyst support and reactants to form product is more important. Now, in a catalytic process any of these reactions can be the rate limiting step. In the whole process any of these out of the 6 processes can be the rate limiting step. Now, let us come back to the steam methane reforming, we know that the catalyst plays a dominant role. It is not only catalyst alone, but the support in the promoter that also plays a dominating role.

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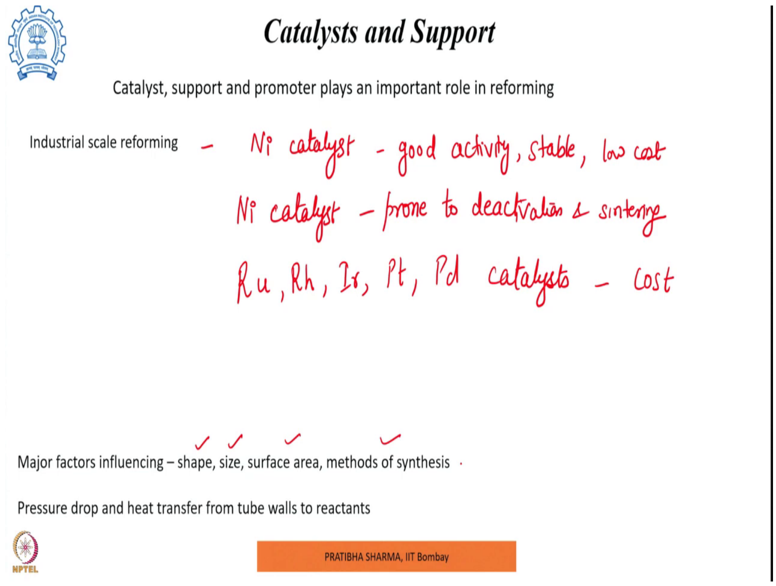

Now, when we talk about industrial scale hydrogen production using the steam methane reforming, primarily the catalyst which is being used is nickel. So, there are several advantages of having nickel catalyst that it is showing activity which is good, it is stable under the operating conditions and it is low cost. However, at the same time there are certain disadvantages or issues associated with the nickel catalyst that it is more prone to deactivation and sintering.

So, in that case there are several other catalyst which has also been looked at by the researchers including the noble metal catalyst, ruthenium, rhodium, iridium, platinum palladium. So, these are the catalysts which have also been looked at for the reforming reaction, but the major issue that comes in while using on an industrial scale is the high cost of the catalyst. Now, there are several factors which also affect are the heat transfer, the pressure drop, the conditions inside the catalyst bed.

And primarily if we look at the catalyst design we have to consider the factors like what is the shape of the catalyst, what is the size of the catalyst, surface area associated, the methods by which these are synthesized that also affect the catalytic process. All these factors can affect the pressure drop, the heat transfer characteristic from the reactor walls to and from the reformer tube walls to the reactant.

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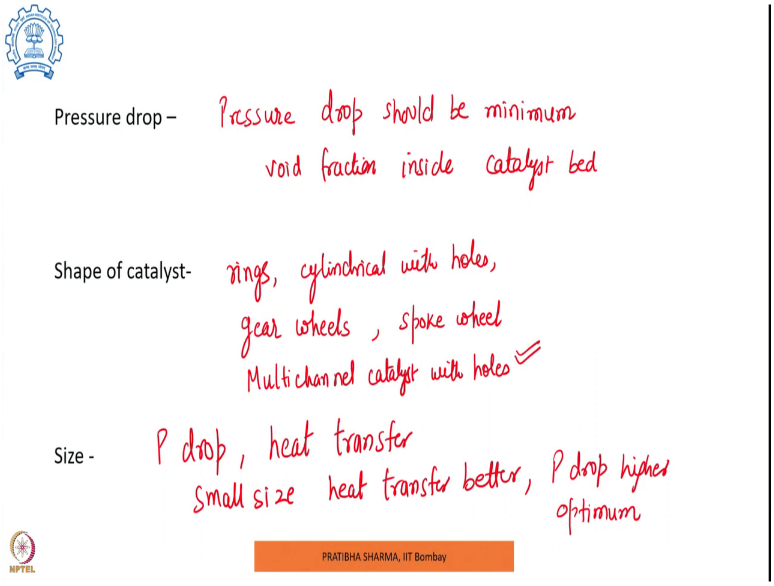

Like for if we see the pressure drop, size has a very important effect in the pressure drop. So, what we want is the pressure drop in the catalyst bed should be low. Now, this pressure drop depends upon the void fraction inside the catalyst bed. And if we say that the particle size of the catalyst is lower then we can see that the pressure drop inside the bed will be higher.

So, there should be an optimum because, we want better heat transfer at the same time we want a lower pressure drop. So, the void fraction should be higher in order to keep that. We need to optimize the conditions inside the catalytic bed. The shape of the catalyst also affects the reforming reaction.

Herein there are several shapes which has been looked at like rings, cylinders, cylindrical shape with holes, then there are gear wheel type of catalyst, spoked wheel type of catalyst, multi channel catalyst have been used they all having holes, so as to have the required flow of the gases inside.

Most widely used one are the multi channel catalyst having several holes. Size again is important here. The size determines the pressure drop at the same time: it will also determine the heat transfer across the bed. Now, for example, if size is lower i.e., for small size of the catalyst heat transfer will be better, but at the same time pressure drop will be higher.

So, there should be an optimum size of the catalyst to be decided so as to have a lower pressure drop at the same time having a higher heat transfer characteristics. Usually the catalyst are supposed to operate stably for long hours typically about 5 years of continuous operation is required without any loss of the activity.

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Now, other than the catalyst, support again is very important and that plays a dominating role. There are several requirements for the support when it is to be used along with the catalyst. We know that support should have a very good dispersion. It should stabilize the catalyst. It should ensure high surface to volume ratio. It should withstand the conditions of operation inside the reformer. It should provide good interaction between the reactants and the catalyst and that will reduce the catalyst deactivation and sintering.

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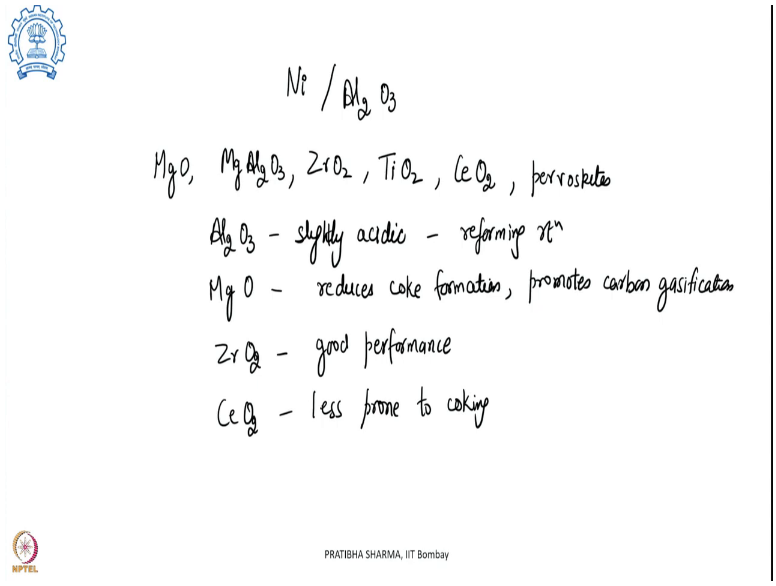

So, these are ideally the requirements when a catalyst support is being looked at. For industrial scale hydrogen production mostly nickel on alumina support is being used as a catalyst in the reformer tubes. Other than alumina there are several other catalyst support which are being studied like magnesium oxide, magnesium aluminium oxide, zirconia, titania, ceria these are the other support which are being studied and reported in the literature.

Now, each of these have their own characteristics like alumina it has slightly acidic character that promotes reforming reaction. However, if we look at magnesium oxide then this reduces coke formation or it promotes the carbon gasification reaction. Zirconium oxide has good performance. So, all of these supports have their own characteristic. Cerium oxide is less prone to coking. So, these are the characteristic of these support materials which have been studied in literature.

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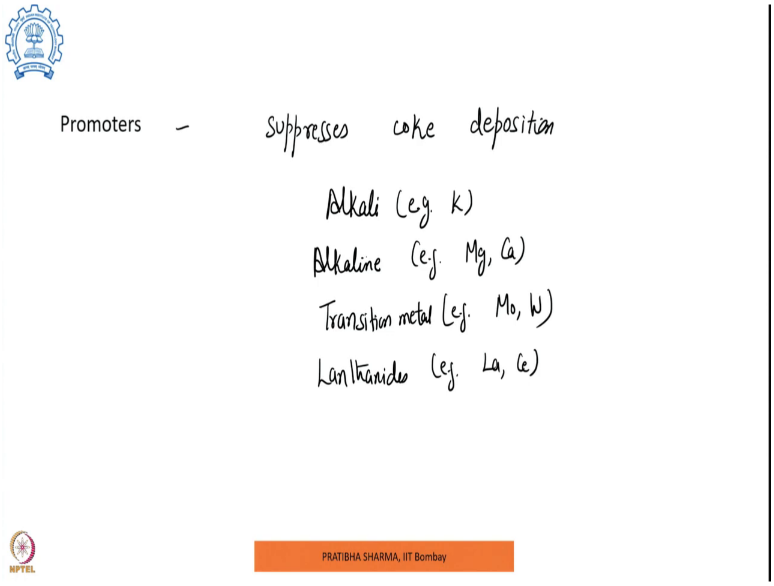

Now, other than the catalyst and support, a small quantity of promoters are added and this addition of promoters suppresses coke deposition onto the catalyst surface. The catalyst promoters are used includes alkali metal elements like potassium, alkaline magnesium and calcium. Transition metal based including molybdenum and tungsten from the lanthanide series, lanthanum and cerium.

So, when a small quantity of these promoters is being added this is beneficial and reduces the carbon formation on the surface of the catalyst.

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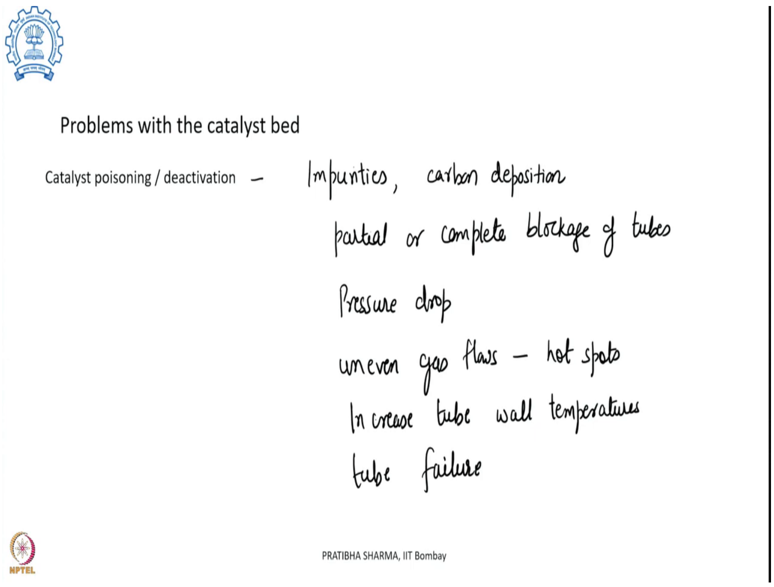

Now, if we look at the catalyst the major challenges which are associated with the catalyst bed, then there are lot many factors that needs to be taken care of which are the primary constraint for the catalyst poisoning or deactivation which is basically caused because of the presence of impurities, because of the carbon deposition.

Now, this carbon deposition has a substantial effect onto the catalyst deactivation. Now what that leads to is either it can cause partial or complete blockage of the reformer tubes and when it causes blockage of the tubes there will be a pressure drop, uneven flows and that uneven gas flows can result into formation of hot spots that can increase tube wall temperature which is highly undesirable, uneven fluxes and that can even lead to a times tube failure. So, this catalyst deactivation is a highly undesirable when it is into the reforming reaction.

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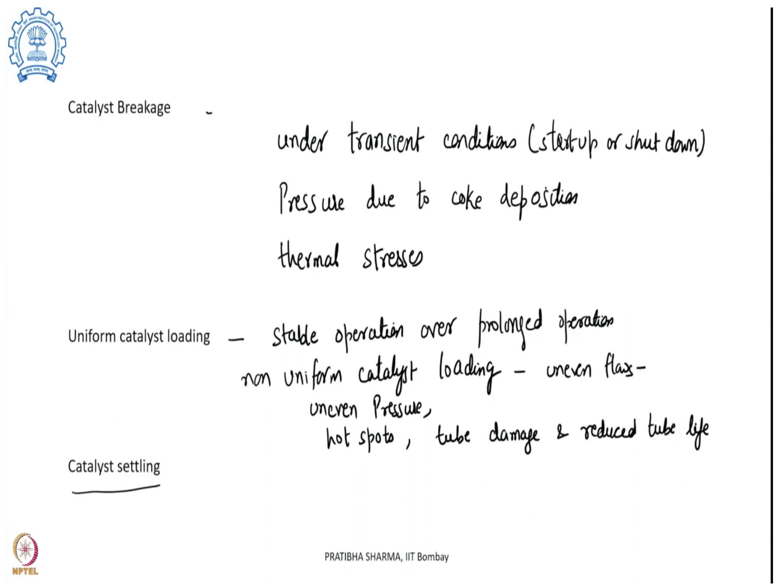

However, for carbon formation it has been known from the thermodynamics that it takes place at a lower temperature below 500 degree centigrade. There can also be problems associated with the catalyst breakage and that catalyst can break under transient conditions. The breakage is mainly observed when it is either starting up or shutting down of the reactor. The catalyst can lose its mechanical strength during that or it can be because of the pressure which is exerted inside the reformer tube.

There can be certain thermal stresses if there is a cooling that can lead to catalyst breakage and this is always undesirable in the reforming process. What is actually required is a uniform catalyst loading and that can lead to stable operation over longer duration for prolonged operation. If however, there is a non uniform catalyst loading then that non uniform catalyst loading can again give rise to several issues.

There will be uneven flows, there will be temperature gradients that will be there, there will be uneven pressure drop inside the column, hot spots will be created and that can lead to tube damage and reduced tube life. So, that is highly undesirable. Besides these there could be a problem which is associated with the catalyst settling and that can also create problems.

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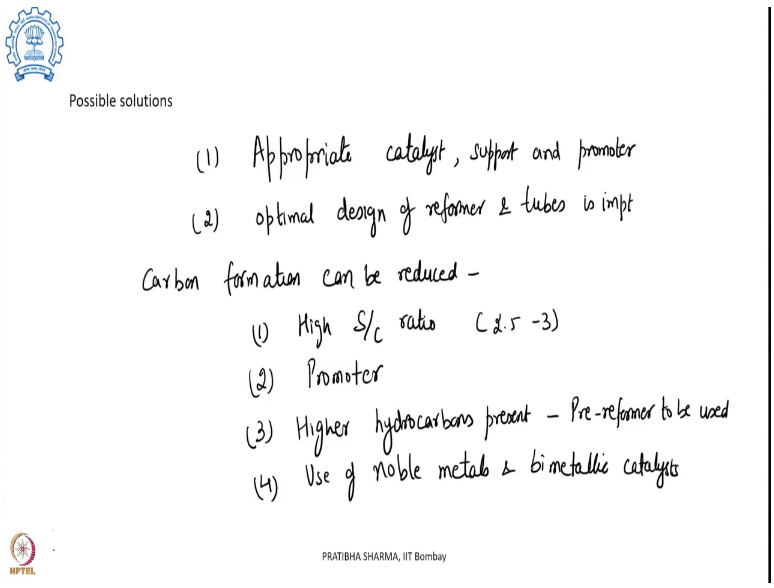

Now, what are the ways to address these? The ways to address these problems is first we have to select the appropriate combination of catalyst support and promoter. Other than that the design of the reactor, of both reformer and tubes is very important.

Now, we talk about the catalyst deactivation: deactivation can be reduced or the carbon formation can be reduced by high steam to carbon ratio and ideally it should be somewhere between 2.5 to 3. At the same time with the proper choice of promoters carbon formation can be reduced. If there are higher hydrocarbons present then a pre reforming unit is essential. And the use of noble metals or bimetallic, although these are expensive, but could be beneficial against the carbon deposition.

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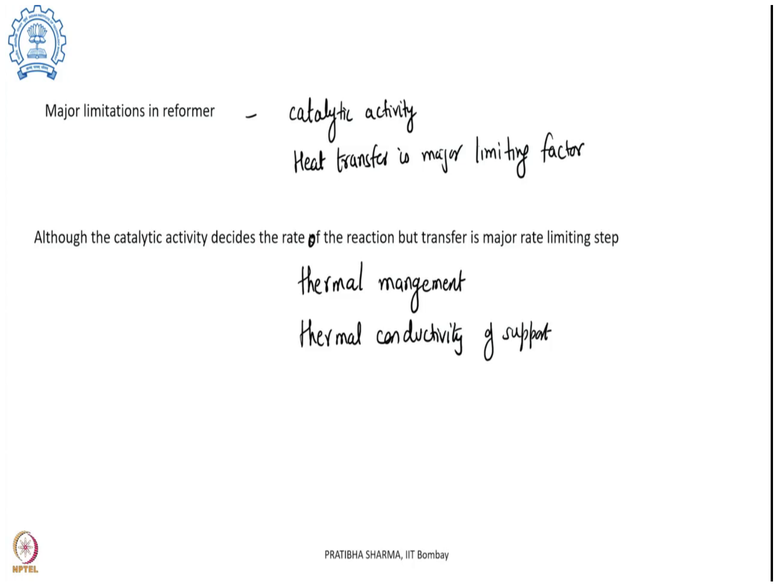

Now, we have seen that there are challenges associated with the reformer and the major limitation in the reformer seems that the catalytic activity could be the major challenge, but it has been observed that the catalytic activity definitely could be the rate limiting step but at the same time the heat transfer characteristics, the heat transfer is prominently or the major limiting factor when it comes to the operation of a steam methane reformer.

Now, although the catalytic activity decides the rate of the reaction, but the heat transfer is found to be the major rate limiting step. So, when it is up to designing the reformer a proper heat transfer or thermal management is very important. At the same time the thermal conductivity of the support is also important. Now, when it comes to designing the reformer there are several heat transfer considerations that need to be taken care of.

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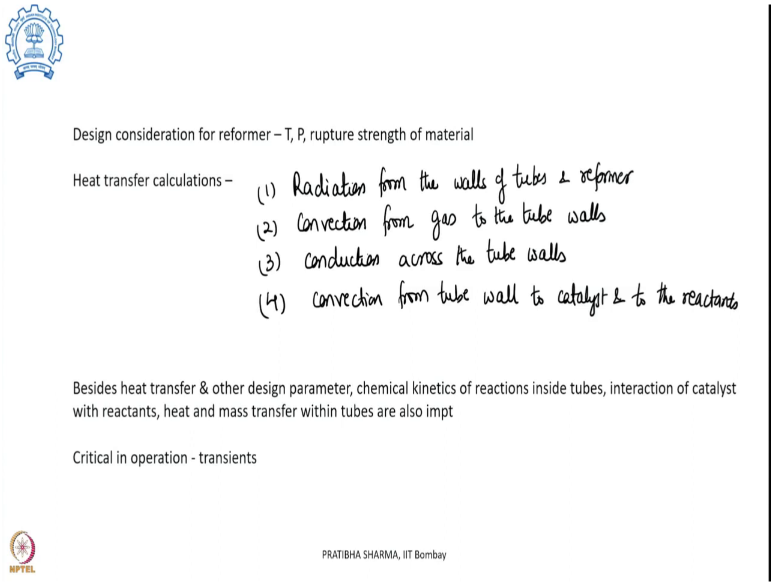

And these design concentrations that need to be taken care of includes the temperature, the pressure that will be there in the reformer, the material with which the reformer tubes are being made and their rupture strength. So, the materials which are highly temperature resistant could be used for making the reformer tubes that can sustain such high temperatures and pressure. Now, when heat transfer calculations are being done, then we have to see the heat transfer not only from the burners, but till the point where heat of reaction goes to the reactants.

So, all the heat transfer aspects needs to be considered - radiation which is taking place from the walls of the tube and the reformer. Then comes the convection from the gas; the combustion gases, the flue gases to the tube walls, conduction across the tube walls, convection from tube walls across the catalyst bed to the catalyst and to the reactants.

So, all these aspects need to be taken care of while designing the reformer and reformer tubes. Now, besides these major heat transfer considerations, also how the kinetics of the reaction inside the tubes is, what is the interaction of the catalyst with the different reactants, what is the heat and mass transfer limitations within the tubes that are also need to be taken care of. However, in a well-designed reformer it is observed that under stable operations these are not much of a problem; however, the major problem arises under the transient conditions of starting up as well as shutting down. So, this is all about the steam methane reforming.

So, in the today's lecture we have seen the entire steam methane reforming process considering all the 4 steps. Thereafter we have seen what are the different catalyst support, promoters which can be used, we have seen what are the requirements in terms of the catalyst as well as support, what are the different design considerations that needs to be taken care of while selecting a catalyst, selecting a support, also the heat transfer characteristics of the reformer, what are the various parameters that needs to be taken care of while designing the reformer and reformer tubes.

Thank you.