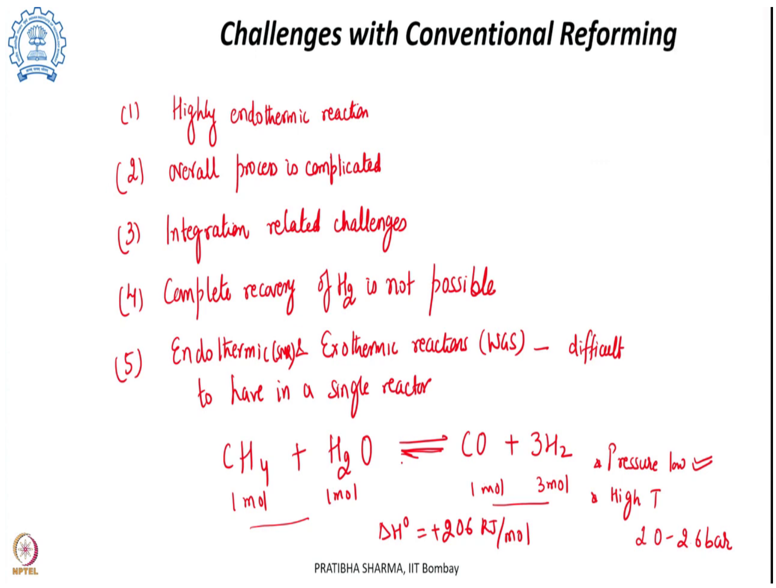
Hydrogen Energy: Production, Storage, Transportation and Safety
Prof. Pratibha Sharma
Department of Energy Science and Engineering
Indian Institute of Technology, Bombay

Lecture - 08
Advanced Methods of Steam Reforming

In the earlier lectures we have seen the conventional Method of Steam Methane Reforming; however, there are certain challenges associated with the conventional steam reforming process.

(Refer Slide Time: 00:33)



And some of these challenges are, the steam methane reforming is a highly endothermic reaction and it requires lot of heat for the reaction to occur. So, a lot of fuel consumption also goes for providing that heat of the reaction. At the same time we have also seen that the overall process is complicated.

Complicated in the sense that there are several steps involved, the number of steps involved are more when it comes to conventional steam methane reforming process. At the same time, some of the steps involved are endothermic in nature like the reforming reaction and some of the reactions are exothermic. So, there are integration related challenges with the different units as such, a lot of thermal management needs to be taken care of so as to use the process energy efficiently.

Now, with all these heat recovery units, the system becomes large and bulky. So, the footprint area required for a conventional reformer is comparatively larger. At the same time, also we have seen that the complete recovery of hydrogen after the purification step, like in pressure swing adsorption we have seen that PSA of gas or tail gas has still certain amount of hydrogen left out. So, complete recovery of hydrogen from the outlet stream is not possible.

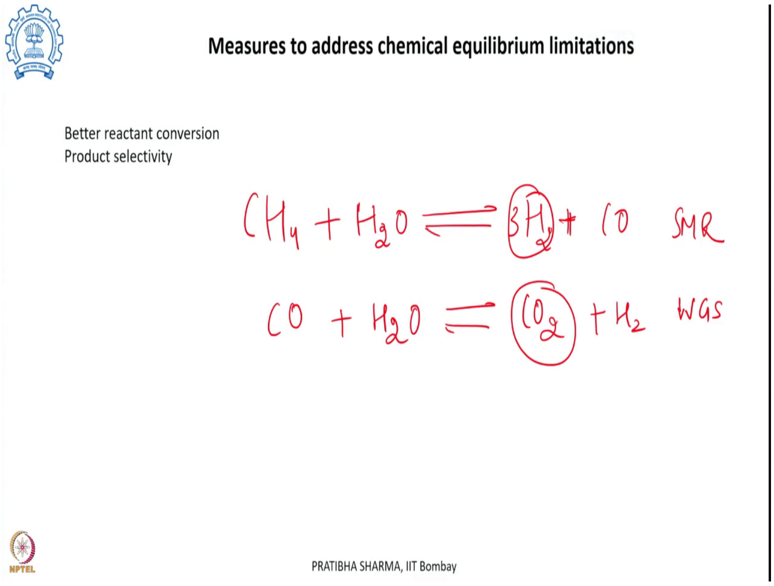
One reaction is endothermic, that is the reforming reaction another reaction is exothermic. To have these reactions, your water gas shift reaction is exothermic reaction SMR is endothermic reaction, to have these reactions in a single reactor under normal operating conditions is very difficult. Besides these we have also seen in the conventional reforming method, there are chemical equilibrium related limitations.

Now, we have seen that when methane reacts with steam to form syngas and we have seen that 1 mole reacts with 1 mole to give a product which is 4 moles. Overall there is a volume expansion, so the reaction is preferred at a lower pressure and higher temperature, because it is a highly endothermic reaction with the heat of reaction being 206 kilojoule per mole.

Now, this increase in this number of moles in the reaction that limits by means of chemical equilibrium limitation should be taken care of and should be done at a lower pressure. But because most of the end use applications require higher pressure, as such to make the reformer compact, getting a high better throughput it operates at a higher pressure of about 20 to 26 or 30 bar.

Now, under that condition being a reversible reaction, the conditions should be such that the reversible reaction or the backward reaction should not be favoured. So, what can be done is, we can have ways of doing that wherein we can address these chemical equilibrium related limitations.

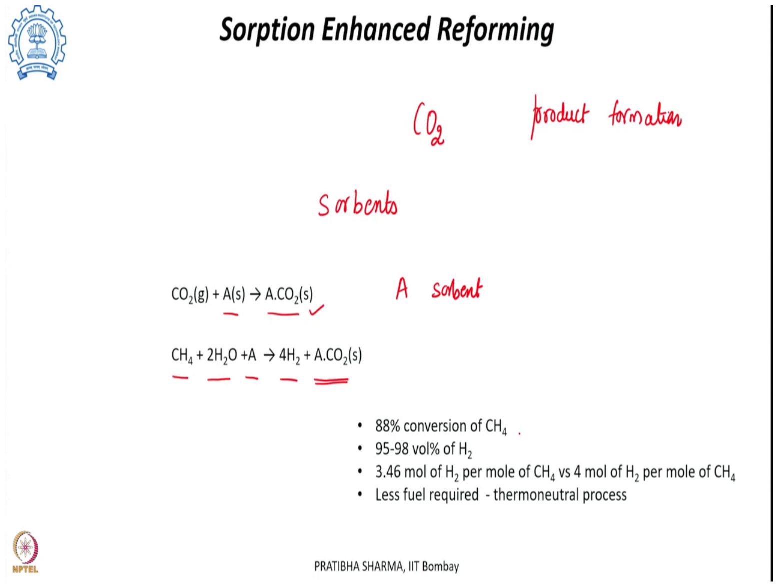
(Refer Slide Time: 05:21)



So, if out of the products which are formed, if we can selectively remove the product, which are being formed. So, whether it is like SMR, hydrogen being formed or in water gas shift, carbon dioxide which is being formed, if these could be removed then the forward reaction would be favoured. And then the limitations of the chemical equilibrium can be taken care of.

This is what is being done in the other methods of steam methane reforming, which we are going to see today. However, the most widely used method is still the conventional steam methane reforming process which we have learned in great detail. These methods which we are going to discuss today, these are still at the demonstration scale, but not being used on a commercial scale.

(Refer Slide Time: 06:42)



Now, one of this method is sorption enhanced reforming. Now, in sorption enhanced reforming, the product carbon dioxide, which is obtained is being selectively removed such that the limitation of the chemical equilibrium is not there and the reaction proceeds towards the formation of the product.

So, the direction of the reaction is that it favours the product formation. Now, how is it done? The carbon dioxide which is being formed in the reaction is being taken up by certain sorbents, which can either chemically combine or it can adsorb the formed carbon dioxide and remove that in the process.

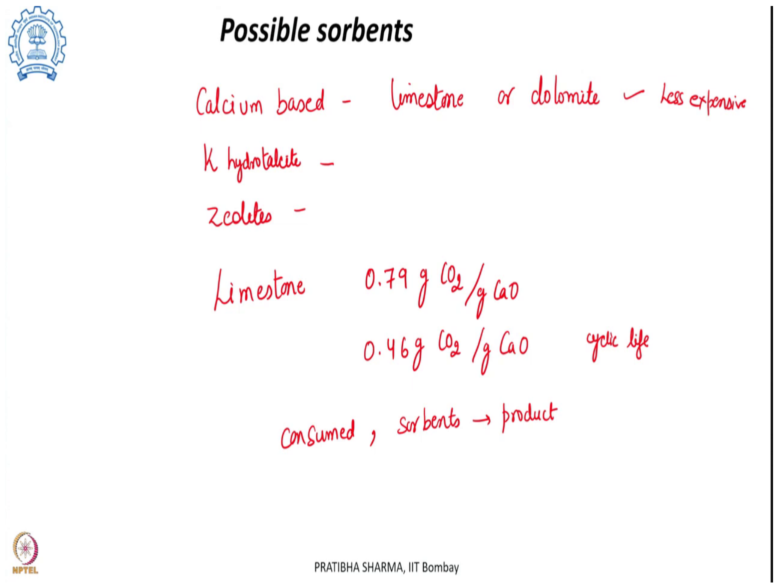
So, if A is a sorbent used here it can combine with carbon dioxide which is being formed after the water gas shift reaction and it can form a compound with it. And when we need the original compound back the regeneration needs to be done. Now, if we look in the presence of carbon dioxide sorbents, the entire steam reforming process looks like methane feedstock reacting with the oxidant, steam in the presence of carbon dioxide absorber sorbent to give hydrogen and the sorbent product, which is formed on reacting with the carbon dioxide.

Now, with this process it has been observed that a higher conversion of methane is obtained, like with this process 88 percentage conversion of methane could be achieved, at the same time the hydrogen which is being obtained in the process is about 95 to 98 volume percent. If we compare it with a traditional steam reforming process, about 3.46 mole of hydrogen is being produced per mole of methane being consumed. As against which was 4 mole of hydrogen per mole of methane being produced.

Now, we will also see that in sorption enhanced reforming process, less amount of fuel is required. Some of the process are endothermic and some of the process are exothermic. So, the required heat of reaction for the endothermic process is being supplied by the exothermic reactions.

So, either the heat required is very less or it is a thermoneutral process. So, the required fuel consumption is also lower, that is the advantage of sorption enhanced reforming process. Now, what are the possible sorbents which can be used for undergoing the sorption enhanced reforming include?

(Refer Slide Time: 10:00)

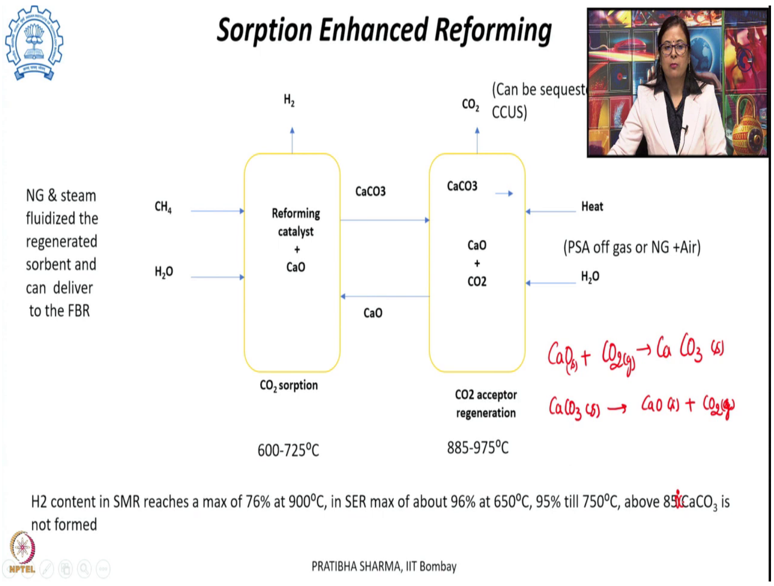


These could be calcium based, mostly these are calcium based sorbents, limestone can be used or dolomite, potassium hydro telsite is being used, then there could be zeolites that can be used. So, there are several possible sorbents that can be used for this particular process. However, it has been observed that the calcium based sorbents are very economical and these are less expensive.

Like if limestone is being used, it is having a very good conversion to or acceptance towards carbon dioxide, it can consume about 0.79 grams of carbon dioxide per gram of calcium oxide however, dolomite although it takes up little lower amount of carbon dioxide, but it has a very good cycle life or it has a very good durability.

Other than that also there are several other sorbents which can be used. In some of the cases these sorbents are being consumed; however, these sorbents converts into a product which can be regenerated back to get the initial sorbent, in the whole process.

(Refer Slide Time: 11:53)



Now, if we look at the process of sorption enhanced reforming. So, the methane and steam, they goes into a adiabatic fluidized bed reactor, wherein all the three reactions takes place, that is important. In the presence of reforming catalyst which is nickel on alumina and carbon dioxide sorbent which is calcium oxide, the three reactions are steam methane reforming, water gas shift and carbon dioxide absorption cross reaction, takes place in a single reactor.

The reaction condition is, the reaction takes place at between 600 to 725 degree centigrade and results into formation of pure hydrogen and very small amount of carbon monoxide and carbon dioxide are still left out. Most of that carbon dioxide is taken up by the sorbent and it is converted into calcium carbonate.

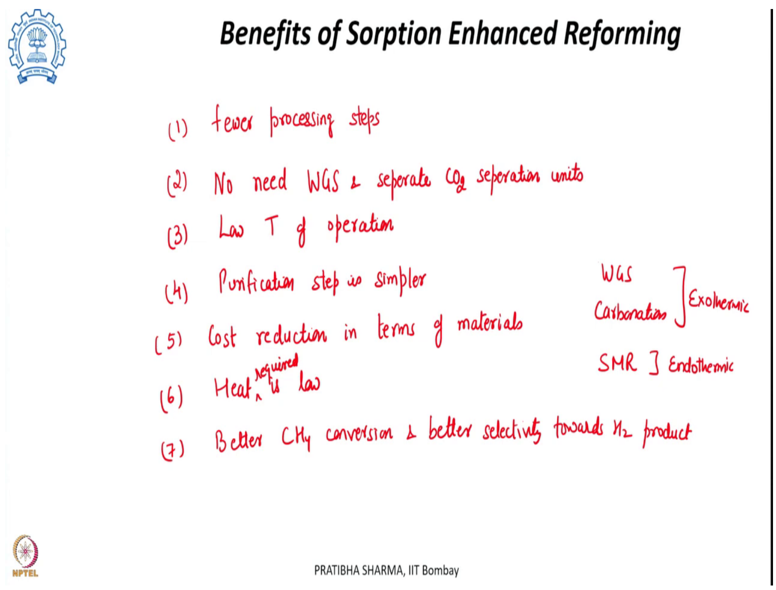
So, the reaction that occurs is calcium oxide reacts with carbon dioxide giving calcium carbonate. However, when calcium carbonate is formed that needs to be regenerated back. So, that calcium carbonate gets back to its initial state forming calcium oxide and gives back the carbon dioxide in a separate reactor, in a separate fluidized bed reactor. Where the sorbent is regenerated back, the required heat of the reaction is being provided either by means of PSA of gas or the natural gas along with air is being fed.

So, natural gas here acts as a fuel to provide the required heating conditions for the regenerator unit. Here in calcium oxide is obtained and carbon dioxide can be used for the carbon capture use and sequestration, because highly concentrated carbon dioxide is being obtained in the process. However, the process of regeneration takes place at higher temperature of 885 to 975 degree centigrade.

Now, when this calcium oxide is fed back to the primary sorption unit or sorption enhanced reforming unit, it is fed along with the natural gas and steam such that the natural gas and steam fluidize the regenerated sorbent and can deliver to the fluidized bed reactor. Now, if we compare with the conventional steam methane reforming process, then in case of conventional steam methane reforming about a maximum of 76 percent of hydrogen was achieved at 900 degree centigrade.

However, in case of sorption enhanced reforming the number is 96 percent, that could be achieved under the reaction condition of 650 degree centigrade. If a temperature is further increased, then 750 degree centigrade, then about 95 percent of hydrogen could be achieved. But above 800 and above 850 degree centigrade, calcium carbonate is not formed and the absorption of carbon dioxide does not occur.

(Refer Slide Time: 15:53)



Now, there are large number of benefits of using sorption enhanced reforming, some of these are clearly evident, that the number of steps which are involved are very low. So, there are very few processing steps which are involved in the process. So, all the three reactions, steam methane reforming, water gas shift reaction as well as carbon dioxide separation are taken care of in a single fluidized bed reactor. There is no need of separate water gas shift unit and its catalyst.

So, the number of process steps involved are reduced. At the same time we have seen that the reaction conditions are comparatively milder. So, the operation temperature is low, the purification stage is simple compared to the conventional deforming method. So, the carbon dioxide which we are getting is highly concentrated; however, certain amount of reminiscent carbon monoxide or carbon dioxide, which is very small in quantity needs to be removed in the purification unit.

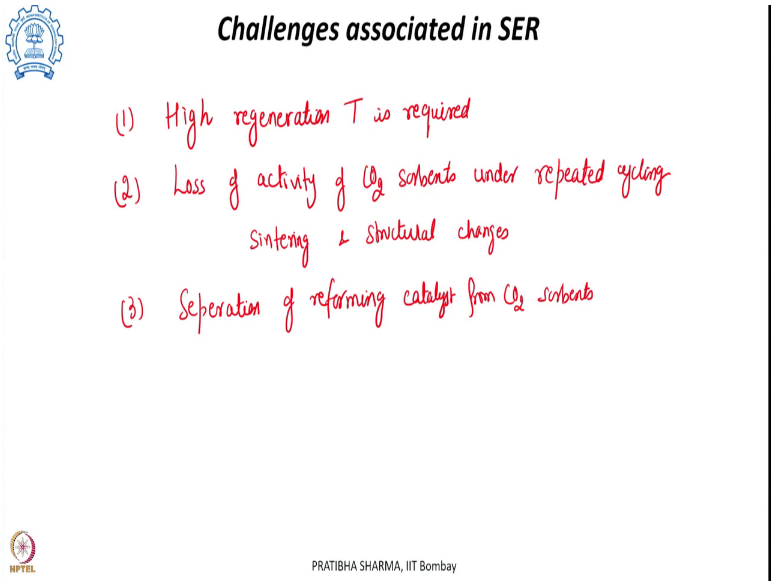
Since most of the carbon dioxide is being removed and we can get pure hydrogen in this way. Since the reaction conditions are mild, there will be a cost reduction in terms of the materials used. Now, when we talk about the conventional reforming, the temperatures that the reformer tube have to sustain is 950 degree centigrade maximum and these are designed for very higher temperatures.

So, as such expensive materials are to be used for the reformer tubes. However, since the reaction temperature does not go to very high temperature, it is about 650 degree centigrade to 725 degree centigrade in the sorption enhanced reforming; as such very expensive material is not required for the reactor construction.

The amount of heat which is required is also low because some of the reactions are endothermic, the remaining two reactions i.e. water gas shift reaction and the carbonation reaction these are exothermic in nature, that provides the required heat of reaction for the endothermic steam methane reaction. So, either a very little amount of energy is required or the reaction undergoes in a thermoneutral manner.

So, the heat required is low or the energy consumption is low the fuel requirement, which is desired for providing the required heat of the reaction is also low in this case. We can achieve better methane conversion and then better selectivity towards the desired product. So, there are many advantages of using sorption enhanced reforming as against the conventional steam methane reforming process.

(Refer Slide Time: 20:14)

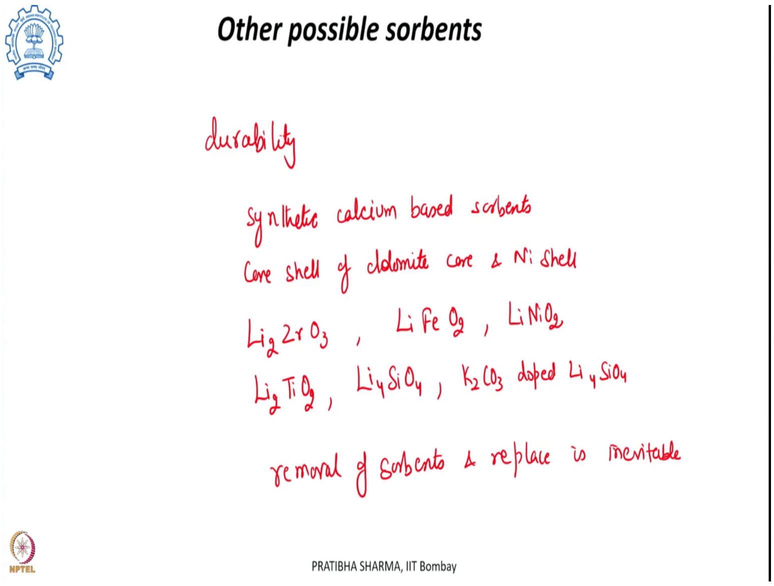


However, other than these benefits that we have looked at there are certain challenges.

The challenge that we have already seen when discussing about the reaction is, that the high regeneration temperature is required. We have saved energy in the sorption process; however, the regeneration of the carbon dioxide sorbent occurs at a higher temperature. So, that is required in the sorption enhanced reforming process. At the same time the sorbent are found to lose their activity, when it undergoes repeated cycling.

The sorbents they break, they undergo sintering; they undergo structural changes and need to be replaced. Besides the separation of the reforming catalyst from the sorbent also needs to be taken care of and that could be a problem that needs to be considered. So, although there are several advantages of sorption enhanced reforming as against the conventional reforming; however, there are certain associated challenges as well.

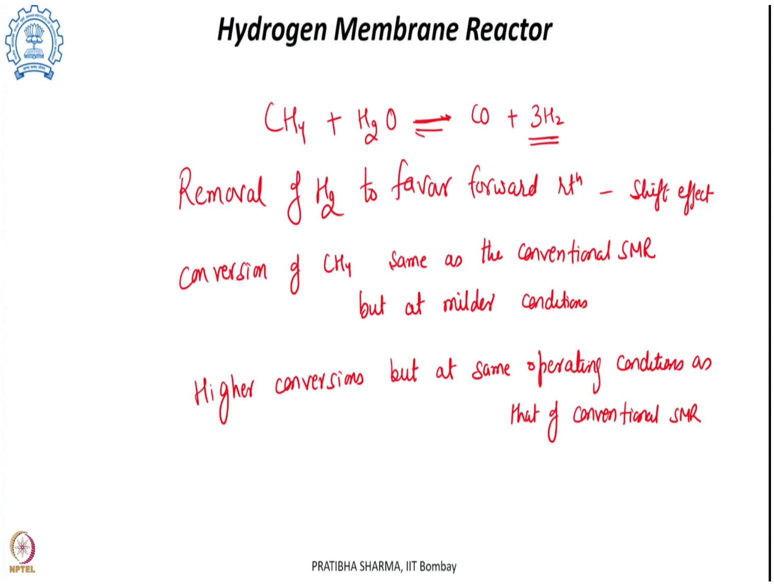
(Refer Slide Time: 22:16)



In order to take care of these challenges like the life of the sorbent is small, they undergo sintering or breaking up, there are several other sorbents which have been reported in literature to increase the durability. So, the durability of the sorbents is the major bottleneck so, there are several other sorbents which have been tried and these are like calcium, synthetic calcium based sorbents.

Then there are core shell structures of say dolomite with nickel, there are several other materials that have also been looked at for sorbents. For example, Li_2ZrO_3, $LiFeO_2$, $LiNiO_2$, Li_2TiO_2, Li_4SiO_4, then K_2CO_3 doped Li_4SiO_4. So, there are several other sorbents which have been looked at. However, the replacement of the sorbents is inevitable. So, you have to remove the sorbents and then replacement is required and that is the challenge in the method of sorption enhanced reforming.

(Refer Slide Time: 24:37)

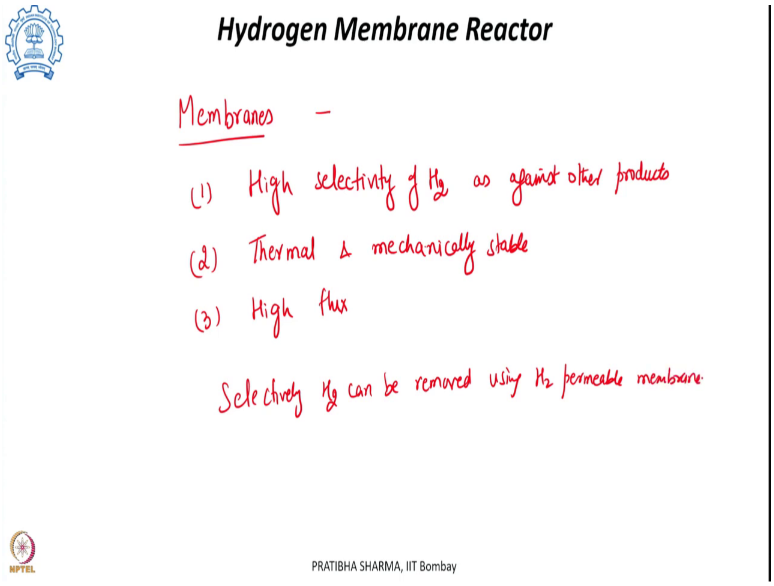


Now, the another method that can be looked at is the hydrogen membrane reactor, again the principle behind that is the same, that is the one of the product selectively is being removed from the reforming reaction and that product, which is being removed is hydrogen in this case. So, hydrogen which is being formed is being removed such that the forward reaction could be favoured and that is done using several certain membranes in a hydrogen membrane reactor.

Now, this removal of hydrogen to favour forward reaction or to take care of the chemical equilibrium related limitation is a shift effect. So, that shifts the chemical equilibrium in the forward direction. Now, there can be two ways, either it can allow conversion of reactant that conversion of methane, which is same as the conventional SMR, but this can be at milder conditions of operation; or it is possible that we can have higher conversions, but at the same operating conditions as that of conventional SMR.

So, that is a choice like, either we can operate under milder conditions and get the similar methane conversion or we can achieve higher conversions at similar operating conditions, than the conventional SMR.

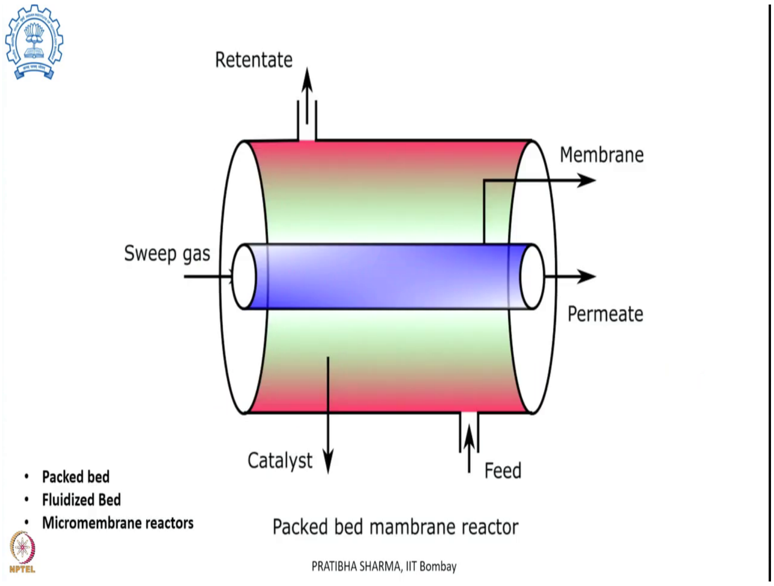
(Refer Slide Time: 26:54)



Now, there are again certain requirements when it comes to hydrogen membrane reactor, these membranes which will be selectively removing hydrogen. They will be selectively removing hydrogen and all the three reactions again will be taking place in the same reactor which is hydrogen membrane reactor, SMR, water gas shift and hydrogen separation will take place in the same reactor. The membranes they need to have good permeability and selectivity towards the desired product.

It should have high selectivity so that it should allow only hydrogen to pass through it. So, they should have high selectivity of hydrogen as against the other product, which could be carbon monoxide, carbon dioxide, unreacted methane. They should be thermally and mechanically stable and they should be able to provide high flux, the flow. So, this selectively hydrogen can be removed using a hydrogen permeable membrane, which should have all these characteristics.

(Refer Slide Time: 28:23)



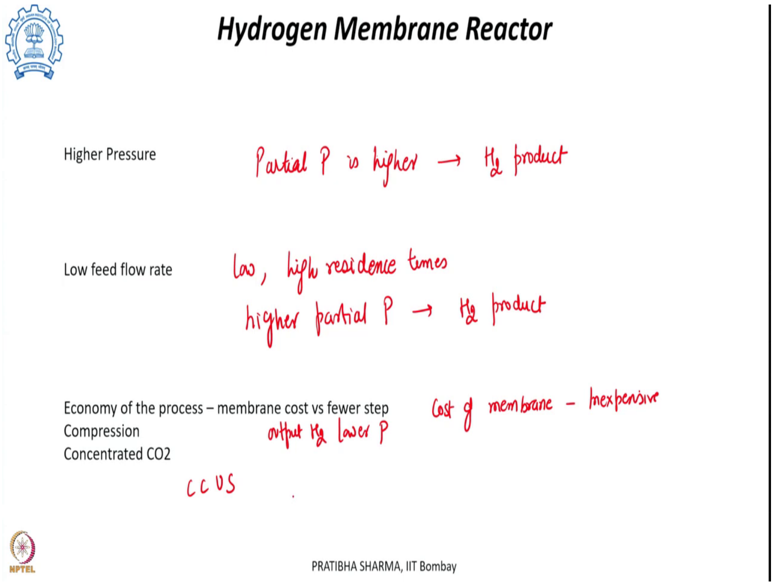
Now, if we see a typical membrane reactor. So, there can be either packed bed reactor or fluidized bed reactor or micro membrane reactor having size from 1 to 1000 micron. So, if we see how the process takes place, herein we have feed entering into the reactor. This is the central membrane which is on a support, the feed enters, undergoes the reaction and selectively hydrogen is permeated across the membrane and being collected.

However, the remaining gas is obtained which is the retentate, this is the basic driving principle for the hydrogen membrane based separation is the partial pressure.

Now, if required there should be a partial pressure on both sides of the membrane or if it is not sufficient enough then a sweep gas is used to provide that. And as such we will get hydrogen. Now, this sweep gas can either be nitrogen or any inert gas. So, this is a catalyst field bed, where in the reaction is taking place, feed enters, hydrogen carbon monoxide and hydrogen syn gases being formed.

Water gas shift reaction takes place, carbon dioxide and hydrogen being formed, hydrogen selectively is obtained product and the remaining gases are obtained. A sweep gas pressure could also be used for getting hydrogen in the process.

(Refer Slide Time: 30:16)



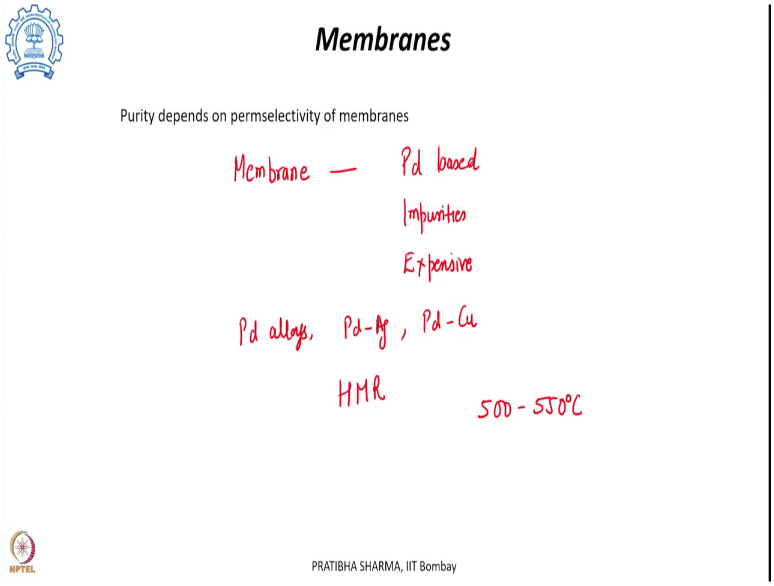
Now, a disadvantage in the conventional reforming method was if the pressure is higher in the conventional SMR method in that case reversible reverse reaction was favoured, because we have seen that is the limitation of chemical equilibrium. However, that could be beneficial when it comes to hydrogen membrane reactor, because the partial pressure across the membrane which is the driving force will determine the permeability.

So, if partial pressure is higher, we can have better product stream. However, another important parameter could be the feed flow rate at which the feedstock is being fed. So, if feed flow rate are low; that means, the reactants get enough time to react and interact. So, the residence time increases, if the flow rates are lower and that creates a higher partial pressure favouring the separation of hydrogen. So, if there is a lower feed flow rate, it will support getting higher separation using a hydrogen membrane reactor.

Now, when it comes to the economics of the process, we have to see that the cost of the membrane should be lower. So, the membranes needs to be inexpensive and that there will be a trade off against the cost of the membranes as against the number of processing steps. It is saving in terms of reducing the number of steps involved. At the same time since the output product hydrogen is obtained at a lower pressure in the process, compression becomes essential for using that hydrogen.

So, the energy is required for compressing hydrogen to higher pressure, either we can use for those utilization end use applications where hydrogen is required at a lower pressure. So, either we have to compress hydrogen to a higher pressure or can be utilized in applications like fuel cell, where low pressure hydrogen is required. At the same time using this method we are getting concentrated carbon dioxide and that can be used for carbon capture use and sequestration and that can reduce the emissions as well from the production site.

(Refer Slide Time: 33:17)

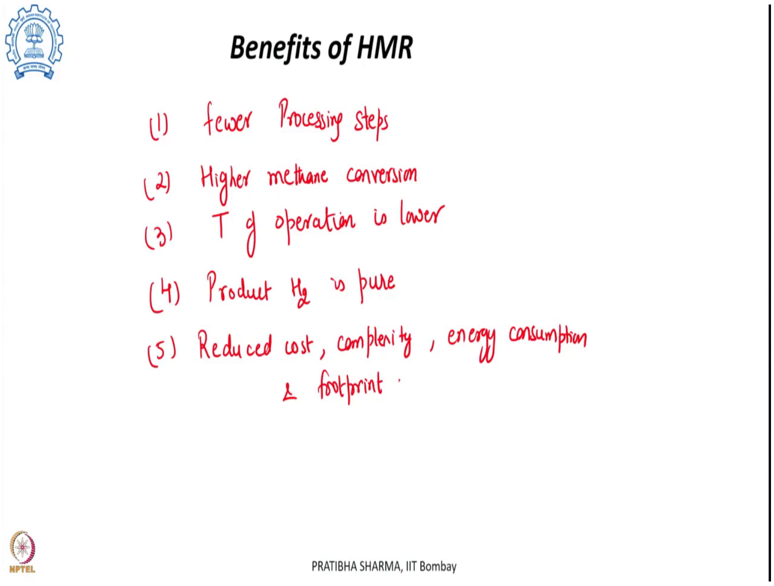


Now, what is the purity that we are going to get of hydrogen that definitely depends upon the selectivity of the membrane. Now, there are different membranes which are being looked at for hydrogen membrane reactor. So, membranes usually palladium based membranes being used. Now, these palladium based membranes have good permeability, but at the same time they have problem like, they are effected by the impurities product present in the gas stream.

So, they get poisoned by the impurities, at the same time these are expensive. So, there are alternate membranes which are researched. So, palladium alloys, palladium silver or palladium copper, based membranes these are considered for the hydrogen membrane reactor. There are several other membranes which are also being looked at and these can be used for the hydrogen membrane reactor.

Now, these membranes, since they can operate at lower temperature. So, the temperature conditions for the hydrogen membrane reactor is 500 to 550 degree centigrade.

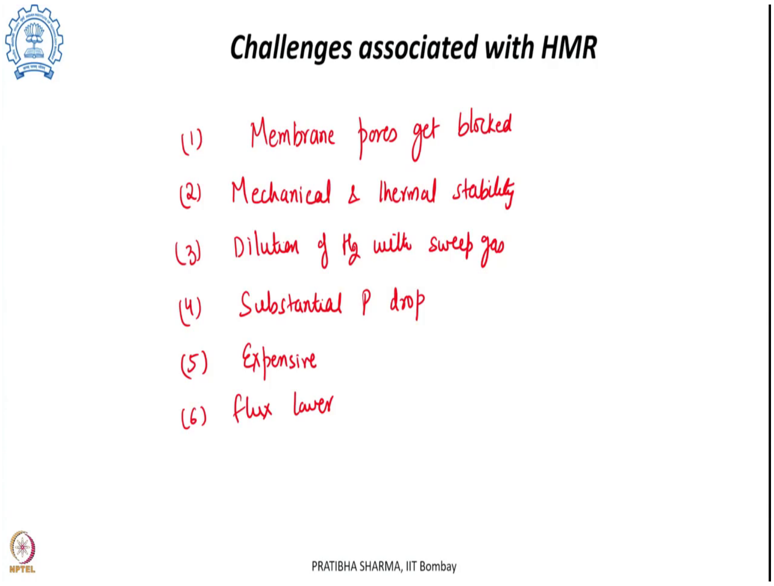
(Refer Slide Time: 34:50)



There are several benefits of hydrogen membrane reactor. The first and foremost that we have already seen is that these involves very less number of processes. So, fewer processing steps, we can get higher methane conversion, temperature of operation is lower with the use of hydrogen membrane reactor.

Product hydrogen which is obtained using the method is pure. Free from the carbon product, cost, complexity, energy consumption and the footprint required for the reformer all are lower. With all these benefits, there are also certain challenges associated with this method of reforming.

(Refer Slide Time: 36:28)



Here the challenges are because of the sintering of the catalyst the membrane pores get blocked, which can prevent further permeation of the hydrogen.

There are challenges associated with the mechanical and thermal stability of the membranes. If we are using sweep gas, then dilution of hydrogen with sweep gas will be there. So, again a purification to get pure hydrogen will be required. There will be substantial pressure drop with the use of membrane, these are expensive. So, we need to see the trade-off between the reduction of the number of process steps as against the membrane cost. And the flux achieved are lower with the membranes based reforming. So, these are the challenges associated with hydrogen membrane based reforming.

So, in today's class, we have seen other than the conventional steam methane reforming two more methods, which are sorption enhanced reforming and hydrogen membrane based reforming, which takes care of the limitations of the chemical equilibrium of the steam methane reforming process. However, both these methods are still not being utilized for industrial scale hydrogen production.

Thank you.