Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 21
Hydrogen Separation and Purification Part-2

In the previous class, we have seen pressure swing adsorption which is the most widely used method for hydrogen purification. In today's class, we will see the remaining methods which can be used for hydrogen purification, like the method which is membrane based separation can be used for either small scale or medium scale separation of hydrogen.

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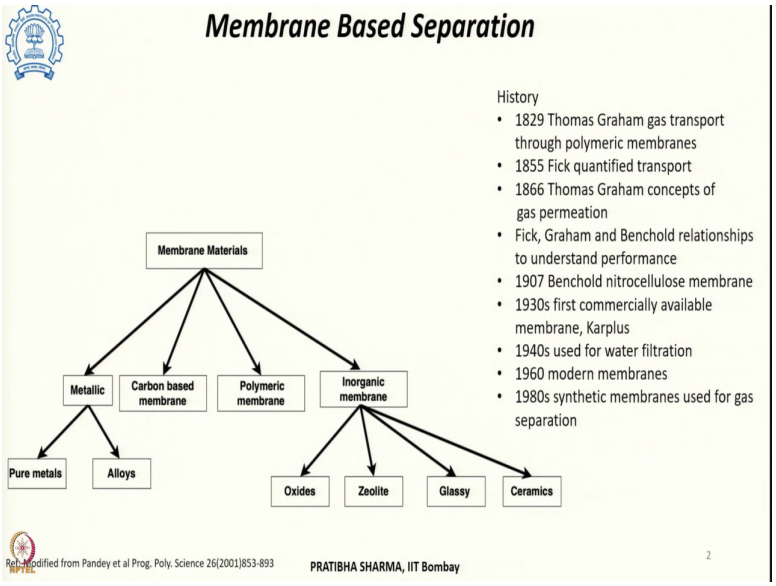

If we quickly look back into the history of the process, it was in 1829 that Thomas Graham, he proposed the gas transport through the polymeric membrane. In 1855, Fick quantified the gas permeation or the transport across these membranes. In 1866, Thomas Graham again he gave the concepts related to the gas permeation, work of Fick, Graham and Benchold, they it was very promising and they gave the various relationship between the different parameters and the performance of these membranes.

In 1907, Benchold he came up with a nitrocellulose type of membrane. This membrane was in fact, first commercialized with the work of Karplus in 1930s. This was first used for water

filtrations in late 1940s. It was in 1960 that the different modern membranes came up. And then, 1980s, the synthetic membranes were widely used for gas separation.

Now, when we look at the membrane based separation to get pure hydrogen, it can be classified depending upon what type of material we are using for these membranes. It can be either metallic membrane. So, it can be pure metallic, it can be alloy, it can be carbon based membrane, polymeric membrane or inorganic membrane. Among the inorganic membranes, these can be oxide based membranes, zeolite based membranes, glassy membranes or ceramic membranes.

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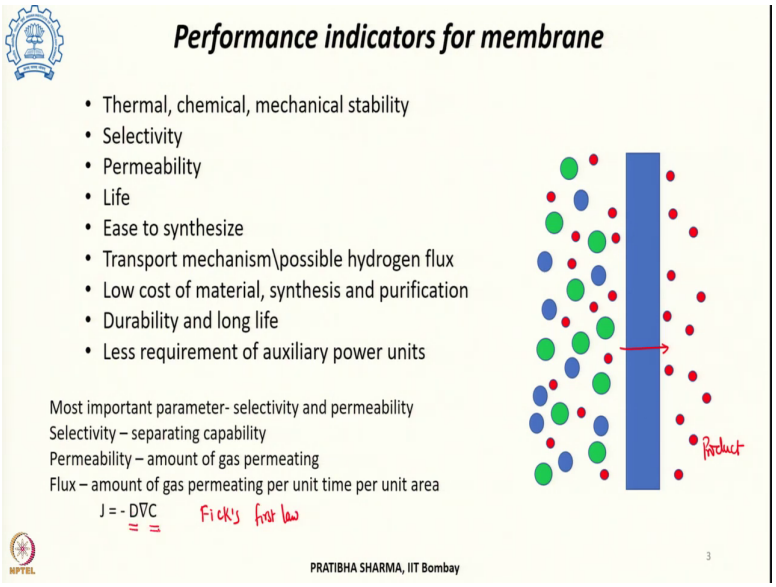

Now, in the process of membrane based separation, when the membrane separates the impure species or the feed gas with several contaminants along with say like the red one being hydrogen. The membrane can selectively permeate certain species through it so that the product side may be concentrated in that particular species. So, in this way we can separate hydrogen from the other contaminants using the membrane.

Now, these membranes should meet several requirements. They should be chemically thermally and mechanically stable; they should have very high selectivity towards a particular species for gas separation or for hydrogen purification it should be hydrogen. So, it should have high selectivity towards hydrogen as against the other species. It should have a high permeability.

So, it should allow to permeate these species, it should have a high life, we should be able to easily synthesize it, the transport mechanism should be such that we could get high flux of hydrogen. The material which is used for synthesis of this membrane the process of synthesis the purification all these should be low cost. The durability of the membrane and the long life is essential at the same time the requirement of any other auxiliary power unit should be less.

Now, the important parameter which characterize a membrane are selectivity, permeability and flux. Now, what do we mean by selectivity? When we have a mixture of gases, the separating capability of the membrane towards one particular species as against the other species is known as selectivity. The permeability is the amount of gas that can permeate through the membrane that defines its permeability; however, the flux is the amount of gas.

So, on the product side the amount of gas that permeates per unit time per unit area. And, this can be given by the Fick's first law which relates it with diffusion coefficient and the concentration gradient.

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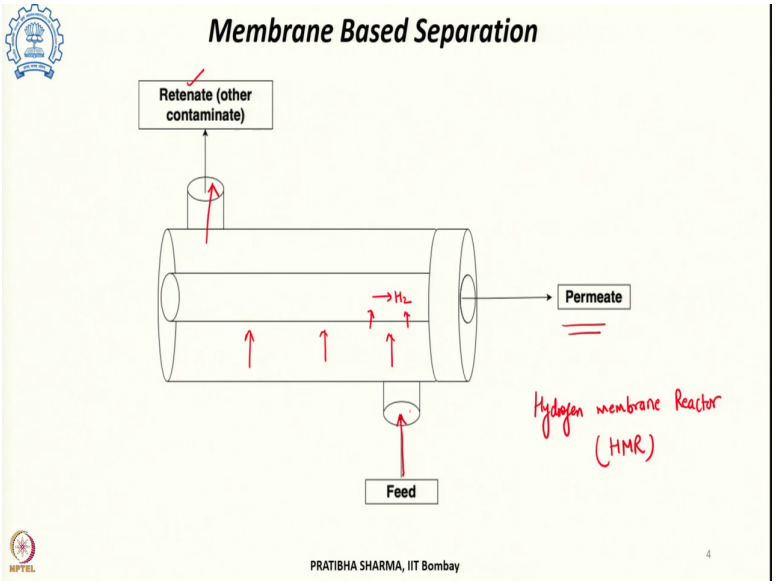

Now, if we quickly look at the membrane based separation method we have feed which is a mixture of gases hydrogen along with the contaminant entering into the membrane reactor. Now, these feed gases when passed through the membrane reactor the component which needs to be separated selectively passes through or permeates through this membrane in our case it is hydrogen. So, that forms the permeate.

The remaining gases which are deprived of hydrogen they come out and that is what we are going to get as a collection of contaminants or the impurities, which is retenate. Now, this membrane based separation we have also earlier seen in the hydrogen membrane reactor in the reforming. So, the concept remain same. So, HMR we have seen earlier when we studied the reforming process.

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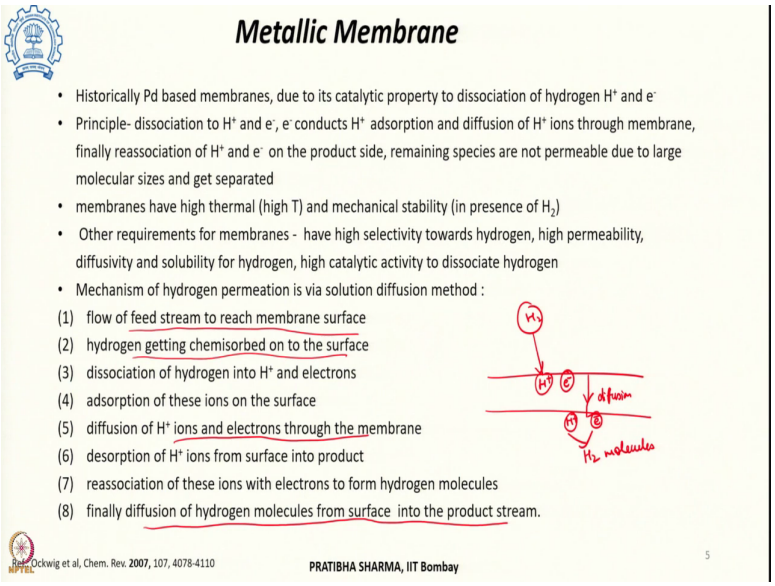

Now, there can be several types of membrane. These can be metallic membrane historically the membrane materials which were metallic. These used to be dense metallic membranes made up of palladium. The palladium specifically was used because it has a good catalytic property towards dissociation of hydrogen. Now, it dissociates hydrogen into proton and electron.

So, the process that follows is this. Dissociation into proton and electron such that this electron conducts and proton undergoes adsorption and diffusion through the membrane; so, it undergoes diffusion through the membrane. And finally, when they reach on to the product side they recombine to give hydrogen molecule. So, this happens for hydrogen, but the remaining species other than hydrogen they are not permeable through the membrane because the membrane is selectively permeable.

And that has a larger molecular size as such we can separate hydrogen from the remaining gaseous mixture. Now, these membranes which are dense metallic membrane they have high thermal stability that is as such we can operate them at high temperature, they have a high

mechanical stability which is essential because we need to operate these membranes in the presence of hydrogen.

The other requirements that this metallic membrane that should meet is they should have high selectivity towards hydrogen, they should have high permeability, high diffusivity and solubility, they should have high catalytic activity to dissociate hydrogen. The mechanism which is used for separation in metallic membrane is by means of solution diffusion.

So, the process is such that when the feed stream flows and reaches onto the membrane surface. The hydrogen gets chemisorbed onto the surface. So, the hydrogen molecule when it reaches onto the surface, it gets chemisorbed onto the surface of the membrane. Finally, it dissociates into H^+ and electron gets adsorbed onto the surface of the membrane. These ions get adsorbed.

They diffuse through the membrane; then they undergo diffusion in the membrane of H^+ and electron. After that on when they come on to the product side they get desorbed. Finally, they recombine to give hydrogen molecule. And this hydrogen molecule finally, undergoes diffusion from the surface into the product stream. So, broadly this is the mechanism by which hydrogen separation occurs in these metallic membranes.

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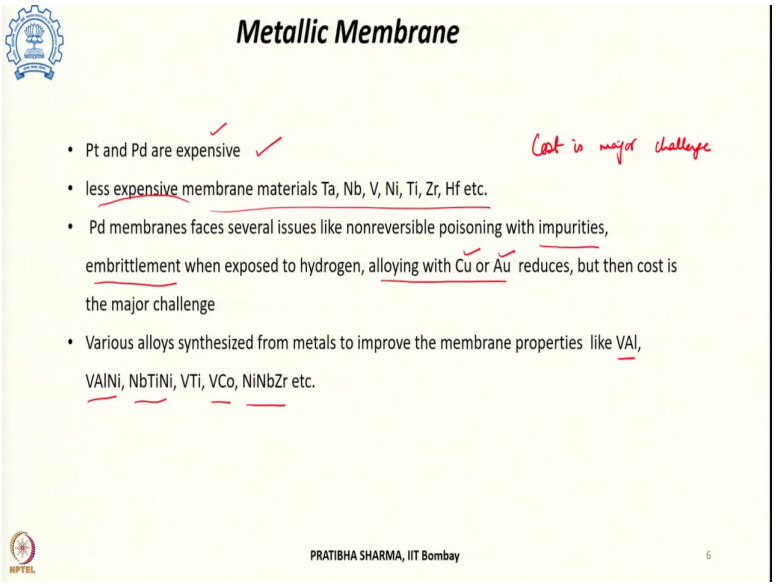

Primarily the membranes which were used for hydrogen separation were platinum and palladium, but then they had several issues like the non reversible poisoning with the

impurities. So, whatever the impurities they used to poison these metallic membranes when they were exposed for long term to hydrogen they undergo embrittlement. Now, in order to address these issues, alloying of these membranes was done with copper or gold, but then the problem was of the cost. So, the cost is the major challenge with these membranes.

Now, compared to palladium and platinum, there are less expensive metals which can be used for separation like tantalum, niobium, vanadium, nickel, titanium, zirconium and hafnium. These are pure metals which can be used for separation. Then, there are alloys which are synthesized from these metals to improve the membrane properties like vanadium-aluminium, vanadium-aluminium-nickel, niobium-titanium-nickel, vanadium-titanium, vanadium-cobalt, nickel-niobium-zirconium and various other combinations various other alloys can be used for making metallic membranes which can separate hydrogen.

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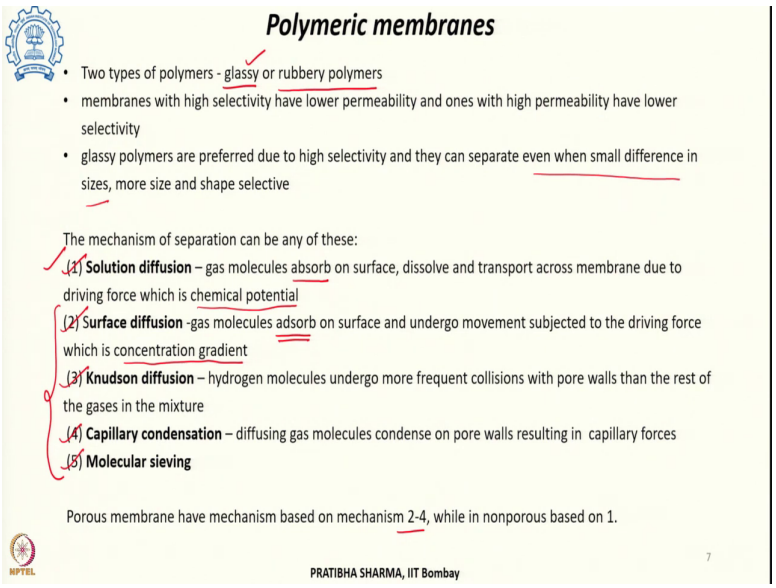

Now, other than metallic membranes there are polymeric membranes which can be used. There are two different type of polymers which can be used either it can be a glassy polymer or a rubbery polymer. Now, the glassy polymer they have high selectivity, but a lower flux; while the rubbery polymers they have a high flux and low selectivity. But among the two the glassy polymers are preferred because they have a high selectivity at the same time they can differentiate between even a small size difference, and then they can allow the permeability.

So, they can separate when the molecules they have a small difference in size. So, they are more size and shape selective. Now, the membranes usually what happens is the membranes which have high selectivity they have a lower permeability; while the membranes which have a higher permeability they have a lower selectivity. So, there is the compromise between the two.

When we consider the polymeric membrane there are different processes by which the separation can be done. There can be either a solution diffusion mechanism that can be responsible for separation. In solution diffusion, the gas molecules they absorb on to the surface and they dissolve and transport through the membrane due to the driving force which is nothing but the chemical potential.

The another method is surface diffusion in which gas molecules adsorb on the surface and again they undergo movement across the membrane diffusion. And that is derived by the concentration gradient in the surface diffusion. The third method could be Knudson diffusion where the there are different species which are present in the mixture they undergo frequent collision.

And the collisions which are experienced with the wall by the hydrogen molecule this is more compared to the other species in the mixture. And in that way, it gets diffused and separated from the gaseous species. Another method could be capillary condensation where the diffusion gas molecule it condenses onto the pore wall. And thereby, it is derived through the capillary forces and then the sieving molecular sieving can be used.

Now, the membranes can be either porous membrane or it can be a non porous membrane. If it is a porous membrane then the mechanism for separation is 2 to 4; however, for non porous membrane it is only the solution diffusion method which operates for the separation process.

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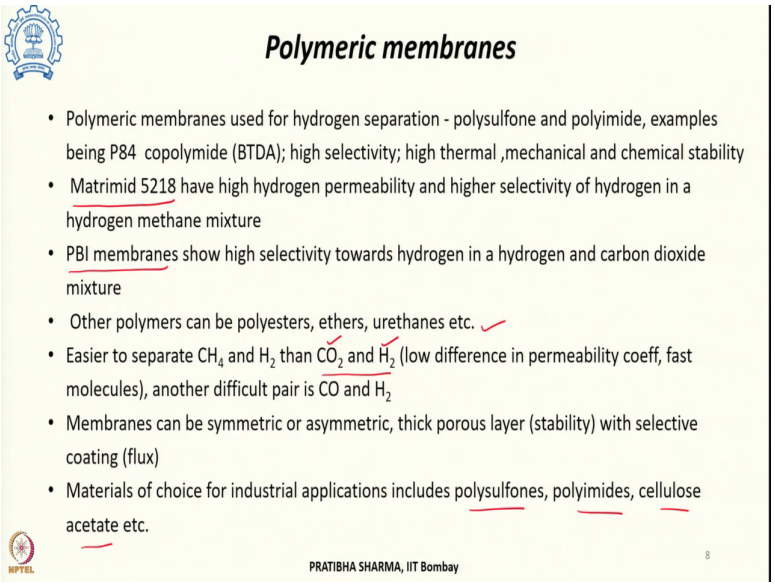

Now, there are different polymers which can be used for membrane synthesis. And the polymeric membrane which can be used for hydrogen separation includes polysulfone and polyamide. These are the well known polymeric membranes which can be used for separation. The example of these are P84 copolyamide BTDA. This particular membrane has high selectivity, high stability, thermal mechanical and chemical stability.

The another membrane which can be used for separating hydrogen from a hydrogen methane mixture is Matrimid 5218. PBI membranes can be used when it is up to separation of hydrogen and carbon dioxide mixture because they have high selectivity towards hydrogen. There can be other polymers which can also be used like polyesters, ethers. It could be urethanes, but it is overall the findings are like it is easier to separate hydrogen from methane compared to hydrogen from carbon dioxide and hydrogen from carbon monooxide

The reason for difficulty in separation between hydrogen and carbon dioxide is they have a lower difference between the permeability coefficient. So, they have very close permeability coefficient at the same time both of these are foster molecules. By foster molecules we mean hydrogen has a high diffusivity and carbon dioxide has a high solubility. So, both of them they can transport and it gets little difficult to separate these.

Now, these polymeric membranes can be either symmetric made up of a single material or these can be asymmetric. In asymmetric membrane, there are two different materials which are used usually it could be a thick substrate a porous layer which can provide strength to the

membrane that is it provides the mechanical stability to the membrane. And over that there could be a selective coating that provides the required hydrogen flux. Now, the materials of choice for industrial applications include polysulfone, polyamide and cellulose acetate membranes.

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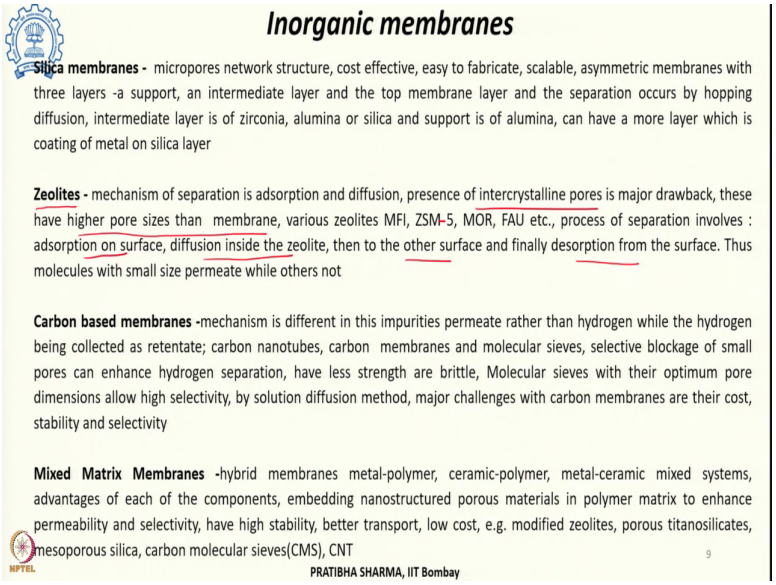

Now, other than the metallic and polymeric membranes there is a wide range of inorganic membranes that can be used for hydrogen separation and purification like the silica membranes. Now, the silica based membranes these are microporous in structure. These are cost effective they can be easily fabricated they are scalable and these are asymmetric type of membrane.

So, they have three different layers. There is a top layer, then there is an intermediate layer and then there is a support layer. And the separation of hydrogen from the mixture occurs by means of hopping diffusion. So, the intermediate layer which is used can be of zirconia, alumina or silica and the support is of alumina. There can be more than that layer there can be a coating onto the metal layer in the silica layer.

Then the next class of materials that can be used are zeolites. In them, the mechanism of separation is basically adsorption and diffusion, but the major drawback with these type of membranes is the inter crystalline pores wherein they have a higher size than the pore size of the membrane.

Now, there are different zeolites which can be used like MFI there can be ZSM5 can be used or MOR or FAU, these are the different zeolite membranes which can be used. The process of separation is first of all an adsorption that takes place on the surface of these membranes then there is a diffusion inside the zeolite membrane. After the diffusion, when it reaches onto the other side of the membrane, it finally gets desorbed from the surface.

Thus the molecules with smaller size permeate and they can be separated from the molecules which are of larger size using the zeolite membranes. Another class of membrane is carbon based membrane, but the mechanism of separation in carbon based membrane is different from the rest of the membranes. In other membranes, we have seen hydrogen gets permeated and separated; in carbon based membranes impurity is permeate rather than the hydrogen while the hydrogen is collected as a retenate.

Now, there are different materials which can be used for carbon based membranes these can be carbon nanotubes, these can be molecular sieves, these can be of other carbon based materials. And, there can be improvement that can be done in carbon based membranes by selectively blocking the small sized pore so that hydrogen separation can be enhanced, but the major problem with the carbon based membranes is they have a lower strength. So, they are brittle.

Now, compared to that molecular sieves the carbon molecular sieves they have optimum pore size, they have higher selectivity, and they are more widely used. The process by which separation occurs in carbon based membranes is solution diffusion method. And the major challenges which are there associated with carbon based membrane are the cost, stability and selectivity.

Now, we can also mix different materials to get mixed matrix membranes taking an advantage of each of the component. So, these are known as hybrid membranes. Now, hybrid could be either metal polymer or ceramic polymer or metal ceramic mixed systems. And each of the component have their own advantages. The example could be like the nanostructured porous materials can be blended or embedded in a polymer matrix.

And with the use of these two, it can enhance permeability selectivity, it can provide better stability, better transport, low cost. The other examples could be modified zeolites, porous, titano silicates, mesoporous silica, carbon molecular sieves, carbon nanotubes.

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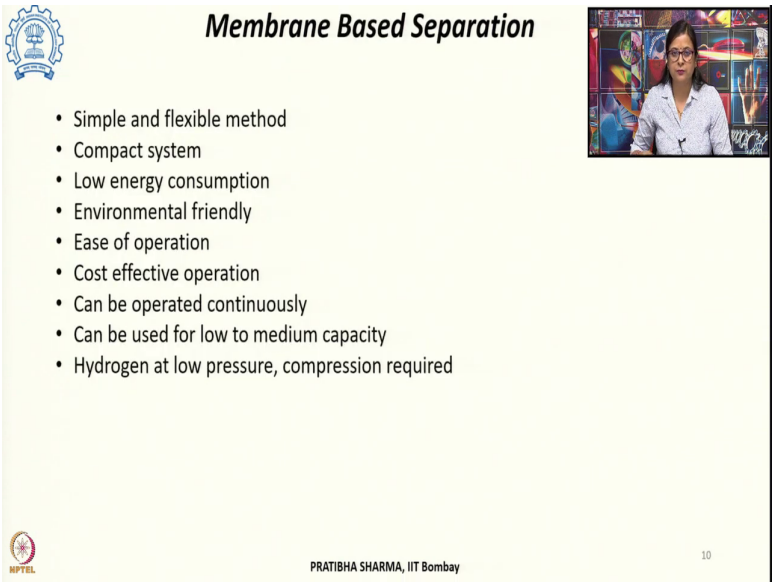

Now, with this membrane based separation method the system which is involved is a simple system. It is flexible, quite compact, it requires less amount of energy, it is environmental friendly, very easy to operate, it is cost effective in operation; however, the capital cost it depends upon the cost of the membrane which is being used. It is a continuous process. So, it can be operated continuously.

However, the membrane based separation is used for a medium to low capacity plants. The major disadvantage with membrane based separation is it gives hydrogen at a lower pressure. So, for applications where higher hydrogen pressure is required, another compressor needs to be integrated and that adds up to the cost as well as energy.

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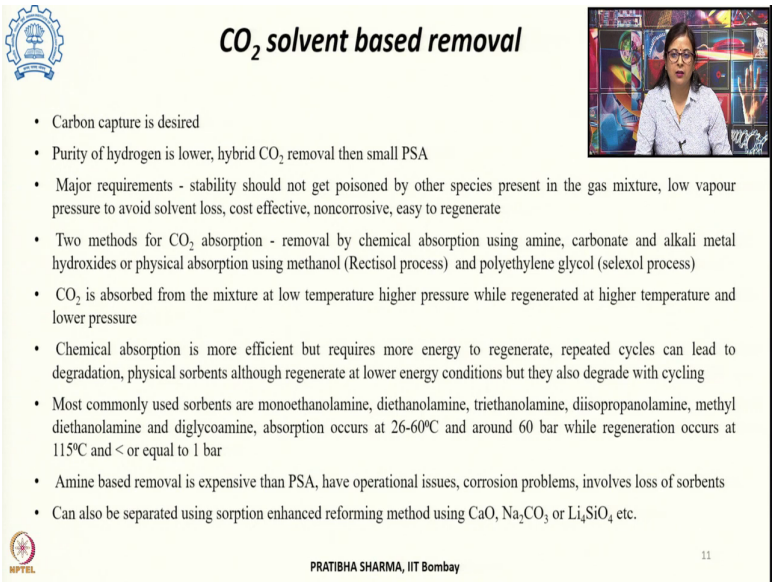

The next method for hydrogen purification is solvent based removal method. Basically, carbon dioxide solvent based removal method is used where the objective is to remove carbon or to do carbon dioxide capture like the pressure swing adsorption is the major method, but in pressure swing adsorption the PSA off gas when it is burned into the burners of steam methane reforming the carbon emissions are still there.

And these carbon emissions, if we want to capture them then prior to a pressure swing adsorption we can use a carbon dioxide solvent based removal method. So, if the carbon content in the feed stream is higher or if the objective is to capture carbon dioxide in the process then carbon dioxide solvent based removal method can be used, but the problem is the purity of hydrogen which is obtained is lower in that case a hybrid carbon dioxide solvent based removal method coupled with a small pressure swing adsorption unit can be integrated.

Now, the major requirement when it comes to the solvents which are used for carbon dioxide separation or removal is these should be stable. And, these solvent should not get poisoned by the presence of other species which are there in the gaseous mixture. At the same time the vapour pressure of these solvents should be low so as to avoid any solvent loss from the process. The solvent should be cost effective, regenerable, non corrosive.

Now, there are two different methods for carbon dioxide absorption which are used. One is using chemical absorption. The different solvents that can be used are amine, carbonate, alkali metal hydroxides or physical absorption like methanol which is which is used in the

Rectisol process or polyethylene glycol which is used in the selexol process. So, the carbon dioxide which is absorbed in the mixture it is typically done at a lower temperature and higher pressure, while the regeneration of the solvent to get back the initial solvent is done at a higher temperature and a lower pressure.

Now, out of the two methods whether it is physical absorption or it is chemical absorption. This chemical absorption definitely is more efficient, but then it forms a stronger bond. So, as such the amount of energy which is required to regenerate back the solvent is higher. At the same time when repeated cycles are performed the solvent can degrade; whereas, in case of physical sorbent although the regeneration occur at a lower energy condition, but then again still the degradation is possible in the repeated cycle.

Now, among the different solvents that can be used or sorbents that can be used for carbon dioxide removal the well known are monoethanolamine MEA, diethanolamine DEA, triethanolamine TEA, diisopropanolamine or methyl, diethanolamine or diglycolamine absorption in these occurs at a lower temperature 26 to 60 degree centigrade around 60 bar pressure; while regeneration occurs at a higher temperature 115 degree centigrade and less than or equal to 1 bar.

Now, amine based removal it involves solvent and the solvents cost at the same time solvent loss. Overall this method is expensive compared to the pressure swing adsorption method. It has operational issues, it has corrosion problems, there are loss of sorbents which are involved in the process. We have also seen earlier the carbon dioxide separation method when we studied reforming.

So, sorption enhanced reforming is an alternate method where carbon dioxide can be selectively reacted with some of the chemicals like calcium oxide or sodium carbonate or lithium silicate. And in this way carbon dioxide can be separated from hydrogen.

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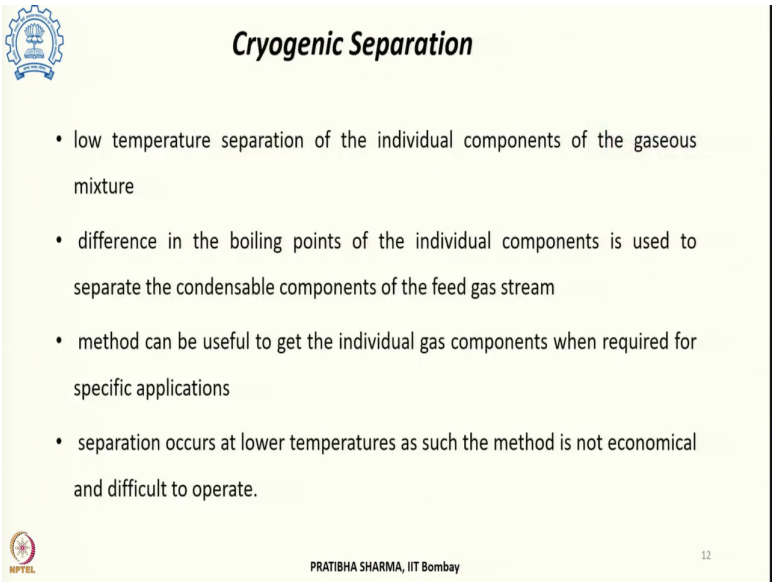

The last method is based on cryogenic separation. Now, as the name itself suggests it is a low temperature separation. In this particular method, the different components of the gaseous mixture can be separately removed. And the mechanism which is used is the difference in the boiling point of individual components which is used to separate the different components of the feed stream.

Now, this method can be useful when the process demands that individual components needs to be separated and can be used. So, if the individual components them themselves have a value which and can be used for a particular process then they can be separated using cryogenic method. However, since the temperature required for cryogenic separation are lower. The method is not economical and it is difficult to operate. Now, to summarize the entire section on hydrogen purification and separation.

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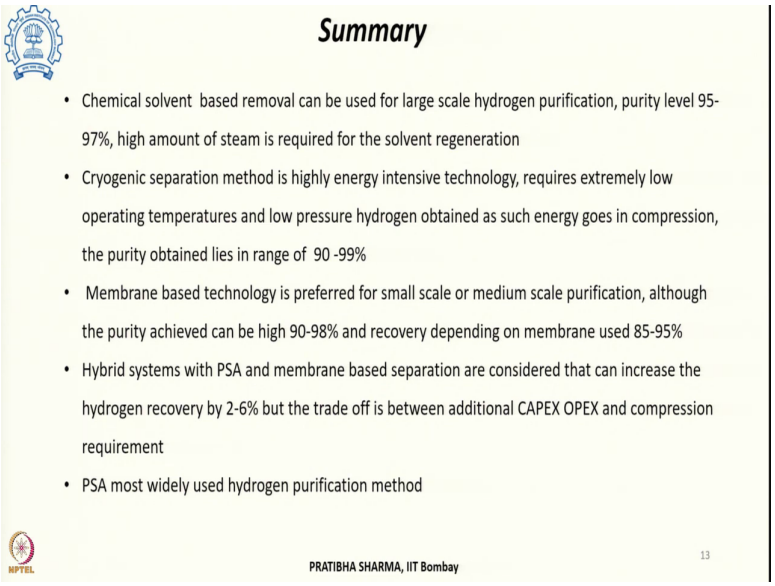

The method we have seen is one of the method is chemical solvent based removal method. Although, this is as like pressure swing adsorption used for large scale hydrogen purification, but the purity level that can be achieved is between say 95 to 97 percent. And at the same time it requires large amount of steam for the solvent regeneration. So, in order to further improve the purity we can use a hybrid along with a PSA.

So, a smaller PSA unit can be integrated with solvent based removal unit. The method of cryogenic separation, it is highly energy intensive because it requires very low temperatures and low pressure hydrogen is obtained. So, compression becomes essential and the purity lies between 90 to 99 percent. The membrane based separation method this is usually preferred for small scale or medium scale purification.

The purity that can be achieved lies between 90 to 98 percent and recovery depending on which membrane we are using can vary between 85 to 95 percent. Now, there can be hybrid systems where in two of such systems can be combined together like PSA with membrane based separation can be considered or carbon dioxide solvent based removal method along with pressure swing adsorption.

Now, like with pressure swing adsorption and membrane based separation, it can although increase the hydrogen recovery by say 2 to 6 percent, but then there remains a trade off to the additional cost that gets added up like CAPEX and OPEX cost. At the same time when it comes to membrane based separation, the required pressures of hydrogen are lower.

So, a compression unit needs to be integrated. So, that again adds up to the energy and cost requirement. And pressure swing adsorption is the most widely used hydrogen purification method among all the methods. That was about the hydrogen purification from the various other contaminants and impurities present in the product gas stream from the various hydrogen production methods.

Thank you.