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Lecture - 20 Hydrogen separation and Purification Part - 1

In the earlier classes, we have seen Hydrogen Production from various hydrocarbons. The product gas from these methods comes along with hydrogen and various contaminants and impurities. Now, depending upon the feedstock used as well as the method which is used for hydrogen production, the product gas from the hydrogen production unit has variety of compositions.

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S.	Method	$H_2(\%)$	CO (%)	<i>CO</i> ₂	CH ₄	Othe
1 \0. 1.	Natural gas reforming	70 – 75	10 - 15	(%) 10 – 15	(%)	N ₂
2.	Methanol reforming	75 – 80	0.5 – 2	20-25	-	
3.	Coal gasification	25 - 35	35 - 45	15 - 25	0.1 - 0.3	N ₂ , S H ₂ O
4.	Biomass gasification	25 - 35	30-40	10 - 15	10 - 20	N ₂ , S, O ₂
5.	Coke oven gas	45 - 60	5 - 10	2-5	25 - 30	N ₂ , S O ₂

Now, steam methane reforming which is the most widely used method for hydrogen production has 70 to 75 percent of hydrogen in it, 10 to 15 percent of carbon monoxide, carbon dioxide, 1 to 3 percent of unreacted methane and some small fraction of nitrogen. In methanol reforming, 75 to 80 percent is hydrogen, 20 to 25 percent of carbon dioxide and a small amount of 0.5 to 2 percent of carbon monoxide.

When the syngas it comes from coal gasification, the major content is carbon monoxide 35 to 45 percent, hydrogen is 25 to 35 percent, CO_2 is 15 to 25 percent and certain amount of methane, nitrogen, sulphur containing impurities and moisture in it. Similarly, for biomass

gasification the hydrogen content is lower 25 to 35 percent, 30 to 40 percent is carbon monoxide, 10 to 15 percent is carbon dioxide and 10 to 20 percent is still methane which is remaining, then nitrogen, sulphur and oxygen.

In the coke oven gas, 45 to 60 percent is of hydrogen, 5 to 10 percent of carbon monoxide, 2 to 5 percent of carbon dioxide, methane 25 to 30 percent and then remaining nitrogen, sulphur impurities and oxygen. Now, in order to get pure hydrogen from the product gas stream from hydrogen production, separation and purification is required. To get pure hydrogen, there are different methods of purification which can be used. Broadly, these can be categorized into four different types the method like adsorption based method.

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Now, in adsorption based method all the impurities or contaminants present in the product gas stream are adsorbed; however, hydrogen remains. The second method is membrane based separation where the membrane selectively allows certain species to pass through it thereby getting the product gas stream which is pure. In absorption based methods, primarily it is used for carbon dioxide solvent based removal, where carbon dioxide can be removed and we can get hydrogen.

And the last method is cryogenic separation. Now, these methods can be categorized into physical or chemical methods. Among the physical adsorption methods; again these can be sub categorized into pressure swing adsorption, temperature swing adsorption and vacuum

adsorption. The low temperature separation method or the cryogenic method can be adsorption based or it can be cryogenic distillation.

Among the membrane based these membranes can be either inorganic membranes or organic membranes. Among inorganic membranes, metallic or carbon based membranes. Organic membranes can be polymer membranes. There could be solvent based removal methods among chemical hydrides, either metal hydrides can be used for purification of hydrogen or it can be another route which is catalysis. Now, we will look in more details about each of these methods.

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The first method which is most widely used for hydrogen purification is the pressure swing adsorption. And in this method we can get ultra pure hydrogen. So, 99.99+ percent purity we can achieve and a high hydrogen recovery with the modern pressure swing adsorption plants even 90 percent hydrogen recovery could be achieved. There could be plant sizes which can be small even 30 normal meter cube per hour to plants reported which are 2,65,000 normal meter cube per hour or 4,00,000 normal meter cube per hour. Just to look a little background.

So, the process was invented by Charles Skarstrom, and he came up with a four step cycle which was further in 1966, the first commercial scale plant which was a pressure swing adsorption plant with four steps and a tail gas drum was integrated with the steam methane reforming. In 1970, the multi bed PSA system was installed. In 1977, the system had ten beds that was installed in Germany.

And thereafter, like in after 1980, the pressure swing adsorption became the major route for hydrogen purification and that replaced the solvent based removal method. Now, if we compare the two methods in solvent based removal method the number of steps involved are more, like SMR thereafter it comes high temperature water gas shift, low temperature water gas shift, carbon dioxide solvent based removal and methanator.

So; however, if we replace it by pressure swing adsorption, we only require a high temperature water gas shift after the steam methane reforming. And with time the process has seen several advancements. A wide variety of mixtures of contaminants can be removed or a wide variety of mixtures can be purified using this particular method.

So, about 40 different types of gases can be separated using the pressure swing adsorption. It is not only used for hydrogen purification, but it is used for various other industrial processes like separation of branched and linear paraffin's, for air fractionation, for air drying. It can be used for carbon capture, for biogas upgradation.

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	Principle of PSA
• Pr	ressure swing – change in P, used to remove the impurities from hydrogen
• Hy	ydrogen in pores/voids of microporous and mesoporous sorbents
• Le	ess adsorbing and more adsorbing species separated
• 01	nce the sorbent gets saturated, it is regenerated, releases all the impurities
• Ga	as molecules get attracted towards surface of high surface area sorbents
• Di	ifferent gas molecules have different affinity, attraction or bonding, they can be separated
• Ac	dsorption is spontaneous process (40-50kJ/mol), exothermic, increases with T \downarrow and P \uparrow
• Ac	dsorption of components of reformate gas – equilibrium
• ec	quilibrium at a particular T, P and composition determines the thermodynamic limit of loading
or	n adsorbent, amount of species adsorbed at const T and varying P defines its adsorption
са	apacity –adsorption isotherms under equilibrium
• De	epending upon binding, different adsorption isotherm shapes, linear is ideal
• Th	his equilibrium information is essential to design process and system (size, sorbents etc)
• 01	nce bed gets saturated, regeneration, based on method TSA or PSA(cycle is fast 1-10 min)
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Now, if we look at the principle of pressure swing adsorption the name itself suggest. So, in short it can be written as PSA (Pressure Swing Adsorption), the name itself suggests that when the pressure is changed because of that the impurities or contaminants they can be adsorbed or desorbed subjected to the change in pressure. And as such we can get pure hydrogen in the process.

Now, there are different sorbents used in the process. These can be microporous or mesoporous. When the feed gas is allowed to pass through the adsorbents then the impurities or contaminants get adsorbed onto the sorbent; however, the hydrogen remains in the pores or voids unadsorbed. So, this is a sort of separation process where a species which adsorbed gets separated from the one which is either less adsorbed or not adsorbing.

Now, once the sorbents they get saturated with the impurities or contaminants then it need to be regenerated back and that has to be done by the change in pressure. So, the pressure swing. Adsorption occurs at a certain pressure that is usually higher pressure and desorption occurs at a lower pressure. So, once the sorbent gets saturated, it has to be regenerated back by reducing the pressure and under that condition it releases all the impurities present in the bed.

Now, what happens when a surface absorbent is exposed to the mixture of gases different components of gas they have different affinity towards the surface. Now, some molecules they get adsorbed they get attracted towards the surface they find a binding towards the surface and then get adsorbed on to the surface. So, the process involves surface adsorption that is why the sorbents required should usually have a high surface area.

Now, since different molecules they show a different affinity attraction or bounding as such they get separated. So, some molecules will be having a lower adsorption some molecules will be having a higher adsorption. And in that way we can separate these molecules. This process of adsorption, it is an exothermic process or it is a spontaneous process with the adsorption energy of 40 to 50 kilo joule per mole. And since it is an exothermic process the adsorption increases as the temperature reduces as well as the pressure increases.

Now, when the gas which is coming from the hydrogen production plant, let us say reformate gas it is onto the surface of the sorbent adsorption of the different components occur except for hydrogen. And at one point of time, the bed or the sorbent gets saturated with the impurities, it comes into equilibrium. So, at a particular temperature, pressure and composition, this equilibrium that actually determines how much amount of impurities that particular sorbent can take.

So, that is what is the thermodynamic limit of the loading of adsorbent. So, the amount of species that can be adsorbed on to it at a particular temperature, at a constant temperature and if we vary the pressure we can get the different adsorption isotherms under that particular

equilibrium state. Now, this adsorption isotherm depending upon what sort of bonding what sort of attraction the molecule feels towards the surface it will have a different shape.

So, different shapes for adsorption isotherms can be obtained, but the preferable one for pressure swing adsorption is that it should be linear that is what is ideally required. If it is non-linear what happens is at some regions of the isotherm may have a lower pressure. Now, in order to desorb such a system we will require even lower than that particular pressure. And in that case the pressure requirement may be as low as it can go to requirement of vacuum that may add on to the cost to the energy efficiency of the process.

So, ideally it should be a linear isotherm. Now, how much amount of hydrogen we are able to recover, what will be the size of the PSA unit, what will be the different sorbents used in the process, all that information of temperature, pressure can come from this equilibrium information. And, once the bed it gets saturated after coming in contact with the impurities, the regeneration of bed can be either done subjected to increase in temperature then the method is called temperature swing adsorption or it can be by changing the pressure lowering down the pressure.

So, it is pressure swing adsorption. Usually, pressure swing adsorption they have a faster cycle about one to ten minutes is a cycle duration, but the temperature swing adsorption it is a slower process. So, it may take hours; this is because the energy which is given to the bed it takes time to provide that energy as well as it takes time to remove that much amount of energy from the bed.



So, if we go into more details about the pressures swing adsorption cycle, the simplest cycle can have two steps an adsorption step and a desorption step. The process is conducted in a fixed packed bed column. When the feed gas enters into a fixed packed bed PSA column at a higher pressure the impurities gets adsorbed into the column and we can get hydrogen as a product in the opposite direction to that of the feed.

Now, once the bed gets saturated with the contaminants then the second step is desorption to get the impurities out of the bed and then the bed gets ready for the next cycle in this process of two step PSA cycle, the hydrogen is obtained at a higher pressure while the impurities are obtained at the ambient pressure or close to ambient pressure. Now, as we can see that there are two steps it is a sort of batch process, but for most of the applications where hydrogen is required like in refineries or other applications a continuous requirement of hydrogen is there.

So, in order to make this batch process, a continuous process more number of bed are added to the process. So, it is not two step actually we can add more number of beds so as to make it a continuous process. Now, when it is integrated with a SMR unit, with a steam methane reforming for hydrogen purification then the after removal of hydrogen the tail gas or the off gas which is obtained from the PSA unit can be used and that can provide the required energy for the steam methane reforming.

So, this tail gas or off gas that is burnt in the burners to provide the required heat of reaction to the reformer tubes. So, that can be still used and improving the energy efficiency of the process. Now, since this tail gas for applications also should be continuous in supply. So, as such a buffer unit or a tail gas drum is used when it is integrated with a SMR process.

This bed it is usually not a static process; inside the bed it is a dynamic process which is going on. So, the temperature, pressure and composition all these varies inside the bed both with respect to time and with respect to the position inside the bed. And even we can add more number of beds like there are processes where we can have the simplest one the two step process.

And we can increase the number of beds to even 16. Now, how many number of beds to be added for getting better hydrogen recovery again there is a trade off? So, we can achieve better recovery by adding more number of beds, but at the same time it adds up to the capital expenditure, operational expenditure, energy requirements. So, that needs to be decided on the basis of economics at the same time the amount of hydrogen that can be further recovered and the cost associated with that hydrogen. So, there is a trade off on the basis of which we can decide

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Now, the traditional or the conventional Skarstrom four step cycle involves four beds. And this there are four steps in the process of pressure swing adsorption. The first step is adsorption step in which the feed gas is fed at a higher pressure to the bed. In the bed which is a fixed packed bed there are layers of different sorbents present. When the gas process or the feed gas passes through this bed, the impurities present in the feed gas they get adsorbed in different layers of the bed.

However, hydrogen remains un adsorbed and that it can be collected at a higher pressure. So, this is the highest pressure step and hydrogen is collect collected on the product side. Now, once the bed gets saturated with impurities then comes the second step; the counter current blow down step. So, after its saturation to regenerate back the bed the pressure is reduced at that time the feed gas is stopped.

So, once the pressure the pressure in the blow down step is not reduced in a single step. So, it is done in a sequence of steps. So, that the different impurities present in the bed gets desorbs and this is known as the depressurization step as well. So, this is subjected to reduction in pressure, the impurities are removed from the bed. Now, the third step involved is a counter current purge step.

By counter current purge step, we mean that the bed is being prepared for the next cycle. This is a light recycle step in which hydrogen which is obtained from the product gas side can be used to purge the bed in such a way that the contaminants which are still remaining in the bed they experience a lower partial pressure and as such certain amount of other contaminants can also come out in the process.

And, the final step is now the bed gets ready for next cycle. We have to again pressurize this bed, that pressurization is done by means of introducing the purified gas which has been obtained from the first step and that recycled purified gas is introduced to again increase the pressure of the bed so that again the first step can be carried out. So, this is the four step cycle of a PSA.

However, we can achieve higher hydrogen recovery by addition of certain more steps. So, like the second step which is the blow down step at this step still substantial amount of hydrogen remains in the bed. And, if it is not removed it may go into the tail gas and then it will be burned off. So, what we can do is we can still add certain step like the pressure equalization step before the blow down step such that we can achieve more of hydrogen recovery. Now, how does this work?

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So, the feed gas which is there are two beds which are kept in contact one bed which is at a comparatively higher pressure compared to the other bed which is at a relatively lower pressure. So, before the blowdown step when the first step is operational, the pressurization step at the end of it still there is lot much amount of hydrogen which is there in the bed. The feed is stopped at that point and the gas flow from the high pressure bed takes place in the co current direction of the feed gas.

Now, since there is a pressure difference between the two beds, this is connected to another bed which is at a lower pressure. Now, the pressure finally, is that is between it is not reduced to the low pressure rather it remains to an intermediate pressure. And, in this way the hydrogen can be transferred to the other bed in a counter current direction.

So, this is a counter current pressure equilibrium step in which the hydrogen which can still be recovered from the pressure first bed can be transported to the another bed, bed II and this particular bed can be used for the re-pressurization for the step number 4. Another method could be providing a purge step. So, the process is still the same as is the pressure equalization equalization step.

The only difference is second bed that can be a bed which can be used for providing purging. So, either it can be the step number 1, can be used for providing the pressurization step or it can provide the purging step using additional beds. Now, these additional beds mean more number of steps involved, more is the complexity of the system, more is the cost associated. So, the various performance indicators that decides the parameters of the process includes hydrogen recovery, how much amount of hydrogen we are able to get from the product stream, how much is the purity of hydrogen which we are getting, what is the energy consumption in the process, what is the productivity, what is the recyclability of both the absorbent as well as the process.

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Now, in this process various sorbents can be used that depends upon what was the feed gas which was fed into the pressure swing adsorption; that means, what was the hydrogen production method, what was the feedstock which was used, what are the impurities present in the feed gas, and also on to the final end use application like what is the purity desired for a particular application.

So, based on that we can select a proper sorbent. Now, since one sorbents cannot remove all the impurities as such there are different sorbents used in the bed. And that choice of a particular sorbents it depends upon which particular component needs to be removed from the feed gas. Also, there is a sequence in which these impurities need to be removed from the feed gas stream.

So, that both the sorbents which is to be used that depends upon the components which need to be removed, at the same time what is the order in which the impurities are removed that all decides what will be the design of the pressure swing adsorption unit. There are wide number of sorbents which are used like alumina, silica gel, it can be molecular sieves, metal organic frameworks, zeolites, activated carbons.

So, there are several sorbents which can be used there are different materials which can be used as sorbents and they have a different affinity towards these impurities. So, now, since a single metal cannot material or single sorbents cannot remove all the impurities we put layers of different sorbents and in that way we improve the purity. Now, the first material to be used is such that it should remove the water content or the moisture.

So, the sequence in which the impurities are removed are first of all water, then carbon dioxide, then methane, carbon monoxide, thereafter nitrogen and argon and finally, hydrogen remains un adsorbed and it is collected. So, this is the sequence of removal of the various impurities in the process. So, water is the first impurity that needs to be removed in the layer 1, for this either alumina can be used or silica gel can be used even activated carbons can also be used for removal of water.

So, the 1st layer can be used for removal of water. It can also be the material can also remove aromatics H2S and HCl. If we look at the different materials in the layer 1, it can be alumina. So, that has a higher loading capacity like alumina can take up 30 moles per kg of the material silica gel comparatively lower, 15 moles per kg activated carbon can still be in between the two like 20 moles per kg, but then it is not preferred because it has a low volumetric capacity.

Now, once the water content is removed. So, the next layer could be towards removal of higher hydrocarbons. So, this could be C3 or C3 plus hydrocarbons can be removed in the next layer. And, it is very essential to remove C3 plus or higher hydrocarbons in the layer 2. The reason being the 3rd layer which is of activated carbon that gets poisoned or that strongly adsorbs the C3 plus and it gets very difficult to then desorb from the layer 3.

So, prior to it enters into layer 3, all these C3 hydrocarbons or higher hydrocarbons needs to be removed in layer 2 which is using silica gel. Now, next layer is of activated carbon. This activated carbon has a different affinity towards different impurities. Wide variety of impurities can be removed using the activated carbons the order of adsorption in this that follows is water higher than carbon dioxide higher than methane higher than carbon monoxide nitrogen and the least one being for hydrogen.

In the activated carbon usually the process which is used for separation is micro pore diffusion. And, if we look at the kinetics of adsorption in activated carbon the fastest one is for hydrogen, then nitrogen, then carbon monoxide, carbon dioxide and methane. Now, once this has been removed in this particular step. So, the next step which is that of the removal of carbon dioxide occurs as well as the lower hydrocarbons in this particular step which is the 3rd step or the 3rd layer of activated carbon.

However, this also can remove several impurities present like H2S and the order that is followed in the activated carbon layer is first of all H2S is removed, then the other hydrocarbons C1 and C2 hydrocarbons then carbon dioxide, unreacted methane can be removed in this 3rd layer which is of activated carbon. This material is less expensive and it has an isotherm which is less non-linear than the zeolites.

At the same time the cost is comparatively less, but the problem with activated carbon is it has a lower adsorption towards CO as such this is because the CO has a lower partial pressure. So, it can only partially remove CO. So, our next layer is further required to remove the CO content, and that is a final layer of zeolite. So, this is also known as a polishing layer which adsorbs the remaining CO present, and it has a higher volumetric loading for the carbon monoxide.

The important thing here is this layer is more respondent or it can adsorb very strongly carbon dioxide and moisture. So, as such the CO_2 and moisture should not reach this layer 4. Now, if what will happen if carbon dioxide or moisture reaches it will form a strong bond and then we will require very high temperatures to remove or very low pressures vacuum pressures to remove that.

So, in order to avoid that the ratio of the layer thickness of activated carbon and zeolite is selected in a manner that CO_2 and H2O do not reach this zeolite layer. Even in the zeolite layer, the order of adsorption is is highest for CO2, then CO, then methane, then nitrogen and hydrogen. With this final layer, we can even reduce the carbon monoxide content to less than 10 ppm. And finally, the un adsorbed product can be there which can be collected at the outlet.

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	Sorbents in PSA
	Requirements from sorbents in PSA:
	Stable in presence of impurities long life
	Low cost
	High loading capacity
	Desorb without vacuum or high T
	High mechanical stability (PSA columns are of several meters height, should not crush with flows)
	High productivity (rate of hydrogen produced to the amount of sorbent used)
	Several sorbents modified activated carbon or impregnated with saline solution, zeolite 5A or 13X modified with
	Na ⁺ , MOF(MgMOF74, UiO66 etc.), combinations of zeolites with activated carbon, or zeolites with MOF, hollow
	fibres
	Performance of PSA – proper design, optimization and use of materials with high loading, multiple beds (adds
	complexity and cost)
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Now, so the various requirement that are from adsorbent in a used in a pressure swing adsorption are that it should be stable in the presence of the various impurities which are there in the feeds stream. And subjected to that it should still have a long life, low cost, it should have a high loading capacity it should desorb without use of vacuum or without requirement of a higher temperature. It should provide mechanical stability. These PSA units' columns are of several meters of height.

So, as such it should be mechanically stable under that much of pressure when there are flows it should not crush, these sorbents should not crush into fine powder. And, we should at the same time get high productivity. This productivity is defined as the rate of hydrogen produced to the amount of sorbents which is being used. So, these are the requirements for the various sorbents which can be used in PSA.

Now, other than the sorbents that we have seen, there can be many other sorbents these are the modified sorbents that can be used like modified activated carbon or impregnated with saline solution or it could be zeolite 5A or zeolite 13X which can be modified with sodium ion or metal organic framework like MgMOF74 or UIO66. There could be combinations of zeolite with activated carbon, zeolites with metal organic frameworks or hollow fibres that can also be used as sorbents.

So, the performance of pressure swing adsorption that depends upon which sorbents is being used, what is the loading percentage of that sorbent with the impurities, designing of that

optimization of the various sorbent layers and then addition of multiple beds, but then the addition of multiple beds again can add to the cost or complexity of the process. So, the pressure swing adsorption operates at an ambient temperature, but subjected to the pressure variation we get the hydrogen purity which can be very high.

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Now, the hydrogen which can be recovered from the processes in the modern plants of around 90 percent there can be different plants with sizes ranging from 30 normal meter cube per hour to 4,00,000 normal meter cube per hour. The energy consumption in the process is less. We can get high purity 99.999 percent purity. There is less investment and operational cost required for it the materials which are used as sorbent they are less expensive.

And wide variety of feed gas obtained from various processes can be cleaned, can be purified using this particular method like the one which can be which is obtained from steam methane reforming or partial oxidation or methane decomposition, gasification, petrochemical or refinery of gas or even coke oven gas. In these processes even if the hydrogen content varies between 30 to 90 percent still that can be purified using the pressure swing adsorption method.

Compared to the carbon dioxide removal method since the number of steps involved is lower. So, the cost saving is more in this particular method. The energy efficiency of the process is higher because the tail gas which is obtained after pressure swing adsorption that can be used to meet the energy requirements in a SMR plant. And this off gas or the tail gas which is obtained from pressure swing adsorption that has a lower heating value of 4000 to 8000 kilo joule per normal meter cube.

In this process the operational life is high it is reported that we can achieve even 30 years of operational life. And the important thing is there is no deactivation problem associated with the sorbents or the poisoning issue that are absent in the process. So, in the next class, we will see membrane based separation method, the cryogenic separation as well as the solvent based removal method for hydrogen purification and separation.

Thank you.