

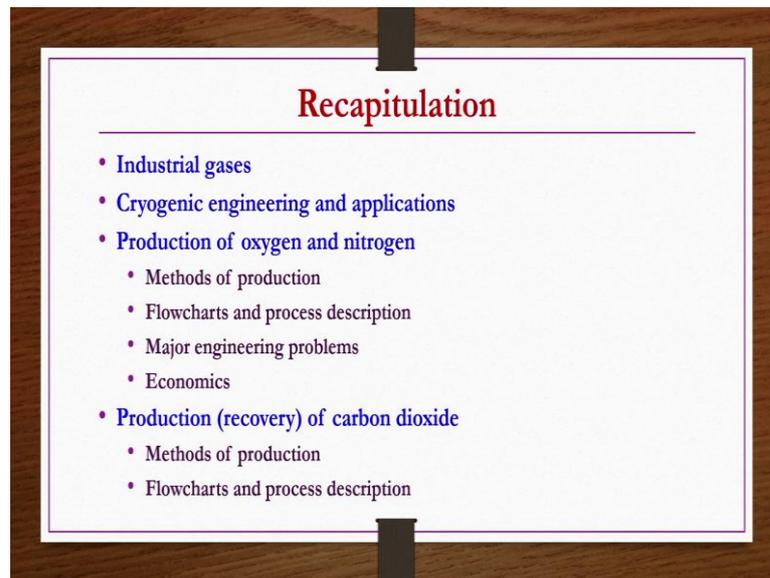
**Inorganic Chemical Technology**  
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**Lecture - 10**  
**Industrial Gases - Hydrogen**

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Industrial Gases Hydrogen. Before going into the today's lecture, what we are going to see? We are going to see a kind of recapitulation of what we have seen in last couple of classes.

We have discussed a few basics of industrial gases, what are the industrial gases, why are they being produced, etcetera those fundamental aspects we have seen. And then, we have seen some applications of these industrial gases as well.

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Then, you know cryogenic engineering how much it is essential from the industrial gases production point of view especially in the liquids and solid forms etcetera. Those things we have seen. We have seen a few applications of cryogenic engineering as well. Not only pertaining to the industrial gases, but also in general.

Then, we have seen the production of oxygen and nitrogen. Under the production of oxygen and nitrogen, we have seen methods of production, flow charts and process

descriptions, what are the major engineering problems, then economics of this oxygen and nitrogen that is the consumption pattern of these two gases also we have seen, right.

Then, further what we have studied? We have seen production of carbon dioxide. Rather, production recovery of carbon dioxide that is what we have seen because we know that this is produced in many of the industrial gaseous production or other processes.

So, it is a kind of recovery of carbon dioxide by different approaches. Those things we have seen. For that two important methods of productions we have seen. And then, we have seen corresponding flow charts along with the process description, ok.

(Refer Slide Time: 02:10)

**Hydrogen**

- It is a very important gaseous raw material for many chemical and petroleum industries
- It has applications both in gaseous and liquid forms; though, liquid hydrogen is more profitable
- Liquid hydrogen is shipped by tank car, truck or barge
- Gaseous hydrogen is shipped in tube trailers
- Metal hydrides as hydrogen sponge are also used for storing hydrogen compactly at moderate pressure
  - Metal hydrides required only 2MPa of pressure for storing compared to 14MPa of compressed hydrogen cylinders
  - Hydrides used are alloys of magnesium-nickel, iron-titanium, lanthanum-nickel and misch metal-nickel

In today's lecture, we are going to discuss about the hydrogen as industrial gas. It is very important gaseous raw material for many chemical and petrochemical industries. For example, some simple example like you know, wherever you have a hydrogenation reaction or hydro treatment you have to do, then definitely this hydrogen is required from the industrial point of view, if you see from chemical engineering point of view, right.

Not only for hydrogenation, but also some other chemicals production like you know ammonia synthesis let us say. So, like that there are several application that this hydrogen gas is having in chemical and petroleum industries, ok. It has applications both in gaseous and liquid forms, but however, production, and then, subsequent storage in liquid form is more profitable from the industry point of view.

Liquid hydrogen is shipped by tank car, truck or barge. Gaseous hydrogen is in general shipped in tube trailers. However, there are other hydrogen storage kind of methods available like metal hydrates are used as hydrogen sponge right for storing hydrogen. In the metal hydrides, they can be stored compactly at moderate pressures because hydrogen is very dangerous.

So, then it is obviously, not preferable to store in very high pressure condition. So, it is better to store them in moderate pressure conditions. So, that way this metal hydrates are you know better option nowadays. Metal hydrates required only 2 megapascal of pressure for storing, whereas, if the same thing if you wanted to store in hydrogen cylinders then 14 megapascal pressure is required, 7 times higher.

So, that is the reason people prefer to have a metal hydrides as hydrogen sponge for the storing this hydrogen, ok. What kind of metal hydrides are often used for the storing of hydrogen? Like magnesium-nickel, iron-titanium, lanthanum-nickel, misch metal-nickel etcetera. These kind of you know metal hydrides have been used or being generated or lot of research is also going on in this area to develop newer kind of material for the storage of hydrogen.

We have seen like in the previous slide that you know we know that it is used as a raw material for production of several chemicals in many of the chemical, and then, petroleum industries, right. Not only hydrogenation reaction or hydro treatment reaction, but also for the production of other chemicals also it is used.

So, what we do now? We see a few examples and in quantity of hydrogen required you know, so that to have a kind of feel how much it is essential. And then, quantitatively also how much quantity is required for a given kind of production that we are going to see in a tabular form.

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**Hydrogen required for production of several chemicals**

Raw material to be hydrogenated	Product	Hydrogen required* (in m <sup>3</sup> ) at 150°C
Phenol	Cyclohexanol	787
Nitrogen	Ammonia	2645
Naphthalene	Tetralin	378
Olein	Stearin	82
Diisobutylene	Isooctane	1600
Carbon monoxide	Methanol	1715

\*per metric ton of product (except synthetic methanol and isooctane which are per cubic meter)

Now, ok let us say phenol you have if you hydrogenate it, then you get cyclohexanol, right. So, how much hydrogen is required at 150 degree centigrade? By the way, this hydrogenation reaction usually occurs at sufficiently higher temperature. But very large pressure higher pressure only in general they occur for majority of the reactions, if not for all, right. So, the pressure has to be higher, so that the hydrogenation take place, in general, if not for all reactions, right.

For each reaction, the optimum temperature and pressure and catalyst etcetera for a optimum production of a product, those things depends on the product to product, reaction to reaction. So, we cannot generalize we cannot compare. So, let us say, if you do these reactions at 150 degree centigrade, and then, see how much phenol is required. Then, you can say from phenol to cyclohexanol if you are producing 787 cubic meters are required, ok.

Let us say, if you wanted to produce ammonia by reacting nitrogen with hydrogen, then 2645 cubic meters are required. And then, if you wanted to produce tetralin from naphthalene by hydrogenating naphthalene, then 378 cubic meters are required. If you want to produce stearin from oleins, then 82 cubic meters of hydrogen required at 150 degree centigrade.

If you wanted to produce iso-octane from diisobutylene, then 1600 cubic meters are required. Whereas, if you wanted to produce methanol from carbon monoxide by

hydrogenation reaction, then 1715 cubic meters of hydrogen is required, ok. So, now you can see how much hydrogen is required. Even we have listed only 4-5 equations here only. There are n number of equation. So, how much hydrogen required is you know, 1, it is very clear, ok. Huge amount of hydrogen required for many of these chemical, and then, petroleum industry related reactions, ok.

Now, we see hydrogen manufacture. The basic method to produce hydrogen is by decomposition of the carbonaceous material because carbonaceous materials in general they have C, H, and O. There may be other inorganic elements may also be there in that one carbonaceous material. But in any given carbonaceous material, however, this C, H, and O are going to be primary components you know constituents of any carbonaceous material. So, that is the primary resource.

(Refer Slide Time: 07:36)

**Hydrogen manufacture**

- It is derived (almost) exclusively from carbonaceous materials
- Raw materials: primarily hydrocarbons and/or water
- Raw materials are decomposed by application of energy (electrical, chemical or thermal)
- Some of the important methods of production includes:
  - Electrolysis of water ✓
  - Steam reforming of hydrocarbons (already discussed) || ←
  - Partial oxidation of hydrocarbons (already discussed) || ←
  - Thermal dissociation of natural gas
  - Steam – iron process
  - Water-gas and producer-gas processes (already discussed)
  - Separation from coke-oven gas (already discussed) and refinery off-gas streams

*Handwritten diagrams on the right side of the slide:*  
 - A circle containing 'CO' and 'CO<sub>2</sub>' with an arrow pointing from 'CO' to 'CO<sub>2</sub>'.  
 - A circle containing 'H<sub>2</sub>O' and 'H<sub>2</sub>' with an arrow pointing from 'H<sub>2</sub>O' to 'H<sub>2</sub>'.  
 - An arrow labeled 'MEA' pointing to the 'CO' circle.  
 - An arrow labeled 'water gas shift' pointing to the 'CO' circle.  
 - An arrow pointing from the 'CO' circle to the 'H<sub>2</sub>' circle.

It is derived almost exclusively from carbonaceous materials, ok. So, raw materials obviously, hydrocarbons and or water. Hydrocarbons if you decompose then obviously, some gases flu gases would be coming, that may be having CO, CO 2, H 2, CH 4 and all that. So, C H 2 may be recovered like that, ok. Raw materials are decomposed by application of certain kind of energy. That energy can be electrical energy, chemical energy or even thermal energy, ok.

Now, we see some of the important methods of production of hydrogen. Electrolysis of water. Steam reforming of hydrocarbons. Partial oxidation of hydrocarbons. Thermal

dissociation of natural gas. Steam iron processes. Water gas and producer gas processes which have been already discussed. Separation from coke-oven gas and refinery off gas streams.

So, here some of the process we have already discussed. The ones which are highlighted in red color font, those things we have already discussed. Let us say steam reforming of hydrocarbons we have studied you know while discussing the synthesis gaseous production.

We have discussed steam reforming of hydrocarbons and partial oxidation of hydrocarbons in the chapter on fuel gases, right. So, when you do naphtha or any other kind of relevant hydrocarbons, if you do the steam reforming or partial oxidation, you get a flu gases. So, they mostly comprise of CO H<sub>2</sub> and then, CO<sub>2</sub>, right.

So, different depending on the process, and then, temperature pressure condition etcetera their composition may vary. Not only these 3, but other components may also be there including the hydrocarbons if the complete reaction does not take place. So, that is also possible, right.

So, but primarily these are the ones which will be having the higher composition, right. So, CO<sub>2</sub> we know that this is usually removed by MEA process or girbotol process, that is mono ethanol amine solutions we used for absorption of the CO<sub>2</sub>, right. Once the CO<sub>2</sub> is being absorbed in that particular solution that solution is reheated to separate out CO<sub>2</sub>, and then, regenerate the absorption solvent. That solvent would be recirculated to the in absorption column this we have seen, right.

So, then in order to remove the CO, what we have done? We have done a water gas shift reaction to convert this CO into CO<sub>2</sub> plus H<sub>2</sub>, right. Then, again that CO<sub>2</sub> is removed by any of the absorption process that we have seen. So, then, primarily H<sub>2</sub> only be remaining. There may be traces of CO or other impurities, then again we have hot concentrated potassium, chromate solutions, absorption etcetera. Those kind of things we use and then, further purify, right.

So, that is what we have seen. Like you know depending on whether your product is H<sub>2</sub> plus CO or only H<sub>2</sub> or producing asteline etcetera, other kind of thing, those kind of

alternative options were there while we were discussing these chapters, right. So, then those things we have already seen. So, then we are not going to repeat again, right.

Same is true for the other things like water gas and producer gas, processes, recovery from or separation from coke oven gas, and then, those things we have already seen. So, the remaining things we try to see now in this particular lecture, ok.

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**Electrolytic method**

- It produces high-purity hydrogen
- This method consists of passing direct current through an aqueous solution of alkali and decomposing water according to:  
$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g); \Delta H = 569 \text{ kJ}$$
- Theoretical decomposition voltage is 1.23 V at STP
- In reality, it varies from 2 - 2.25 V because of overvoltage of hydrogen on electrodes and resistance of cell itself
- Commercial cell that electrolyzes 15% NaOH solution, in which
  - iron cathode and nickel-plated-iron anode electrodes used
  - electrode compartments are separated by asbestos diaphragm
  - operates at 60 - 70°C
  - nickel plating of anode reduces oxygen overvoltage

So, let us start with electrolysis of water, so electrolytic method. It produces high purity hydrogen. Not only for this process, electrolysis process is in general are good for a high quality high purity you know production. High purity products if you wanted to get, and then, if it is possible to do electrolysis then better to go for the electrolysis.

But the problem with this such kind of process are the they are expensive and then, small capacities only you can do such kind of disadvantages would be there. So, those things also we are going to see anyway. So, here also the same is true. It produces high purity hydrogen, ok.

This method consist of passing direct current through an aqueous solution of alkali and decomposing water according to the reaction  $2 H_2 O$  liquid giving rise to  $2 H_2$  gas, and then, one  $O_2$  gas with delta H 569 kilojoules which indicate this reaction is endothermic and required lot of energy.

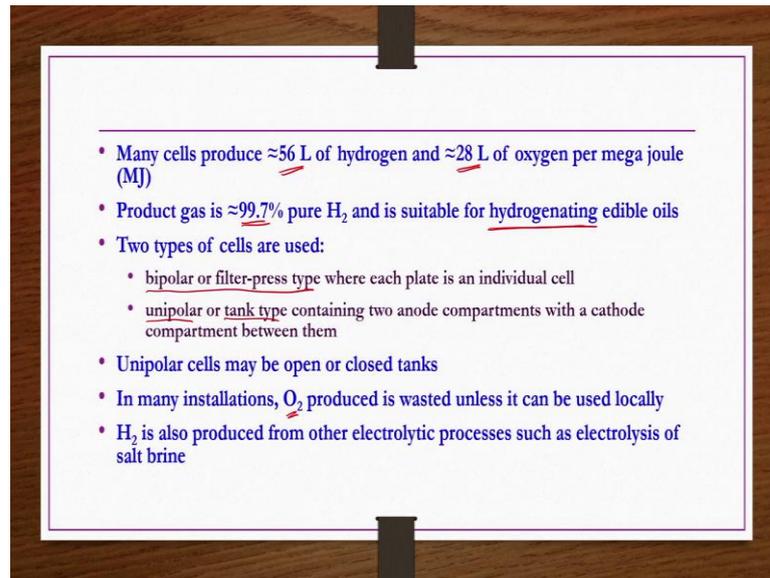
So, now this process is electrolytic process. So, then energy has to be provided through electrical means. The energy should be provided through electrical means. So, how much voltage is required for this reaction to occur in order to get H<sub>2</sub> from water by electrolysis? That is theoretically 1.23 volts at standard temperature pressure conditions, right.

However, there are certain kind of issues like you know over voltage issues. And then, cell resistance also because these are done in the form of cells in as in compartments. So, then resistance of the cell itself may be having some kind of additional voltage requirement, because of that one, the required you know in reality whatever the voltage that should be provided for this reaction to occur that is very much higher compared to the theoretical decomposition voltage.

How much it is in general? Between 2 to 2.25 volts because of over voltage of hydrogen on electrodes and resistance of cell itself, ok. Commercial cell that electrolyzes 15 percent of NaOH solution, in general in such kind of commercial cells, what are the electrodes, and then, those details we are going to see now here. Iron cathode is used whereas, the anode is nickel plated iron, ok.

And then, electrode compartments are separated by as best as diaphragm. Often operates at 60 to 70 degree centigrades. And then, whatever the nickel plating has been done on the anode that reduces the oxygen over voltage as well, ok. So, that is the advantage of having the nickel plating on the anode, ok.

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Many cells produce in general 56 litres of hydrogen and 28 litres of oxygen per megajoule of electrical energy that is supplied to the process. If you supply 1 megajoule of electrical energy for the process to get the hydrogen, how much do you get? 56 litres of hydrogen and 28 litres of oxygen you get. In such kind of processes, often this oxygen is wasted or it is not recovered or stored until and unless it is useful on site, but most often it is wasted.

Product gas whatever you get that is 99.7 percent pure  $H_2$  and it is even suitable for hydrogenating edible oils. Such high purity is more than sufficient for hydrogenating many of the edible oils. Cells are important in this electrolysis process. So, it is essential to know how many types of cells are in general available.

Two important types of cells are available. One is bipolar or filter-press type cells, where each plate is an individual cell. Another one is unipolar or tank type containing two anode compartment cells with a cathode compartment between them, right. Unipolar cells may be open or closed tanks. In many installations,  $O_2$  produced is wasted until and unless it can be used locally wherever this  $H_2$  is produced.  $H_2$  is also produced from other electrolytic processes such as electrolysis of salt brine solution etcetera.

So, that is about few basic details about electrolysis process to produce hydrogen, ok. There are many technical engineering aspects there, but those things are not

important from the course point of view. So, but that is the reason we are not discussing them.

Now, we see second method, coal gasification process. As we already know now that carbonaceous materials are you know sources or raw material for production of hydrogen, by different methods. You may be decomposing carbonaceous material by applying the energy, energy in different forms, like electrical energy, thermal energy or chemical energy to get the hydrogen. Because this carbonaceous material mainly composing of C, H and O. So, that H may be you can recover somehow, right.

So, natural gas and then, hydrocarbons are being depleting very faster. So, because of such reasons you know nowadays coal has been considered as a resource for hydrogen production, ok. So, that is the reason now we see coal gasification process to get hydrogen.

Actually, coal gasification can be done for many other products also like you know for other synthesis gas productions etcetera also one can do, fine. It can also be done for the you know combustion purpose also, usually people use for you know electricity production etcetera. Those things also there. But now the coal gasification we are doing only in order to produce H<sub>2</sub>. Accordingly, we see discussions.

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**Coal gasification process**

- Gaseous and liquid HC feedstock reserves depleting fast, thus, coal as source of hydrogen receiving importance
- Reactions of coal gasification:
  - Gasification:  $C + H_2O \rightarrow CO + H_2$
  - Water-gas shift reaction:  $CO + H_2O \rightarrow CO_2 + H_2$  (should be controlled to give  $CO:H_2 = 1:3$ )
  - Boudouard reaction:  $C + CO_2 \rightarrow 2CO$
- At sufficiently high pressure, produced  $H_2$  will hydrogenate some of carbon to  $CH_4$ 
  - $C + H_2 \rightarrow CH_4$
  - $CO + 3H_2 \xrightarrow{\text{Catalyst}} CH_4 + H_2O$
  - Methane gas produced was known as "synthetic" natural gas
    - subsequently it is called as "substitute" natural gas (SNG)
- Operating range of P and T in gasifier: atmospheric to 6.9MPa and 800 - 1650°C respectively
- Higher pressure and lower temperature results in formation of larger amount of methane

Gaseous and liquid hydrocarbon feedstock reserves are depleting fast, because of that reason coal a source of hydrogen receiving much importance these days. So, if you take coal as basic raw material, and then, see how to get the hydrogen from it or you have to see the reactions of coal gasification.

What are the reaction that may often occur in coal gasification, that is gasification reaction? Gasification is nothing, but reacting with the steam. When you react the coal with steam you get CO plus H<sub>2</sub>, then because of the water gas shift reaction this CO may be reacting with the steam again to give CO<sub>2</sub> plus H<sub>2</sub>.

This reaction is controlled to give CO divided by H<sub>2</sub> is equals to 1 by 2, that is one mole of CO if you reacting here under water gas shift reaction, you should get 3 moles of H<sub>2</sub> such a way that the conditions has to be maintained. Then, Boudouard reaction where coal reacts with the CO<sub>2</sub> to give carbon monoxide. This carbon monoxide will again react with the steam to get carbon dioxide and hydrogen, right.

So, now what we have? We are already having H<sub>2</sub>, right. Under this gasification process, if the conditions are such a way that the pressure is very high then whatever this H<sub>2</sub> is produced that will hydrogenate some of the carbon to form methane, ok. But you do not want methane to be formed. But however, it is possible without your you know willingness if you maintain the pressure high. So, you should not maintain high pressure.

Because as I already mentioned hydrogenation reaction, most of the hydrogenation reaction temperature may be moderate, but the pressure has to be high, right. If the pressure is high, so then whatever the hydrogen is present in the system that will be hydrogenating the other components, other carbonaceous material also, ok.

So, let us say, C plus H<sub>2</sub> giving rise to CH<sub>4</sub> is one possibility. CO which is already formed, because of the gasification, that again getting hydrogenated in the presence of appropriate catalyst to give CH<sub>4</sub>, and then, water is forming, right. So, like this you know different options are there.

So, then different reactions may be there. So, then the CH<sub>4</sub> whatever is there. Earlier it was known as synthetic natural gas, but synthetic, and then, natural are you know contradictory words. So, then people started calling it substitute natural gas SNG, ok. But

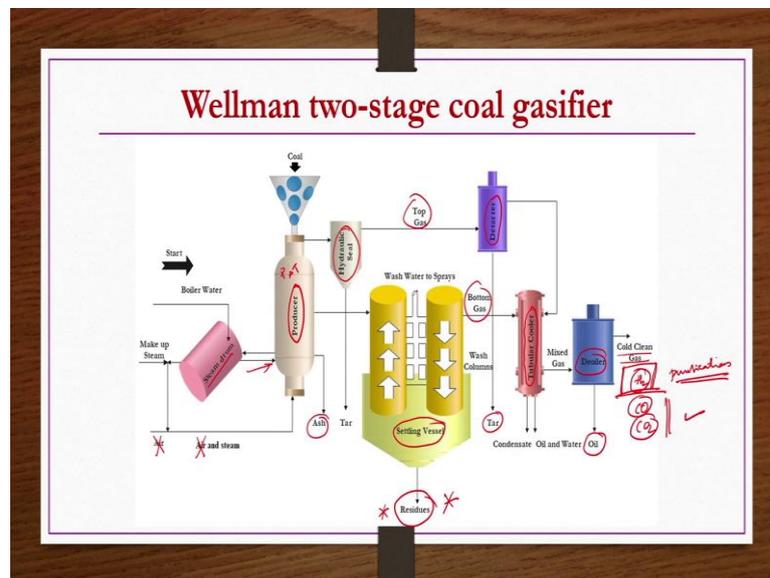
however, our interest is not this one as far as this lecture is concerned. Our interest is this one only.

So, what we have to do? We have to reduce the pressure or we have to maintain the pressure as much low as possible in gasification process. So, that there is no hydrogenation taking place. Only gasification, may be some combustion pyrolysis you cannot avoid them anyway, even if you maintain low pressure. So, you know, but at least you can avoid hydrogenation, so methane formation would be less.

Operating range of P and T in the gasifier are atmospheric pressure to 6.9 megapascals are the pressure condition ranges. And then, 800 to 1650 degree centigrades the temperature conditions in the gasifier. As I mentioned already high pressure, and then, lower temperature results in formation of larger amount of methane.

So, what you have to do? You have to maintain low pressure, and then, high temperature, so that gasification reaction these reaction primarily take place, but not these ones, ok.

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Now, we see Wellman two-stage coal gasifier process. This is a process here. So, what we have? We have a gasifier which is also known as the producer, ok. It is a continuous process to this reactor coal is continuously fed. Actually, in this reactor required temperature and pressure are maintained as per the reaction.

If you wanted to produce SNG, then pressure is maintained high and then, temperature is maintained low. If you want to avoid formation of methane or you want more gasification and combustion to take place, then you maintain low pressure and high temperature.

The same reactor may be used for the production of both hydrogen as well as the SNG, ok. To this reaction which is at certain desired temperature and pressure, you are allowing steam to enter, right the steam you are getting by applying the boiler water in a steam drum. So, that the steam would get generated and that steam you can pass it to the gasifier.

Or what you can do if the produced steam is not sufficient enough you can take external steam. And then, make up along with the air. And then, send it to the reactor or gasifier along with the air and steam both together you can feed in depending on what reaction you are preferring to have. If you preferring to have some combustion reaction also along with the gasification then you can allow air. But if you are preferring only gasification primarily, then you do not supply air, only steam you supply, ok.

So, when this reaction takes place, there are two types of gases would be evolved, top gases, bottom gases, ok. And then, ash should be forming at the bottom that would be collected as a bottom product from the bottom of the gasifier continuously. This reactor is a continuous one.

Top gases are you know which are more volatile, and then, can raise to the top of the column even at low temperature, those gases. So, those gases whether it is top gases or bottom gases, when they are coming out of the reactor which is operating between 800 to 1600 degree centigrade roughly as per requirement.

So, obviously, the outlet gases would be at high temperature. The temperature would be controlled by passing it through hydraulic seal. Then, top gases are allowed to pass through detarrer, where tar is removed. And then, top gases are further sent to tubular cooler. So, that further cooling of these gases can take place to room temperature or atmospheric temperature conditions.

The bottom gases that are coming out of this reactor, they are also at high temperature. And they may also be containing some lighter hydrocarbon. So, then they those things

has to be removed, and then, the gases has to be cooled down. For that water wash water is used actually, right.

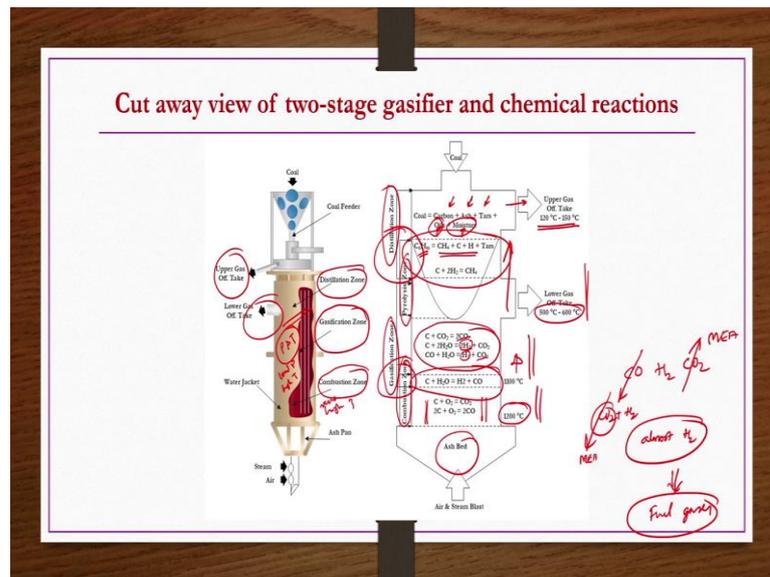
In the settling vessel see whatever the impurities that are dissolved in the water they will be collected in the settling vessel, and then, they will be taken as a residues. These residues are also not kind of wasted. They are having so many organic constituents that can be used for production of other chemicals, because any carbonaceous material is a kind of a pool of wealth, you can produce so many things, ok.

The bottom gases you know they are further sent to the tubular cooler to further reduce the temperature. And then, mixed with the top gases and then, send to deoiler. Deoiler are some kind of adsorption columns, something like glycerine etcetera are provided here to remove traces of gases like you know H<sub>2</sub> CO etcetera or in some light hydrocarbons will also be absorbed by these oils, right. And then, spent oil is collected from the bottom, right.

So, cold clean gases are collected from the top. These gases would be consisting of hydrogen primarily, but in addition to that one CO, and then, CO<sub>2</sub> may also be there. So, one has to further do the purification steps. So, what type of purification steps are possible? That we are going to see once again anyway. Some of them we have already seen previously, ok. So, once you do the purification you get the hydrogen as per required purification standard that you follow.

Now, as I was mentioning in the gasification reaction, not only H<sub>2</sub> formation CO CO<sub>2</sub> formation, methane formation, etcetera would also be taking place. So, all that depends on the temperature and pressure conditions. So, it is important to understand what kind of reactions occurring across the different cross section or different heights of the you know gasifier. That is what we are going to see now.

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So, this cut view of the same gasifier shown here. So, it is having 3 zones, one is the combustion zone which is at the bottom, at which the temperatures are very high temperatures very high temperatures. Then, just above that one there is a gasification zone, the temperatures are still high.

Then, above that one there is a pyrolysis zone that is not shown here, then above that one there is a distillation zone where the temperatures are nominal. Alright, nominal in the sense between 150 to 200 degree centigrades something like that.

From the coal is coming here, this is a coal feeder. Inside this gasifier we are maintaining certain temperature and pressure as per our product requirement. So, now, here we want more hydrogen, so low pressure, and then, high temperatures are being maintained. Some reaction would be taking place. Whatever the upper gas would be there that is the top gases. Top gases in the sense which are more volatile and quickly rises to the top of the column.

So, those taken out from the vent off here whereas, the lower gases or bottom gases are taken off from just above the gasification zone from here, ok. Whatever the ash is there that is collected in the ash pan, and then, discarded continuously. This process goes on continuously.

Now, if you see the reactions point of view what kind of reactions are occurring, the same thing is pictorially shown here actually. So, now, we have a combustion zone, we have a gasification zone, pyrolysis zone and distillation zone.

So, coal whatever is there it is a carbonaceous material. So, then we have carbon, ash, tar, oils moisture etcetera all of them would be present here. So, in distillation zone temperature is maintained between 120 to 150 degree centigrade, sometimes up to 200 degree centigrades. So that, when this distillation zone operated at certain range of temperatures the sum of the oils moistures etcetera are collected from the top.

Remaining are mostly hydrocarbons, after that you know, that can be those hydrocarbons may be represented as  $C_n H_n$  that may be you can write as  $CH_4$  plus C plus H plus plus tars etcetera. So, here the temperature from this onwards to the towards the upper ones is between 500 to 600 degree centigrade temperature is maintained, right. So, that pyrolysis takes place and then, some methane etcetera are also forming along with other gases. So, this zone is known as the pyrolysis zone, right.

So, these are you know, some of the zones are you know intermixing with respect to the temperature because the zones you know they have represented with respect to the temperature of operation, right, ok. So, this is the pyrolysis zone which is operating at 500 to 600 degree centigrade, and then, from here the lower gases are taking off.

Further temperature higher temperature you can see, further lower section of the gasifier which operates around 1000 to 1100 degree centigrades. Here most of the reactions are producing  $CO$ ,  $H_2$ ,  $CO_2$  kind of products that you can see, ok. So, now, what you see? In gasification zone mostly you are getting  $H_2$ ,  $H_2$ ,  $CO$ ,  $CO_2$ . So,  $CO_2$  you can remove by the MEA process, girbotol process. And then,  $CO$  you can convert to the  $H_2$  plus  $CO_2$  by water gas shift reaction. And then, you can do similar analysis.

If you maintain, that is possible if you maintain the temperature less than 1100 or 1000 degree centigrades something like that and pressure is low pressure, not the high pressure, right. But however, if you further increase the temperature then more combustion kind of reactions are taking place, where primarily you get  $CO_2$  and  $CO$  only, ok. So, ash is collected at the bottom.

Now, what you can see? Some of these zones are intersecting. That is because the range of temperature at which these are working it is not very specified like you know between 500 to 600, it is a 100 degree centigrade range, ok. So, like this now the combustion may also occur at 1100 degree centigrade and 1000 degree centigrades as well. So, at that temperature gasification is primarily occurring.

So, these kind of you know sections are there at which you know either of the process, I mean you cannot distinguish them as a specifically combustion zone or gasification zone, a kind of buffer zones are present in between these zones, ok.

So, this is what about you know gasification, coal gasification process. So, here we are getting CO, H<sub>2</sub>, and then, CO<sub>2</sub> mixture. There may be methane and other kind of impurities are there. So, that purification etcetera you can do. This you can take out by MEA process. This you convert to CO<sub>2</sub> plus H<sub>2</sub> by water gas shift reaction. And then this again you remove by MEA process or any other suitable process.

Now, after that you almost you know H<sub>2</sub> would be there in the flue gas because these gases whatever are there you have to process them for subsequently for these kind of removal. These removal and then, water gas shift reaction how to do that we have already discussed. And then, removal of CO<sub>2</sub> that we have already studied further conversion of CO to CO<sub>2</sub> and H<sub>2</sub> that also we have seen how to do, right.

Then, after that only almost pure H<sub>2</sub> is there. If at all any traces of CO, CO<sub>2</sub> methane etcetera are there how to remove them, those things also we have seen in the previous week, when we were discussing about the fuel gases. So, we are not repeating them. But in addition to these purification methods there are additional purification methods are also there, those things we are going to see anyway in today's lecture.

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**Cracked ammonia process**

- By cracking or thermal dissociation of ammonia, a mixture  $N_2$  and  $H_2$  can be prepared in 1:3 ratio by vol.
- Final gas mixture can be used for hydrogenation because  $N_2$  is inert
- Cracking process include following steps:
  - vaporizing the liquid ammonia from cylinders
  - heating it to  $870^\circ C$
  - passing it over an active catalyst and
  - then cooling it in HE where incoming gas is vaporized
- Often a single 68 kg cylinder of anhydrous  $NH_3$  produces  $190 m^3$  of cracked ammonia
- This is equivalent to contents of about 33 hydrogen cylinders

The slide includes a diagram of a heat exchanger (HE) represented by two vertical parallel lines. To the right of the HE, there is a circled  $N_2$  with an arrow pointing towards the HE, indicating the cooling of incoming gas.

Now, we go to the next method, cracked ammonia process. Cracked ammonia process is basically, if you wanted to tell about it in one single line. So, you take the ammonia liquid, and then vaporize it and then, apply high temperature 800 degree centigrade or something like that.

And then, whatever the gases are there, that you pass through suitable catalyst. So, then ammonia will be decomposed into nitrogen and then, hydrogen, right. So, you got this hydrogen, because nitrogen is anyway mostly inert for most of the applications, ok. That is what nothing, but the cracked ammonia process.

However, we see steps again here as well. By cracking or thermal dissociation of ammonia a mixture of  $N_2$  and  $H_2$  can be preferred in 1 is to 3 ratio by volume. Final gas mixture can be used for hydrogenation as well because  $N_2$  is inert anyway. Cracking process include following steps vaporizing the liquid ammonia from cylinders, because ammonia is filled in cylinders usually that you have to vaporize.

Then, heating it to 870 degree centigrade, then passing it over an active catalyst. Then, cooling it in heat exchangers where incoming gas is vaporized. So, by this process you can get  $H_2$  and  $N_2$ , ok. So, how much amount of  $H_2$  you get by this process if you wanted to see, let us say a single 68 kgs cylinder of anhydrous ammonia you take and then do this process, you get 190 meter cube of cracked ammonia. Cracked ammonia is nothing, but decomposed one that is in form of  $H_2$  and  $N_2$ .

So, this is equivalent to contents of about 33 hydrogen cylinders, right. If you take 68 kgs of anhydrous ammonia, then you get 33 hydrogen cylinders quantitatively. This is cracked ammonia process.

Now, what we do? We have a comparison of hydrogen production alternatives. We have seen different methods that are available, now including steam reforming, coal gasification, electrolysis etcetera, so we have a comparison from engineering point of view.

Engineering point of view several things would be there. So, these things are efficiency you have to see, then environmental impact you have to see, advantages, disadvantages etcetera, and then, production cost etcetera all of these things are important from industrial viewpoint, right. So, then those things we are going to discuss for each and every; for a 4 important processes.

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	Steam Reforming	Coal gasification	Electrolysis	Thermo-chemical decomposition
Approximate Thermal Efficiency	• 70	• 60 – 65	• 32 (SPE i.e., Solid Polymer Electrolyte) • 21 – 25 (KOH)	• < 55
State of art	• Well-known technology	• Mature technology available	• Proven and reliable technology	• Research stage
Environmental effects	• Depletion of natural gas • Depletion of light HCs	• Coal mining impacts • Air pollution (but less than via electricity from coal)	• Pollution problems with electricity generation	• High efficiency means less resources use • Possible release of harmful chemicals
Advantages	• Currently cheapest method	• Cheapest and most secure near-term alternative to CH <sub>4</sub> reforming	• Small plant size • Can also use non-fossil fuel	• Can also use non-fossil fuel
Disadvantages	• Scant long-term potential (due to CH <sub>4</sub> supply issues)	• Main limitation is exhaustion of coal resources; • Large plant size	• High cost • Low net energy efficiency	• Materials problems in reactant containment • Large complex plant
Estimated H <sub>2</sub> production cost	• 7.17 (\$/GJ product as on 1980)	• 10.02 (\$/GJ product as on 1980)	• 21.05 (\$/GJ product as on 1980)	• Not applicable

What are they? Steam reforming of hydrocarbons, coal gasification, electrolysis and thermo chemical decomposition processes. What are we going to see under each process? We are going to see approximate thermal efficiency how much, state of art, environmental effects, advantages, disadvantages, and then, estimated H<sub>2</sub> production cost.

Steam reforming of hydrocarbons is the best approach that is available. Its efficiency is also very high, 70 percent. And it is a well-known technology that is already being implemented in majority of industries. Environmental impacts obviously, natural gas or hydrocarbons naphtha etcetera are being used for the reforming, so that to get synthesis gas or hydrogen gas. So, they will be depleting. Apart from that there is no other environmental effect anyway.

Advantages if you see, this is currently cheapest method that is available for production of a synthesis gas and hydrogen gas. Disadvantages, is CH<sub>4</sub> supply issues are there because of that one scant long term potential is there, right. Estimated H<sub>2</sub> production cost per gigajoule of product as on 1980 if you see, 7.17 dollars only, ok.

Coming to the coal gasification, efficiency is still better, 60 to 65 percent. And then, it is also mature technology that is available. Environmental effects since you need coal, coal mining has to be done. And then, impacts of coal mining whatever are there, they will all be considered here also as environmental effect.

Air pollution would obviously be there, if you are using coal, whether you are doing gasification, combustion, pyrolysis whatever you do, but however, here in this process to get hydrogen from coal gasification, pollution is less compared to that electricity from coal when you try to produce, ok. It is also cheapest, and then, best next to the steam reforming process, ok.

Disadvantages limitation is exhaustion of coal resources. Coal resources are already depleting very faster. So, if you also produce hydrogen from the coal, they will be further faster depleting. But the plant size is very big this coal gasification that is one issue. Estimated production cost is 10.02, slightly higher compared to the steam reforming. Electrolysis, its efficiency is very low 30 to 21 to 25, depending on what type of electrolyte solution you are using.

It is a proven and reliable technology of course. Pollution problems may be there with electricity generation. The advantages is that it is a small plant size, you do not need big setup for that, big-big plants are not required. It can also use non-fossil fuel, but the disadvantages are the production cost is very high, high cost, production cost itself is 21.05 that is too much high compared to the other two processes. Low net energy

efficiency that we have seen. Not even half of what it is by steam reforming. So, these are the disadvantages.

Coming to thermo chemical decomposition efficiency is less than 55 that is maximum 55 percent is attained. And then, it is still at research stage. Coming to the environmental effects high efficiency means less resources use and possible release of harmful chemicals are the issues. They can also use non-fossil fuel. And then, materials problems in reactant containment, and then large complex plant is another issue.

The estimated production cost we cannot evaluate because it is at research stage. So, this is a kind of comparison if you are producing hydrogen by 4 different methods. So, what you can understand from all these 5 bullet points shown here. That is in terms of efficiency, state of art, environmental impacts, advantages, disadvantages and then, production costs from all these point of view, steam reforming is a better option for the production of hydrogen as per the current existing technology available.

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**Hydrogen purification processes**

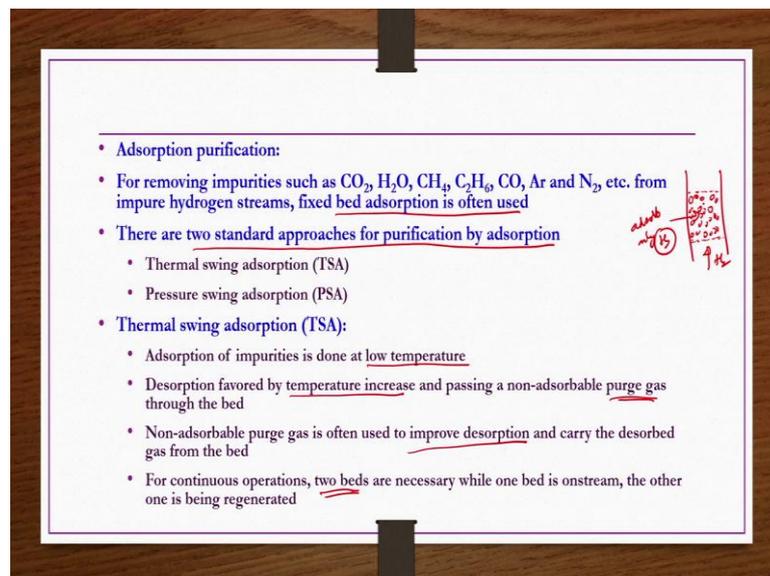
- **CO removal:**
  - If CO is present in high concentrations then it is converted to hydrogen by water-gas shift reaction  $\text{CO}_2$   $\text{H}_2$
  - Remaining CO removal is done by scrubbing the mix gas in solutions of complex copper ammonium salts
- **CO<sub>2</sub> and H<sub>2</sub>S removal: Many commercial processes available**
  - Monoethanol amine (MEA) or Girbotol process ✓
  - Hot potassium carbonate process ✓
  - Physical solvent processes

Now, we see hydrogen purification processes. CO removal, carbon monoxide removal. If CO is present in high concentration then it is converted to the hydrogen by water gas shift reaction, that we know in presence of iron oxide. And then, when you react CO with the steam, then what happens? You will get CO<sub>2</sub> plus H<sub>2</sub>. CO<sub>2</sub> can be removed by MEA solutions etcetera. So, then you have the pure H<sub>2</sub> only or high concentration H<sub>2</sub> only you will be having, right.

Remaining CO if at all that is present traces of CO still present, they can be removed by scrubbing the mixture gas in solution of complex copper ammonium salts. So, these steps also we have seen under steam reforming of hydrocarbon section when you are discussing about synthesis gas. So, we are not discussing them again.

If at all CO<sub>2</sub> and then, H<sub>2</sub>S are there, so many commercial processes are available. Some of them we have already discussed, like monoethanol amine solution or girbotol process that is absorption of CO<sub>2</sub> in these solutions. And then, removing this CO<sub>2</sub> from the spent liquid by heating it those process recovering MEA, and then sending back to the absorption tower. All those things we have seen. So, we are not studying them again. Hot potassium carbonate process, and then, physical solvent processes are also there

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• Adsorption purification:

- For removing impurities such as CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO, Ar and N<sub>2</sub>, etc. from impure hydrogen streams, fixed bed adsorption is often used
- There are two standard approaches for purification by adsorption
  - Thermal swing adsorption (TSA)
  - Pressure swing adsorption (PSA)
- Thermal swing adsorption (TSA):
  - Adsorption of impurities is done at low temperature
  - Desorption favored by temperature increase and passing a non-adsorbable purge gas through the bed
  - Non-adsorbable purge gas is often used to improve desorption and carry the desorbed gas from the bed
  - For continuous operations, two beds are necessary while one bed is onstream, the other one is being regenerated

*Handwritten notes in red ink:*  
adsorb  
H<sub>2</sub>  
CO<sub>2</sub>  
H<sub>2</sub>O  
CH<sub>4</sub>  
C<sub>2</sub>H<sub>6</sub>  
CO  
Ar  
N<sub>2</sub>

Now, adsorption purification process is another important method that is available for purifying the hydrogen in the gaseous mixture. So, what are the different types of adsorption purification steps are available, those things we are going to see now. For removing impurities such as CO<sub>2</sub>, H<sub>2</sub>O, methane, ethane, CO, Ar, N<sub>2</sub> etcetera from impure hydrogen streams, fixed bed adsorption is often used, right.

There are two standard approaches for purification by adsorption. Fixed bed in the sense nothing, but you know you have a column as we know already, cylindrical column is there. And then, this column is packed with some kind of packing material, only certain portion of this one. And then, bottom and top are closed with a you know mesh, ok.

So, now, the gases whichever you wanted to absorb, they adsorbed on that one they should be passed through such kind of packed material. So, then the packing whatever is there that on to that one this H<sub>2</sub> would be adsorbed.

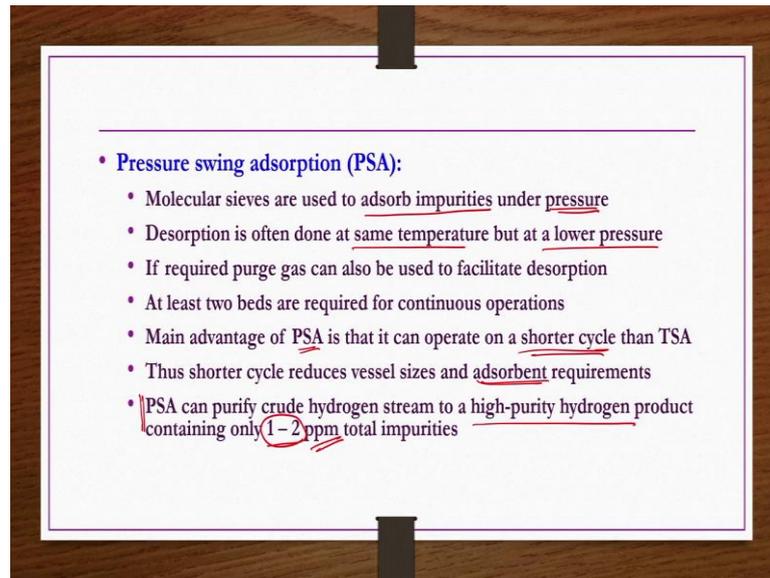
And then, later on once sufficient adsorption has been done because this material packing material is chosen such that adsorb only H<sub>2</sub> if you are trying to purify H<sub>2</sub>. Or if you are trying to remove other kind of impurities accordingly you have to select the materials, packing material accordingly.

H<sub>2</sub> once it is adsorption equilibrium, if it is achieved. So, further adsorption may not possible. Then, what you can do? You can stop the flow of H<sub>2</sub>. And then, you do the de-adsorption, desorption you do to recover the pure H<sub>2</sub> from the packed material, ok. Packing material whatever we have used for the packing.

So, this can be done either by pressure conditions or by temperature conditions. Based on that one two approaches are there, thermal swing adsorption and pressure swing adsorption. In the thermal swing adsorption what happens? Adsorption of impurities is done at low temperatures. And then, further desorption is favored by increasing the temperature and passing a non-absorbable purge gas through the bed.

The use of this purge gas is that you know it improve the desorption efficiency and then, carry forward the desorbed gases from the bed as well. For that reason this purge gases are allowed while doing the desorption. While doing desorption only you use this purge gases. For continuous processes at least two beds are necessary, one bed would be on stream, the other one is being generated.

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Next is pressure swing adsorption, PSA. Here molecular sieves are used to adsorb impurities under the pressure. Under pressure conditions, what you do? You different types of molecular sieves have been developed. So, these molecular sieves are very good for adsorption of different gases. So, similarly hydrogen can be adsorbed. But, when you use this molecular sieves for adsorption of certain kind of gases onto them, you have to use pressurized conditions.

Desorption is often done at same temperature, but at lower pressure. Temperature you maintain same temperature at which you are doing the adsorption, but the pressure you have to decrease substantially to desorb the hydrogen that is being adsorbed onto the molecular sieves, ok. So, that is how it is done.

So, first you have to adsorb. Do the adsorption, so that only because this material, the adsorption medium whatever is there they are selected such a way that only hydrogen is being adsorbed in those material. So, as much hydrogen as possible, you adsorb first. Once the equilibrium has attained, then you stop the adsorption, and then, you apply the desorption conditions, and then, get the pure H<sub>2</sub> only. Because while doing the desorption only H<sub>2</sub> is present in the adsorption medium, right.

Because while doing the adsorption only H<sub>2</sub> is being adsorbed in adsorption medium whereas, the rest of the impurities are passed out while the adsorption itself. If required purge gas can also be used to facilitate desorption. And at least two beds are required for

continuous process here as well. Main advantage of this one PSA over TSA is that shorter cycle time. Because cycle time in the sense adsorption followed by desorption.

Once it is, one cycle is complete how much are you recovering, and then, what is the duration of cycle that will define you know economics not only from the equipment size wise, but also from the operational cost wise. So, that is these two are very important. If the shorter cycle is there, so smaller equipments can be used, ok. And then, if the equipment for the adsorption is smaller, so obviously, adsorbent or you know adsorption medium requirement would also be less.

PSA can purify crude hydrogen stream to high-purity hydrogen product containing only 1 to 2 ppm of total impurities only. Only this much of impurities are there. Such a good process is this PSA.

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**Cryogenic liquid purification:**

- Impure hydrogen stream is also partially purified by cooling to suitable cryogenic temperatures
  - So that impurities be condensed and separated as a liquid stream
  - This is often used for bulk removal of light HCs from hydrogen in refinery off-gas
- Purity of product obtained depends upon
  - vapor pressure of the impurity and
  - high impurities are not readily removable in most cases
- Higher purification may obtained by Linde cycles which remove low-boiling contaminants in a hydrogen gas stream at 2.1 MPa and  $-180^{\circ}\text{C}$  by washing successively with
  - liquid methane (to remove  $\text{N}_2$  and  $\text{CO}$ ) and
  - liquid propane (to remove  $\text{CH}_4$ ) to give 99.99% pure hydrogen
- Final purification obtained by using activated carbon, silica gel or molecular sieves ||
- Low temperatures for washing with liquid nitrogen or for fractionation are also used to remove impurities ✓

Next purification approach is cryogenic liquid purification. It is used for bulk removal of impurities often. How? Impure hydrogen stream is also partially purified by cooling to suitable cryogenic temperatures.

How to define? Let us say you have this  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  etcetera, these gases are there and these things are you know your impurities. So, you have to select a temperature, so that you know only these things would be condensed, not the other one.

How you decide that one? That you can decide based on the vapor pressure of the impurities, ok. So, that the impurities be condensed and separated as a liquid stream.

This is often used for bulk removal of light hydrocarbons from hydrogen in refinery off gases. So, if you wanted to recover hydrogen from the refinery off gases then cryogenic is a best option because refinery off gases would also contain lot of hydrocarbons, lighter hydrocarbons as well along with the other impurities.

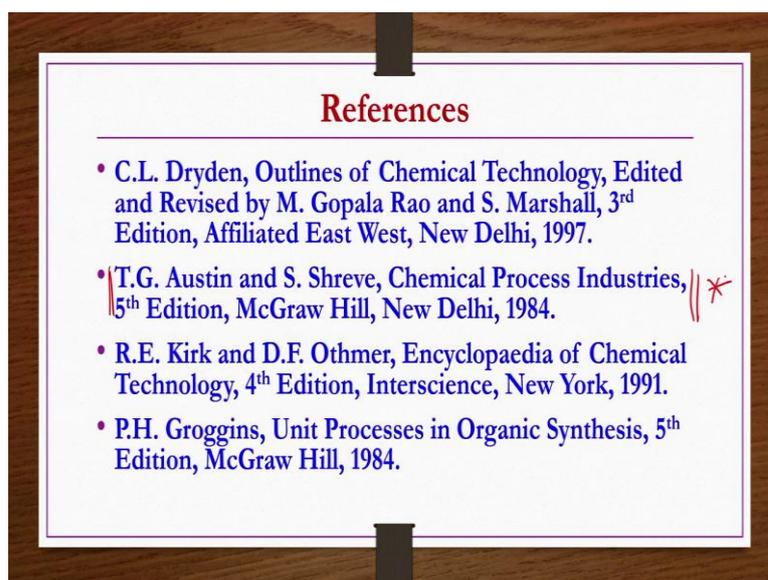
Purity of product obtained obviously, depends upon vapor pressure of the impurity. Impurities are not readily removable in most of the cases. Higher purification may be obtained by further Linde cycles, which remove low-boiling contaminants in hydrogen gas stream at 2.1 megapascal and minus 180 degree centigrade by washing successively with liquid methane to remove  $N_2$  and CO.

And then, liquid propane to remove  $CH_4$ . While removing  $N_2$  and CO it is possible that methane may also be coming along with the  $H_2$ , right. So, that methane should also be removed. So, then liquid propane is usually used to remove this methane, traces of methane from the mixture gas. Then, you get more than 99.99 percent pure hydrogen.

Final purification obtained by using activated carbon, silica gel, and or molecular sieves depending on purity that you required. Low temperature for washing with liquid nitrogen or for fractionation are also used to remove impurities in general.

So, that is all about hydrogen production and then, purification of hydrogen; or removing impurities from the gaseous mixture to get the pure hydrogen, how to do all that thing we have seen, right. Some of the technologies, some of the processes, we have seen in the today's lecture. And then, some we have already previously seen.

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Coming to the references of this lecture. All these details may be found in these books. But this particular lecture has been prepared from this book *Chemical Process Industries* by Austin and Shreve.

Thank you.