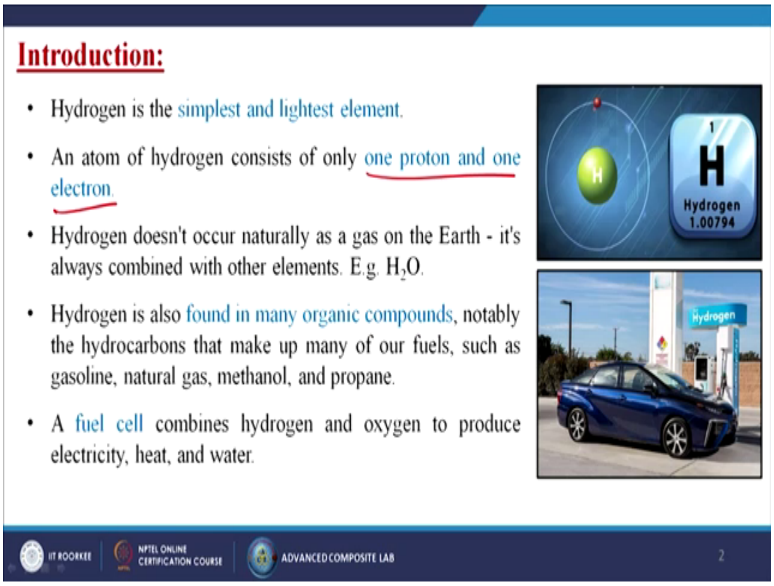
Selection of Nanomaterials for Energy Harvesting and Storage Applications
Prof. Kaushik Pal.
Department of Mechanical and Industrial Engineering
Indian Institute of Technology, Roorkee

Lecture – 06
Hydrogen Energy: Introduction & H 2 Production from Fossil Fuels and Biomass

Hello my friends, now we are going to discuss Hydrogen Energy Introductions and Hydrogen Production from Fossil Fuels and the Biomass. So, basically in this particular lecture, we are going to discuss about the what is hydrogen energy and how we are going to produce the hydrogen from the fossil fuels and the biomass? So, basically hydrogen can be produced by different methods, but in this particular lecture we are going to discuss about only that hydrogen generation from fossil fuels and the biomass.

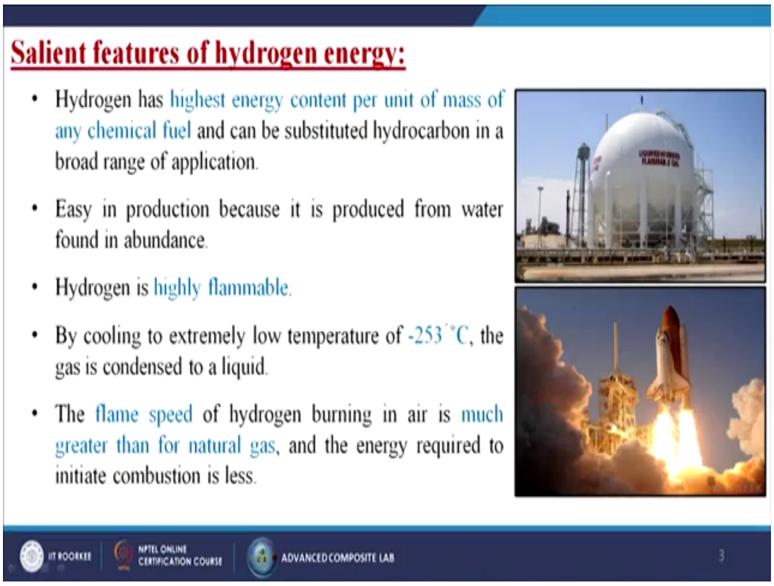
(Refer Slide Time: 00:55)



So, basically in introductions we can say that hydrogen is the simplest and the lightest element. So, it is coming the first in the periodic table. So, an atom of hydrogen consists of only one proton and one electron itself in the outer cell. Hydrogen does not occur naturally as gas on the earth its always combined with other elements like water. So, water is a 2 hydrogen atoms and the 1 oxygen atoms over there. Hydrogen is also found in many organic compounds notably the hydrocarbons that makes up many of our fuels such as gasoline, like natural gas, like methanol or maybe the propane. A fuel cell combines hydrogen and oxygen to produce the electricity, heat and the water.

So, nowadays the researchers are extensively working on the fuel cells basically they are trying to produce the electricity or maybe the heat or maybe the water from the hydrogen itself. So, now, what are the salient features of hydrogen energy?

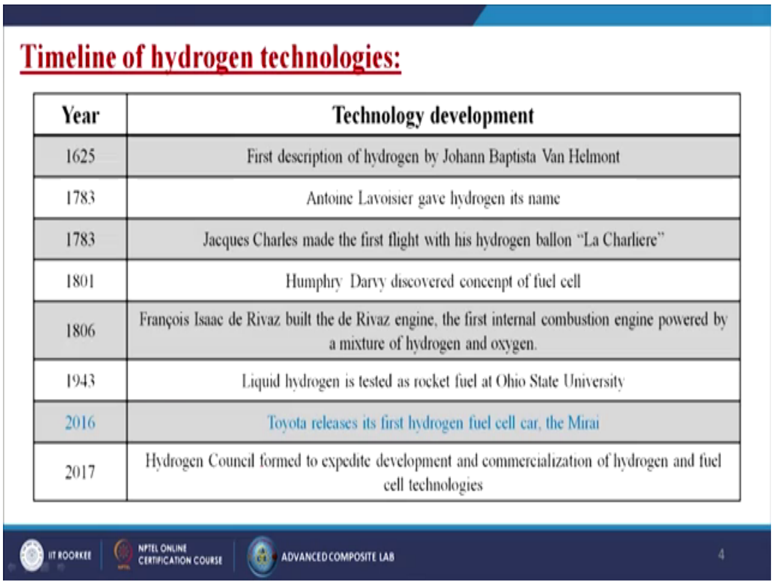
(Refer Slide Time: 01:58)



So, hydrogen has highest energy content per unit of mass of any chemical fuel and can be substituted hydrocarbon in a broad range of applications. Easy in production because it is produced from water found in abundance because nowadays are we are wasting too much of water. So, from that particular waste water we can produce the hydrogen very easily. Hydrogen is highly flammable by cooling to extremely low temperature of minus 253 degree centigrade the gas is condensed to a liquid.

The flame speed of hydrogen burning in air is much greater than for natural gas and the energy required to initiate the combustion is very very less.

(Refer Slide Time: 02:44)

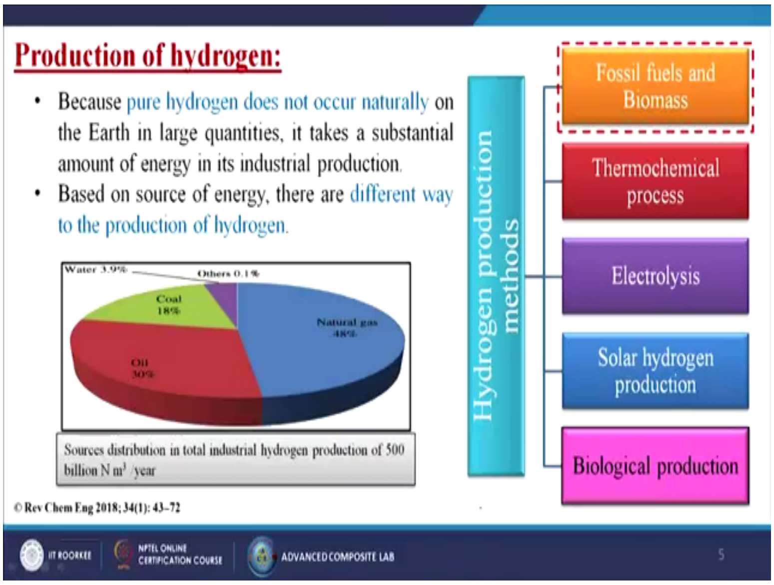

Timeline of hydrogen technologies:

Year	Technology development
1625	First description of hydrogen by Johann Baptista Van Helmont
1783	Antoine Lavoisier gave hydrogen its name
1783	Jacques Charles made the first flight with his hydrogen ballon "La Charliere"
1801	Humphry Darvy discovered concept of fuel cell
1806	François Isaac de Rivaz built the de Rivaz engine, the first internal combustion engine powered by a mixture of hydrogen and oxygen.
1943	Liquid hydrogen is tested as rocket fuel at Ohio State University
2016	Toyota releases its first hydrogen fuel cell car, the Mirai
2017	Hydrogen Council formed to expedite development and commercialization of hydrogen and fuel cell technologies

Now, let us go to the history for the hydrogen technologies. It has been started in the year of 1625. So, first description of hydrogen by Jan Baptist Van Helmont, then slowly we have come to the year of 2016 where Toyota release its first hydrogen fuel cell car the Mirai, then in 2017 hydrogen council formed to expedite development and commercialization of hydrogen and fuel cell technologies.

So, first initially the hydrogen has been identified then people have tried to make the hydrogen as a fuel cell or maybe some other generating electricity or maybe the heat or maybe the power, then at last 2016 the Toyota has already invented a car which is run by the hydrogen and 2017 one hydrogen council has been formed who is looking after the whole hydrogen generations and the storage system throughout the world. Now, how we can produce the hydrogen basically?

(Refer Slide Time: 03:49)

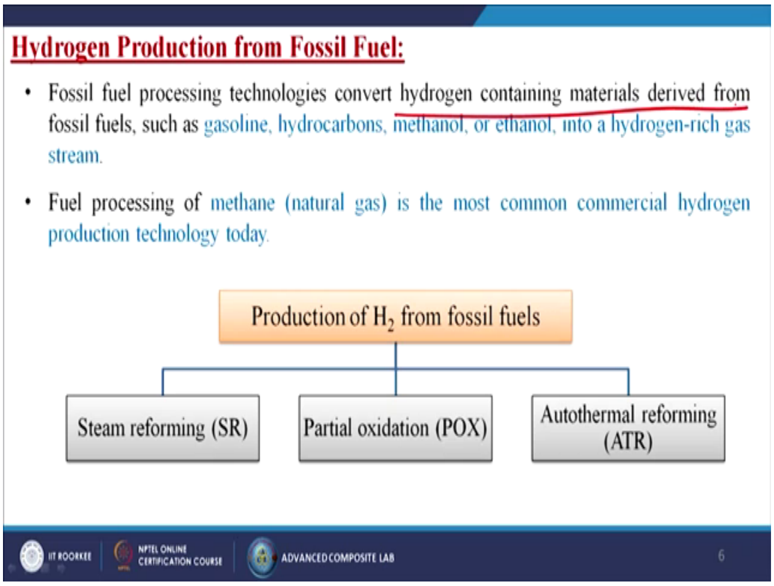


So, because pure hydrogen does not occur naturally as I already explained in our previous slides, on the earth in large quantities it takes a substantial amount of energy in its industrial production. Based on source of energy they are a different way to the production of hydrogen. So, what are those? Like hydrogen production methods basically we can do it by the fossil fuels and the biomass at the onset of these particular lecture, I have informed you that there are so, many process by which we can produce the hydrogen.

So, first one is the fossil fuels and the biomass second one is the thermo chemical process, third one is called the electrolysis, fourth one is the solar hydrogen productions and the last one is called the biological productions. So, basically in these particular lecture we are going to discuss about the hydrogen productions from the fossil fuels and the bio mass. So, basically this is the source distribution in total industrial hydrogen production of 500 billion natural meter cube per year. So, now, you can see that natural gas is taking 48 percent, then after that it is oil 30 percent, coal is 18 percent like water 3.9 percent and others is very very negligible that is 0.1 percent.

Now, we can see that from this particular image after certain time or maybe certain years these natural gas oil and coal will be finished from the earth. Now for the energy generations we have to only concentrate about this part only. So, that is why nowadays scientists researchers are giving the maximum attention to this particular part itself. Now how we are going to do the hydrogen production from fossil fuel?

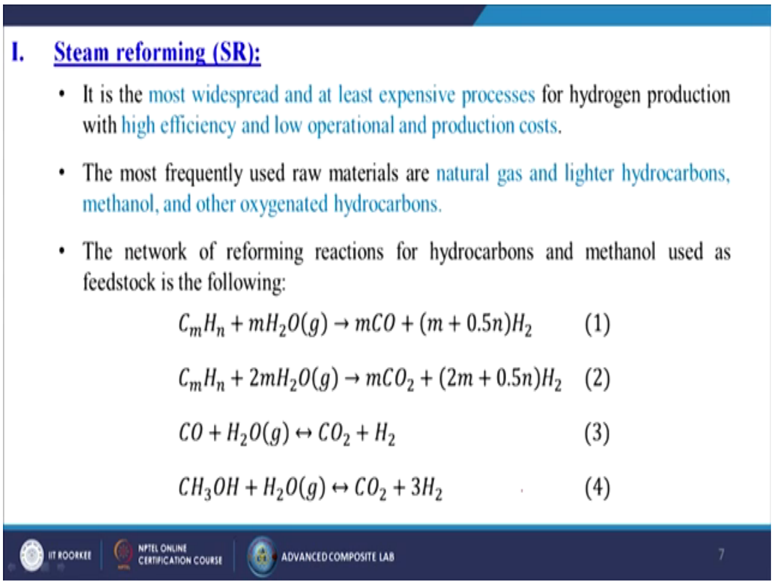
(Refer Slide Time: 05:39)



Fossil fuel processing technologies convert hydrogen containing materials derived from fossil fuels such as gasoline, hydrocarbons, methanol or ethanol into a hydrogen rich gas stream. Fuel processing of methane natural gas is the most common commercial hydrogen production technology today so; that means, from the methane we are generating the hydrogen.

So, now production of hydrogen from the fossil fuels can be performed by three way, that is first one is called the stream reforming in short basically we are calling it as SR, then next one is called the partial oxidation that is called the POX and the last one is called the auto thermal reforming or maybe the ATR. So, ATR is basically the addition of these two.

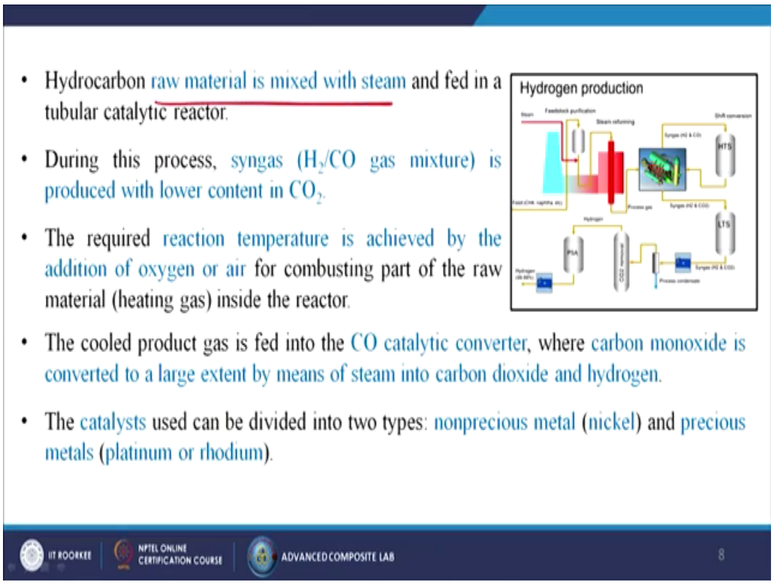
(Refer Slide Time: 06:26)



Now, first let us discuss about the steam reforming. It is the most widespread and at least expensive process for hydrogen production with high efficiency and low operational and production costs. The most frequently used raw materials are natural gas and lighter hydrocarbons like methanol and other oxygenated hydrocarbons.

The network of reforming reactions for hydrocarbons and methanol used as feedstock is the following. So, by these reactions we are going to produce the hydrogen. So, every steps basically we are the hydrogen, but maximum we are getting at the fourth stage itself. So, now, you can see that while doing this maybe some chemical reactions is taking place. So, that is why it is not up to that much because it can produce some kind of toxic gases or maybe it can produce some kind of harmful elements which is not good for the environment itself.

(Refer Slide Time: 07:29)



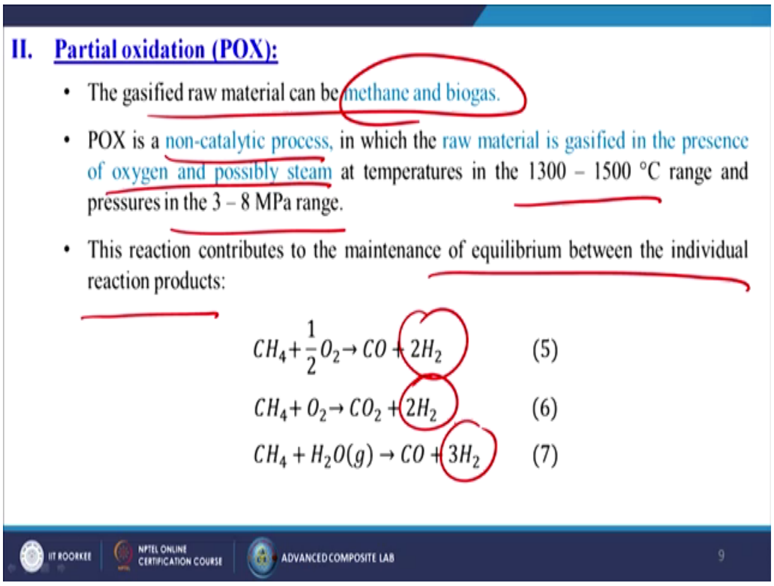
So, hydrocarbon raw materials is mixed with steam and fed in a tubular catalytic reactor. So, here you can see the steam is going into the feedstock and then from here the feed is going which is nothing, but the methane or maybe some kind of petroleum products like naphtha and then feedstock purifications is taking place over there because feed is here.

The steam is directly joining with the purified feed itself and then the steam reforming is taking place in these particular zone. Now after reactions what is happening? It is generating the hydrogen and carbon dioxide both we are doing the pressure swing adsorption. So, basically we are segregating the carbon dioxide gas from there and then ultimately we are getting the hydrogen as a pure gas 99.99 pure hydrogen basically we are getting from these particular technology.

So, during these process syngas which is the combination of hydrogen and carbon monoxide gas mixture is produced with lower content in carbon dioxide. The required reaction temperature is achieved by the addition of oxygen or air for combusting part of the raw material inside the reactor; that means, high chemical reactions is taking place in this particular zone itself. The cooled product gas is fed into the carbon monoxide catalytic converter, where carbon monoxide is converted to a large extent by means of steam into carbon dioxide and the hydrogen.

The catalyst used can be divided into two types; one is called the non precious metals that is like nickel and another one is called the very costly metals or maybe the precious metals like platinum or maybe the rhodium.

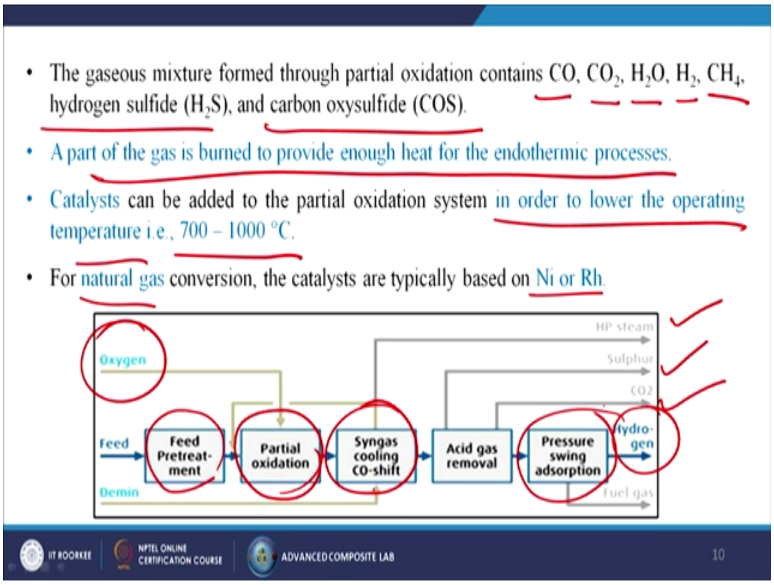
(Refer Slide Time: 09:14)



Now, the second part is called the partial oxidations which is nothing, but the POX. The gasified raw material can be methane and the biogas. POX is a non catalytic process in which the raw material is gasified in the presence of oxygen and possibly steam at temperatures in the 1300 to 1500 degree centigrade range and pressure is required 3 to 8 mega Pascal range.

The reaction contributes to the maintenance of equilibrium between the individual reaction products; here also we are getting the plenty of reactions that is methane with the oxygen itself. But here we are not going to add any kind of catalyst in the first case we are going to add the catalyst for the hydrocarbon case, but here we are not going to utilize any kind of catalyst its a normal reaction is taking place.

(Refer Slide Time: 10:11)

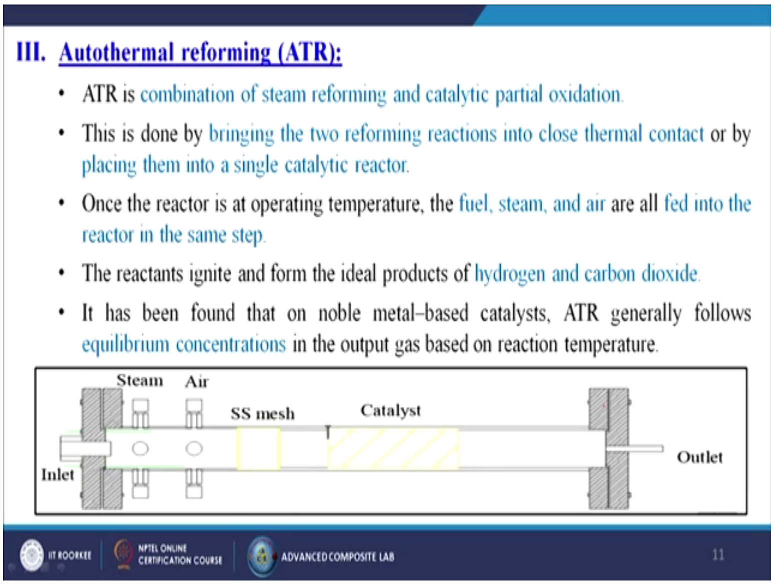


The gaseous mixture formed through partial oxidation contains carbon monoxide, carbon dioxide, water, hydrogen, methane, hydrogen sulfide H 2 S and the carbon oxysulfied. A part of the gas is burned to provide enough heat for the endothermic process. Catalysts can be added to the partial oxidation system in order to lower the operating temperature if my material cannot sustain that particular temperature.

Then just to reduce the reaction temperature sometimes we are adding catalyst over there and that is also in between 700 to 1000 degree centigrade when we are trying to do the reaction. For natural gas conversion the catalysts are typically based on nickel or maybe the rhodium. So, in this particular case what happened? My feed is coming; feed pretreatment is taking place in this particular case now we are adding the oxygen, so, partial oxidation is taking place and then syngas cooling CO-shift is taking place in this particular case.

Now, we are adding the demin in these particular portions through that HP systems steam are coming, high pressure streams are coming over there then if we go the further step from syngas cooling co shift to the acid gas removal, then we are taking out the sulphur and then we are taking out the carbon dioxide; that means, every reaction stages we are taking out the other non required gases over there and then at last only the hydrogen is left, which as a pressure swing adsorption we are taking the hydrogen gas over there.

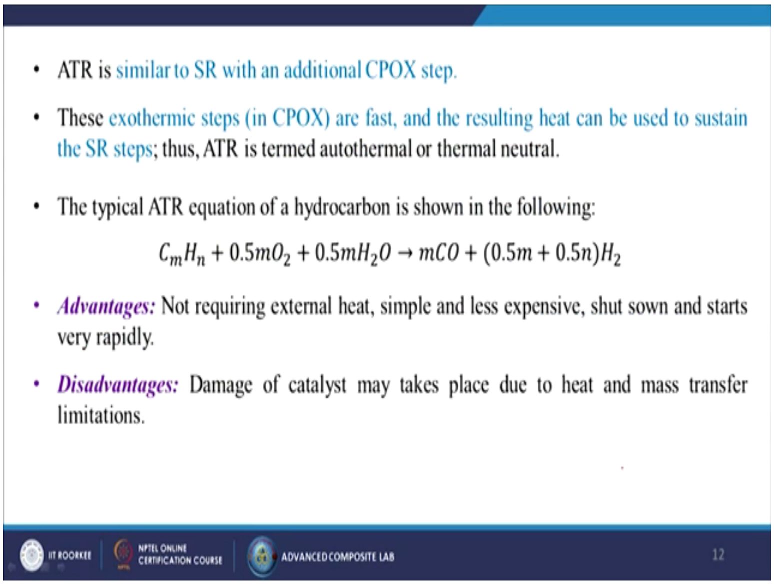
(Refer Slide Time: 11:51)



Next add one is called the autothermal reforming or maybe in short it is called the ATR. ATR is a combination of steam reforming and the catalytic partial oxidation as I told already. This is done by bringing the two reforming reactions into close thermal contact or by placing them into a single catalytic reactor. Once the reactor is at operating temperature the foil steam and air are all fed into the reactor in the same step. So, you can see steam is going inside, air is going inside the reactants ignite. So, in this particular case we are doing the ignitions over there. It has been found that an noble metal based catalysts ATR generally follows equilibrium concentration in the output gas based on the reaction temperature.

So, now through this mesh the whole steam and air is passing out, then after that we are putting the catalyst. So, reaction is taking place and then after that as a outlet the gases whatever the gas has been produced through this reaction is coming out or maybe we are taking it out.

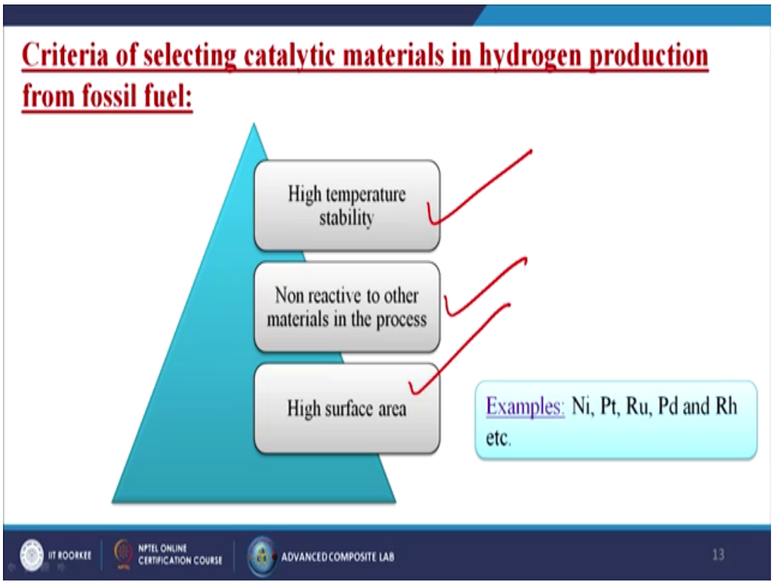
(Refer Slide Time: 12:56)



So, ATR is similar to SR with an additional CPOX step. These exothermic steps in CPOX are fast and resulting heat can be used to sustain the SR steps thus ATR is termed auto thermal or maybe the thermal neutral step. The typical ATR equation of a hydrocarbon is shown in the following. So, simple this is the reaction is taking place inside the system. Advantages not requiring external heat simple and less expensive shutdown and the starts very rapidly; that means, the reaction can takes place automatically we no need to put any kind of other heat or may be the pressure from the outside.

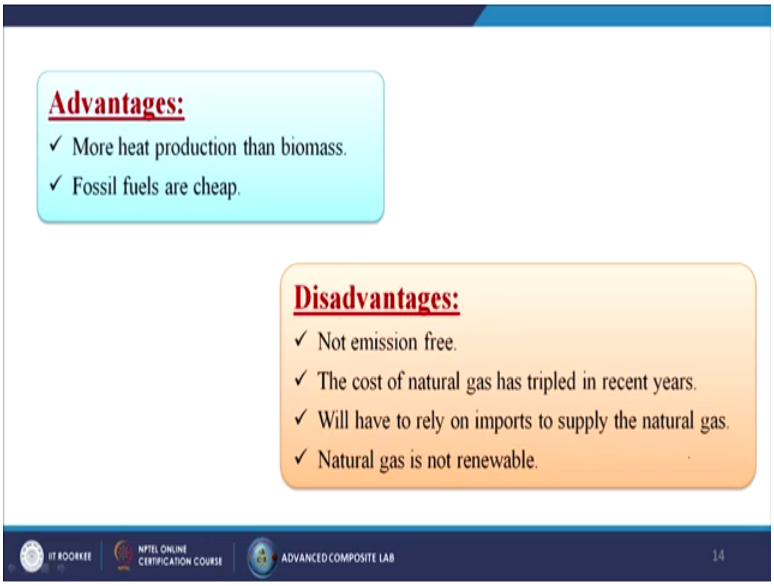
Disadvantages damage of catalyst may takes place due to heat and mass transfer limitations yes the material can degrade so, that is the problem over here. Now what are the criteria for selecting the catalytic materials in hydrogen production from fossil fuels?

(Refer Slide Time: 14:01)



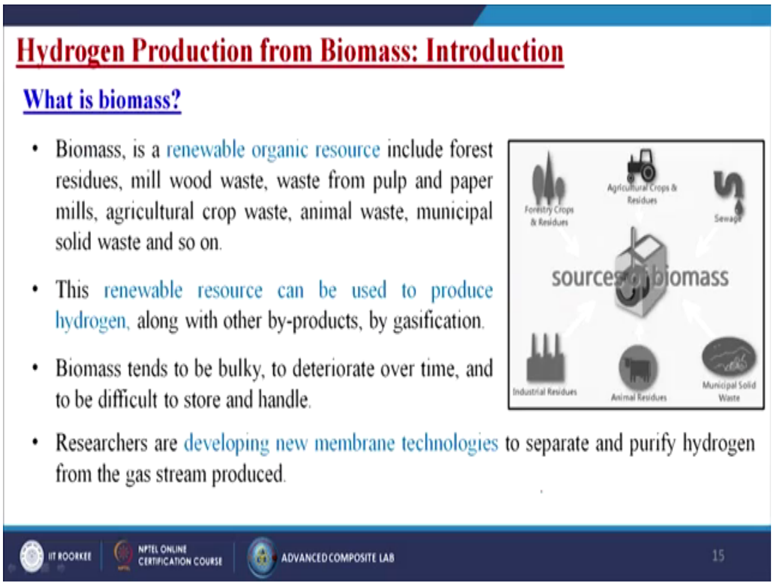
It should have high temperature stability non reactive to other materials in the process it is having high surface area what are the examples of this kind of catalytic material like nickel, platinum, ruthenium, palladium and the rhodium. So, these all are the examples basically. What are the advantages?

(Refer Slide Time: 14:22)



More heat production than the biomass fossil fuels are cheap biomass will come later next of course, it is having certain disadvantages too not emission free. As I told already when the chemical reaction is taking place maybe it can generate some kind of toxic gases or maybe the carbon monoxide gases which is very very harmful to the environment itself. The cost of natural gas has tripled in recent years we will have to rely on imports to supply the natural gas because from our country point of view we do not have a enormous source. So, simple we are importing those gases from the outside natural gas is not the renewable one.

(Refer Slide Time: 15:04)

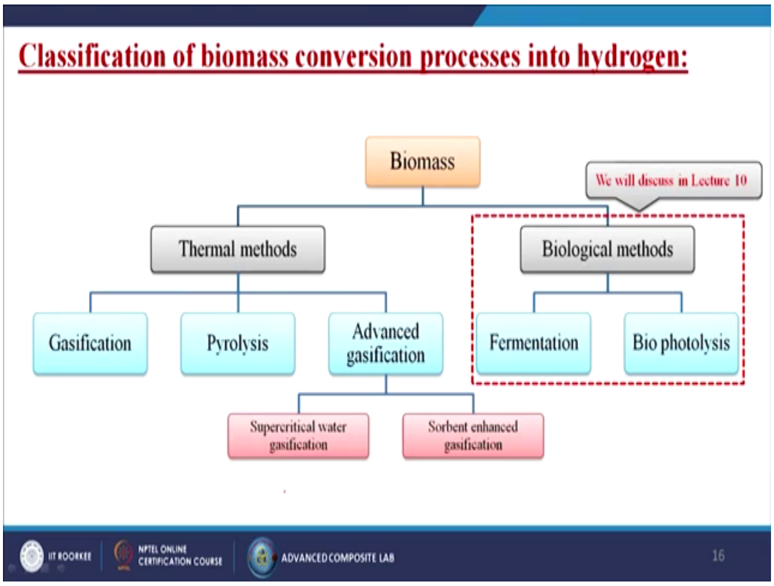


Now, we are going to discuss about the second part that is hydrogen production from the biomass. Till now we are discussing about the hydrogen production from the fossil fuels. So, as a introduction we can say that what is let us know that what is biomass. So, biomass is a renewable organics resource includes forest residues, mill wood waste, waste from pulp and the paper mills, agricultural crop waste, animal waste, municipal solid waste and so on.

So, from the source itself you can understand that why we are trying to work on this particular technology, because these all are the materials is basically its a waste and the problem of these materials to store or maybe for the biodegradability problem. So, if we are able to utilize these materials. So, we can reduce the pollutions to the environment itself.

So, this renewable resource can be used to produce hydrogen along with other byproducts by the gasification. Biomass tends to be bulky to deteriorate over time and to be difficult to store and handle. Researchers are developing new membrane technologies to separate and purify hydrogen from the gas stream produced.

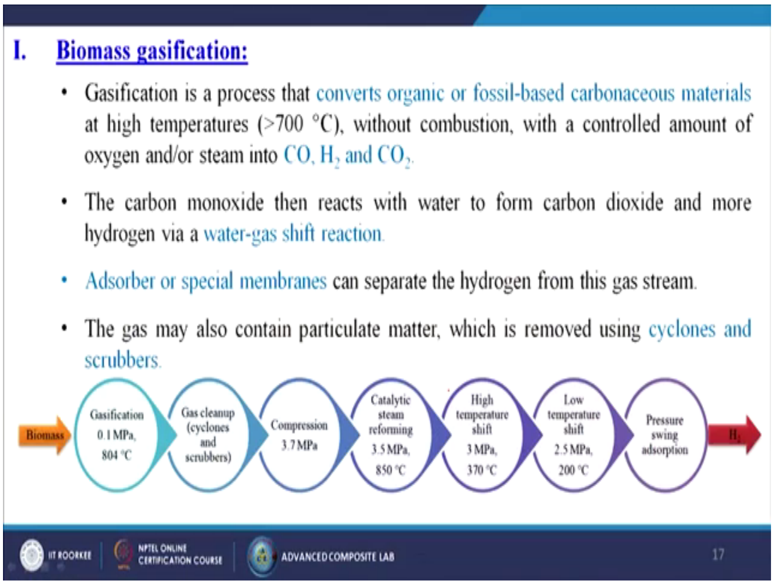
(Refer Slide Time: 16:23)



Now, what is the classification of biomass conversion process into hydrogen? So, biomass basically that is divided into two parts; one is called the thermal methods another one is called the biological methods. So, in thermal methods we can do the classifications by pyrolysis by advanced gasification.

Advanced gasification is also having divided into two part; one is called the super critical water classifications and the sorbent enhanced gasifications and if we talk about the biological methods which we are going to discuss in our lecture number 10. So, basically that can be also done by two methods; one is called the fermentations another one is called the bio photolysis. So, just let us discuss about the biomass gasifications.

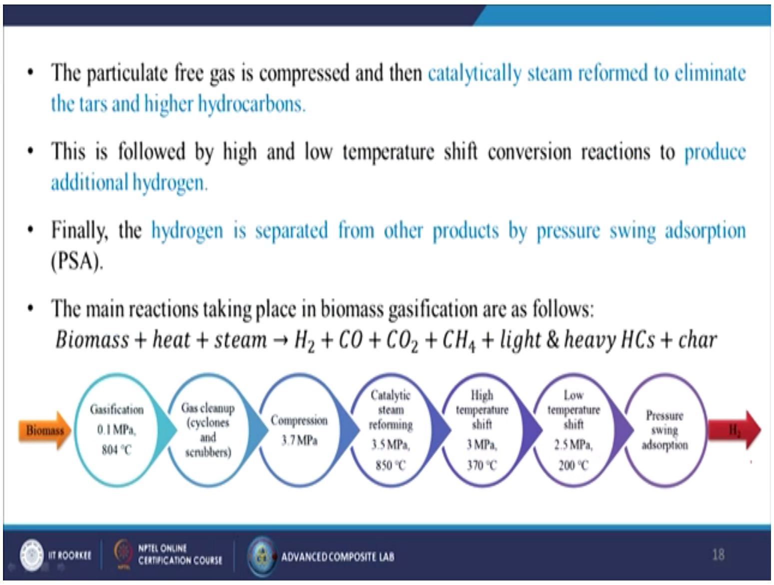
(Refer Slide Time: 17:12)



So, gasification is a process that converts organic or fossil based carbonaceous materials at high temperature. High temperature is more than 700 degree centigrade without combustion with a controlled amount of oxygen and or steam into carbon monoxide hydrogen and the carbon dioxide gas. The carbon monoxide then reacts with water to form the carbon dioxide and more hydrogen via a water gas shift reaction. Adsorber or special membranes can separate the hydrogen from this gas stream. The gas may also contain particulate matter which is removed using cyclones and the scrubbers. So, like this biomass first is gasification at 0.1 mega Pascal and 804 degree centigrade, then next is that gas clean up like cyclones and by scrubbers then compression is taking place up to 3.7 mega Pascal.

Catalytic steam reforming at 3.5 mega Pascal at 850 degree centigrade high temperature shift at 3 mega Pascal at 370 degree centigrade, then low temperature shift at 2.5 mega Pascal pressure with 200 degree centigrade and the pressure swing absorption is taking place and at last we are going to get the hydrogen gas.

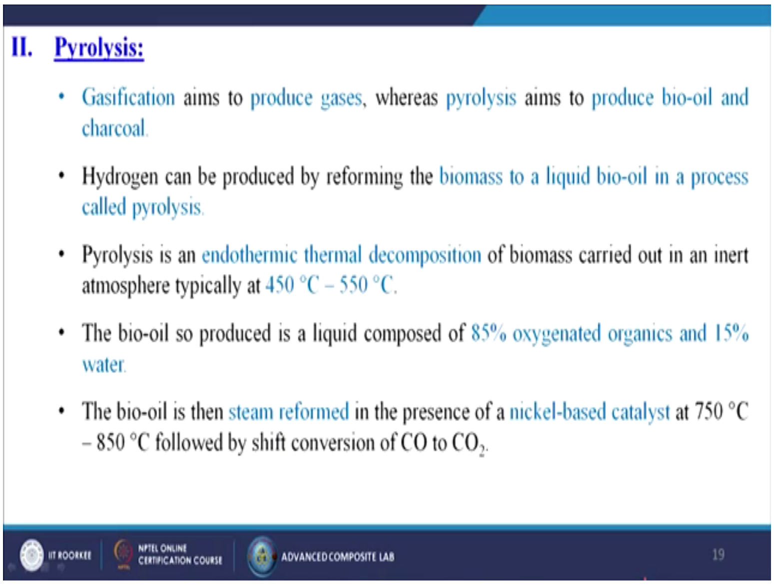
(Refer Slide Time: 18:34)



The particulate free gas is compressed and then catalytically steam reformed to eliminate the tars and higher hydrocarbons. This is followed by high and low temperature shift conversion reactions to produce additional hydrogen over there. Finally, the hydrogen is separated from other products by pressure swing adsorption which is called the PSA system.

The main reaction taking place in biomass gasification are as follows; biomass plus heat plus steam it will produce hydrogen carbon monoxide, carbon dioxide, methane, light and heavy hydrocarbons and the char. So, this is the whole system at last we are going to get the hydrogen gas. Now we are going to discuss about the second part that is called the pyrolysis.

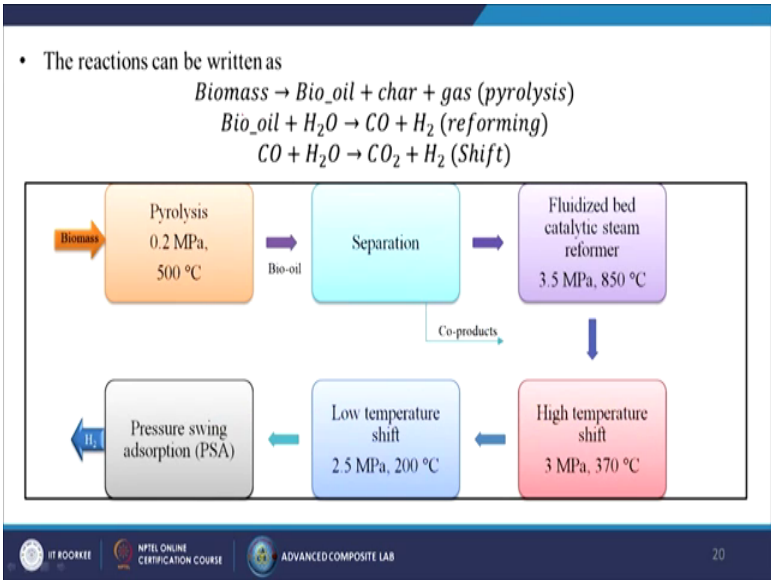
(Refer Slide Time: 19:29)



Gasification aims to produce gases where pyrolysis aims to produce the bio oil and charcoal. Hydrogen can be produced by reforming the biomass to a liquid bio oil in a process called pyrolysis. Pyrolysis is an endothermic thermal decomposition of biomass carried out in an inert atmosphere typically at the temperature of 450 degree centigrade to 550 degree centigrade.

The bio oil so, produced in a liquid composed of 85 percent oxygenated organics and 15 percent water. So, basically this is a one kind of chemical reaction process. The bio oil is then steam reformed in the presence of a nickel based catalyst at 750 degree centigrade to 850 degree centigrade followed by shift conversion of carbon monoxide to carbon dioxide.

(Refer Slide Time: 20:21)

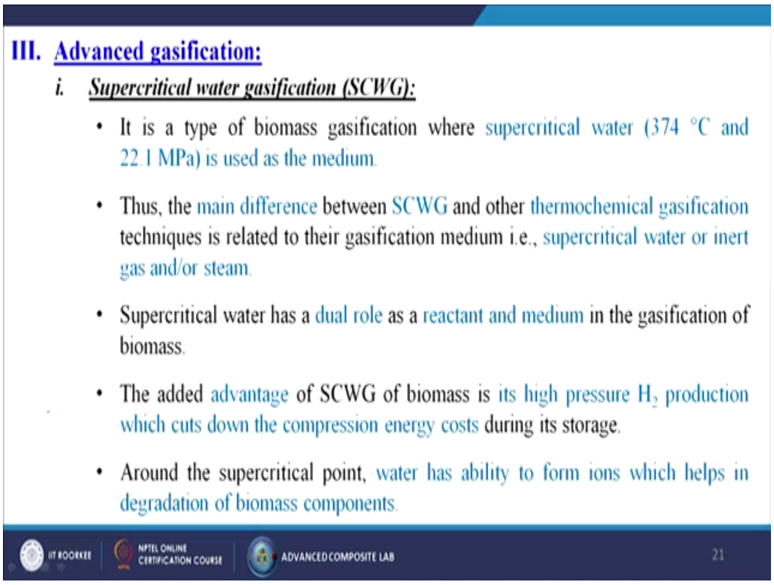


The reaction can be written as biomass. So, by pyrolysis reactions it is producing bio oil char and that gas. Bio oil plus H 2 O, if we add the water it will produce the carbon monoxide and the hydrogen by reforming process. Then carbon monoxide if we again add it with water itself. So, it will produce that carbon dioxide and hydrogen by the shift process.

So, basically first initial stage from the biomass we have to produce the bio oil, then by reforming process and by shift process we can generate the hydrogen. So, biomass as I told already pyrolysis is taking place with pressure 0.2 mega Pascal at 500 degree centigrade it is producing the bio oil. Then we are doing the separation process over there and then only we are taking the fluidized bed catalytic steam reformer with 3.5 mega Pascal at 850 degree centigrade, then we are doing the high temperature shifting over there which is 3 mega Pascal at 370 degree centigrade, then low temperature shift at 2.5 mega Pascal at 200 degree centigrade.

So, from high temperature to we are bringing the material to the low temperature and then we are doing the pressure swing adsorption. So, basically we are segregating the carbon dioxide gas from there and then ultimately we are getting the hydrogen as a pure gas.

(Refer Slide Time: 21:47)

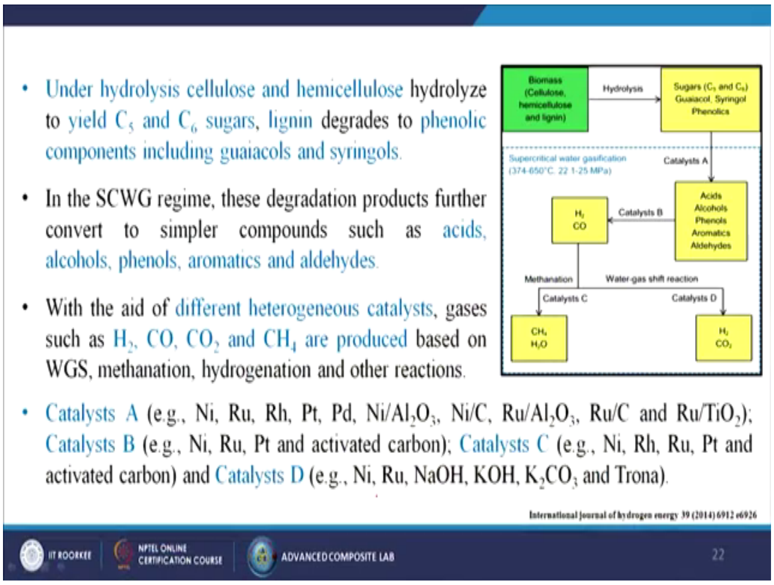


Then the third one is called the advanced gasification. So, basically it is also divided into two parts; one is called the super critical water classifications SCWG it is a type of biomass gasification where supercritical water at 374 degree centigrade and 22.1 mega Pascal pressure is used as the medium. Does the main difference between the SCWG and other thermochemical gasification techniques is related to their gasification medium, supercritical water or inert gas and steam or may be the only steam itself.

Supercritical water has a dual role as a reactant and medium in the gasification of biomass. The added advantages of SCWG Supercritical Water Gasification of biomass is its high pressure hydrogen production which cuts down the compression energy costs during its storage; that means, it does not need any kind of segregations of other byproducts.

Around the supercritical point water has ability to form ions which helps in degradation of biomass components. So, that maybe the little bit advantage to this particular system.

(Refer Slide Time: 23:06)

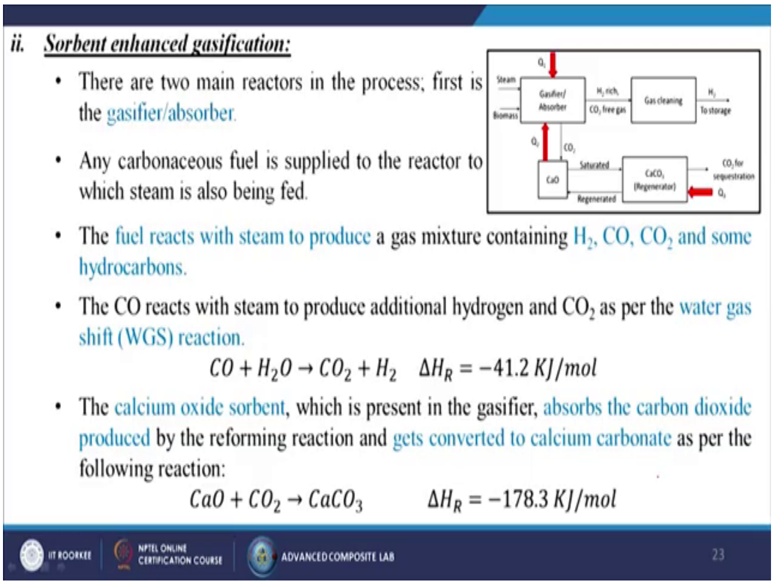


Under hydrolysis cellulose and hemicellulose hydrolyze of yield C 5 and C 6 sugars lignin degrades to phenolic components including guaiacols and syringols. So, basically these two products are preparing. In the SCWG regime these degradation products further convert to simpler compounds such as acids, alcohols phenols aromatics and the aldehydes. With the aid of different heterogeneous catalysts gases such as hydrogen, carbon monoxide, carbon dioxide and methane are produced based on WGS, methanations, hydrogenations and other reactions.

There are so many types catalysts basically we are using it has been divided into their applications. So, if we talk about the catalyst A group. So, basically its nickel, ruthenium, rhodium, platinum, palladium sometimes nickel alumina composites nickel carbon or maybe the ruthenium Al 2 O 3 like this if we talk about the catalyst B like nickel, ruthenium, platinum and activated carbon if we talk about the catalyst C series its like nickel, rhodium, ruthenium, platinum and activated carbon.

And if we talk about the catalyst D series then it should be nickel, ruthenium, sodium hydroxide, potassium hydroxide, potassium carbonate and the trona. So, this all about the biomass production by this particular technology.

(Refer Slide Time: 24:40)

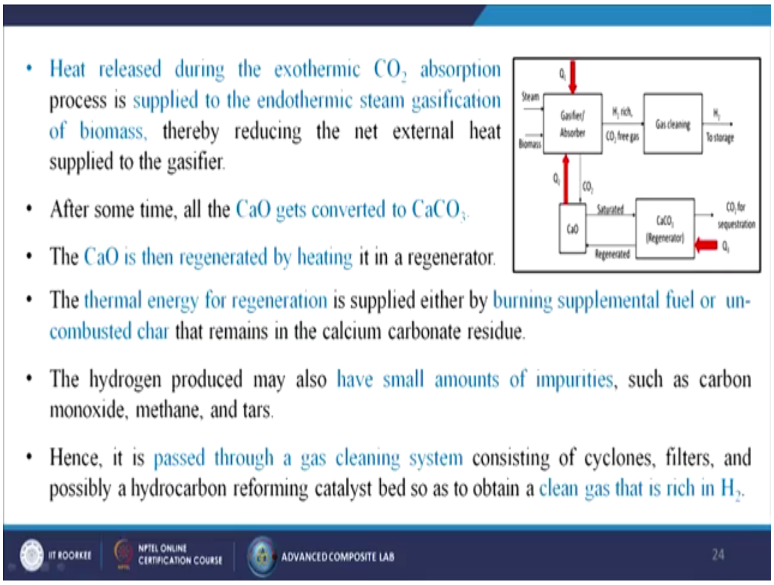


Next second one is called the sorbent enhanced gasification. There are two main reactors in the process first is the gasifier or maybe the absorber. So, this one is the number 1. Any carbonaceous fuel is supplied to the reactor which steam is also being fed. So, we are putting the steam and biomass as a inlet inside the system. The fluid reacts with steam to produce a gas mixture containing the hydrogen carbon monoxide, carbon dioxide and some hydrocarbons when the reaction is taking place.

So, basically the carbon monoxide it is coming. The carbon monoxide reacts with steam to produce additional hydrogen and carbon dioxide gas as per the water gas shifts reaction which is nothing, but carbon monoxide plus water it will produce the carbon dioxide plus hydrogen and some kind of heat energy over there. So, like this way we are getting the hydrogen rich and carbon dioxide free gases over there, then we are doing the gas cleaning and we are getting the pure hydrogen for the storing systems.

So, in this particular chamber what is happening? Whatever the carbon dioxide gas has been produced from the first chamber it is coming and it is reacting with the calcium oxides and then it is forming the calcium carbonate regenerations, it is again going back into the system itself. So, continuously the hydrogen gas is produced from this particular technology.

(Refer Slide Time: 26:05)

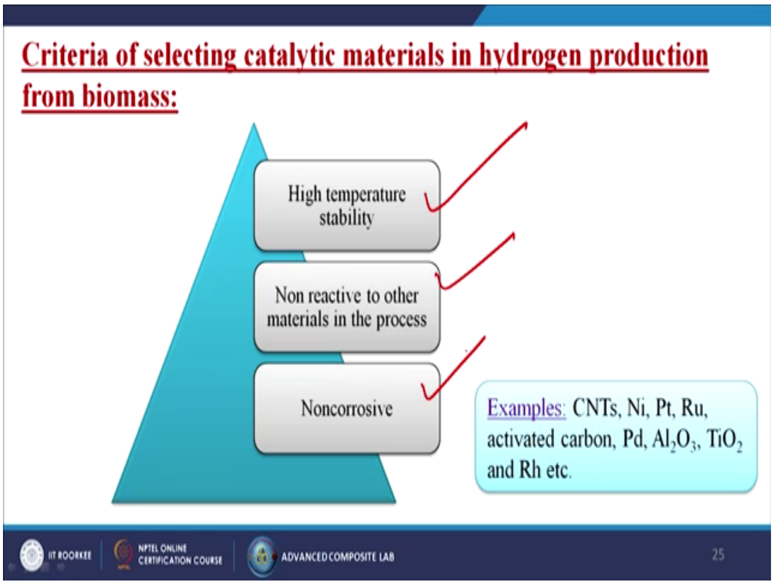


Heat released during the exothermic carbon dioxide absorption process is supplied to the endothermic steam gasification of biomass thereby reducing the net external heat supplied to the gasifier. After some time all the calcium oxide gets converted to the calcium carbonate. So, in this particular case so, whatever the calcium oxides were using whole calcium oxide after reaction with the carbon dioxide it is forming the calcium carbonate.

The CaO is then regenerated by heating it in a regenerator; that means, when again we are heating this one again it is forming the calcium oxide. So, that is why situations and then after that the regeneration is taking place. So, the thermal energy for regeneration is supplied either by burning supplemental fuel or maybe the uncombusted char that remains in the calcium carbonate residue.

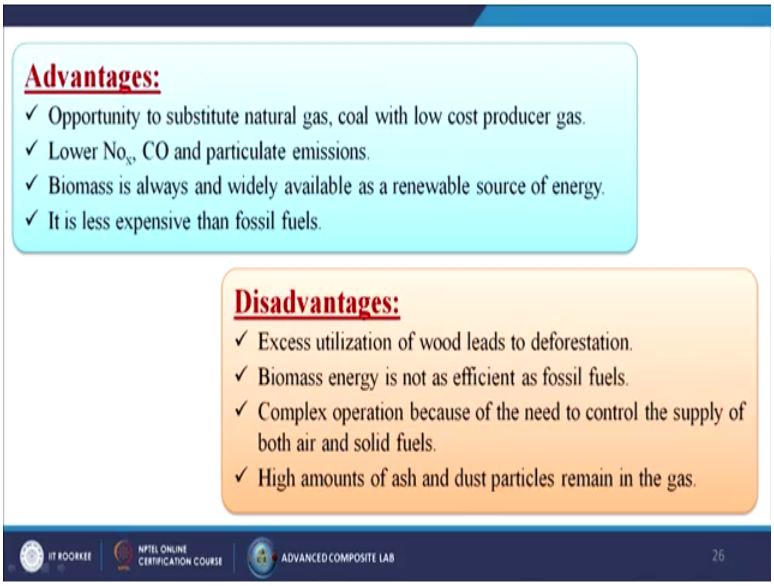
So, maybe a less extra fuel is required from the outside or maybe through this reaction whatever the char is forming, through that char also again it can come back to its original position. The hydrogen produced may also have small amounts of impurities such as carbon monoxide, methane and the tars. Hence it is passed through a gas cleaning system consisting of cyclones, filters and possibly a hydrocarbon reforming catalyst bed so, as to obtain a clean gas that is rich in hydrogen itself. So, in this particular case we are getting. Now, what are the criteria of selecting catalytic materials in hydrogen production from biomass?

(Refer Slide Time: 27:39)



So, the material should have high temperature stability, non reactive to other materials in the process and it should be non corrosive type. Examples like carbon nanotubes, nickel, platinum, ruthenium, activated carbon, palladium, alumina, titanium dioxide and the rhodium. So, these all are the catalyst materials basically we are using. Now what are the advantages?

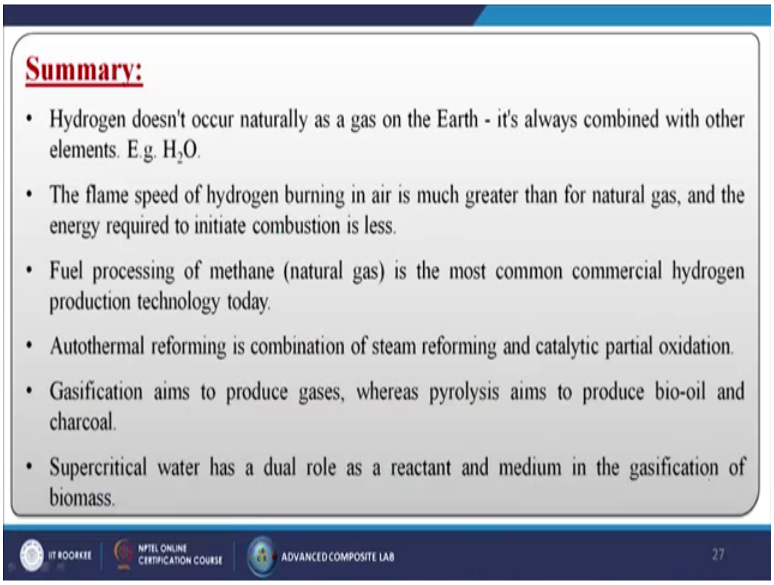
(Refer Slide Time: 28:07)



Opportunity to substitute natural gas coal with low cost producer gas lower No x; that means, lower toxic gases carbon monoxide and particulate emissions, biomass is always a widely available as a renewable source of energy it is less expensive than the fossil fuels.

Of course there are certain disadvantages also; excess utilization of wood leads to deforestation which can create a direct problem to the pollutions or maybe to the environment. Biomass energy is not as efficient as fossil fuels complex operation because of the need to control the supply of both air and the solid fuels, high amount of ash and dust particles remains in the gas itself. Now we have come to the last slide of these particular lecture. So, in summary we can say that hydrogen does not occur naturally as a gas on the earth its always combined with other elements like water.

(Refer Slide Time: 29:05)



The flame speed of hydrogen burning in air is much greater than for natural gas and the energy required to initiate combustion is very very less; that means, hydrogen gas is highly flammable products. Fuel processing of methane means from the natural gas itself is the most common commercial hydrogen production technology today. Autothermal reforming is combination of steam reforming and the catalytic partial oxidation. Gasification aims to produce gases where pyrolysis aims to produce the bio oil and charcoal and through bio oil we are producing the gas itself.

So, it is a maybe I can say rather its a two step process. Supercritical water has a dual role as a reactant and medium in the gasification of the bio mass. So, this is the whole summary of these particular lecture.

Thank you.