Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 17
Hydrogen Production from Biomass Part - 3

So that was the pyrolysis part and now moving to the biomass gasification. So, gasification is another way of having a higher yield of hydrogen without looking into multiple reactors like we have seen in the pyrolysis. Where we do pyrolysis in one reactor and a hydrogen yield or hydrogen enhancement in the separate reactor.

So, we have already understood the gasification pyrolysis and the combustion part. So, typically gasification as the name suggest conversion of biomass solid fuel to the gaseous fuel. Gaseous fuel, easy handy to use to store to transport unlike the biomass which is a little inconvenient for multiple use; so, that is the simple thing why a gasification is done.

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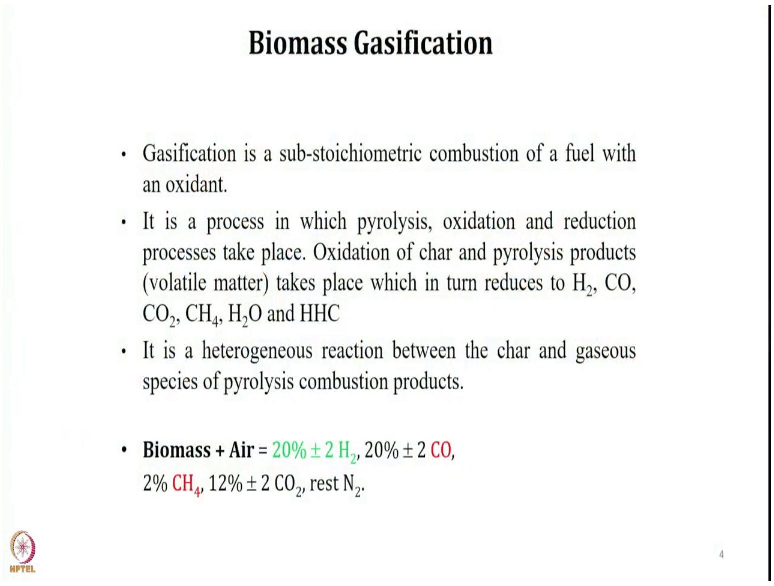

So, now gasification is a sub stoichiometry combustion of a fuel; so, typically less amount of oxygen that we are supplying. So, gasification it involves pyrolysis, oxidation, and the reduction process.

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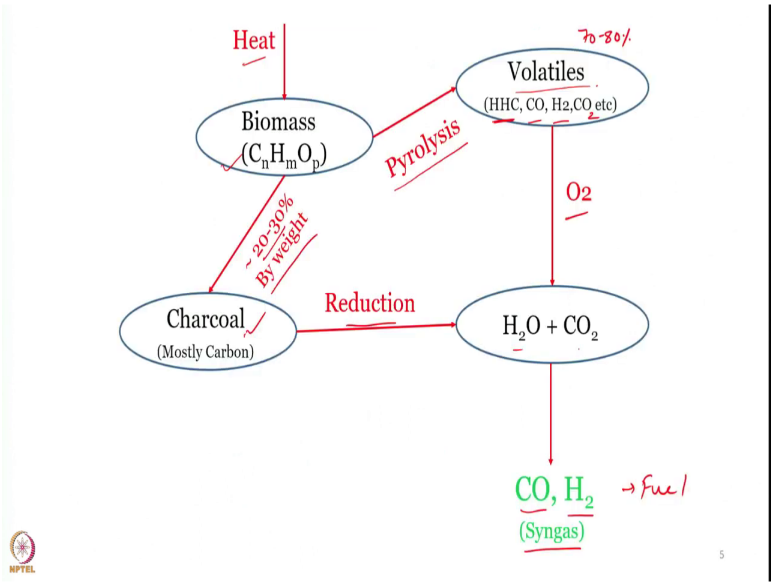

In the next slide; so, typically biomass we know it contains the $C_nH_mO_p$ and then when we heat it. When we heat it what we get is, it undergoes pyrolysis and we get the volatiles, volatiles are nothing but your combination of higher hydrocarbon. As we have seen in the earlier pyrolysis process also it gives you carbon monoxide, hydrogen, CO_2, etc. But also, it gives the charcoal around 20 to 30 percent of charcoal by weight and volatile is around 70 to 80 percent by weight.

So, these two now in combustion process we burn all as we have seen in the example of the match stick both are burnt. But here, in gasification what we do is, we only allow the volatiles to undergo combustion and what we get is H_2O and CO_2. Now, the rule comes of the charcoal, charcoal acts as a reducing agent which reduces H_2O and CO_2 to carbon monoxide and the hydrogen and these two are fuel.

So, these two are the good fuel though carbon monoxide is a poisonous gas, but we know that it is a very good fuel. And also carbon monoxide is one of the substrate or the feedstock to give us more hydrogen through water gas shift reaction that we will see in the subsequent slides. So, this together is called the synthetic gas or in short syn gas.

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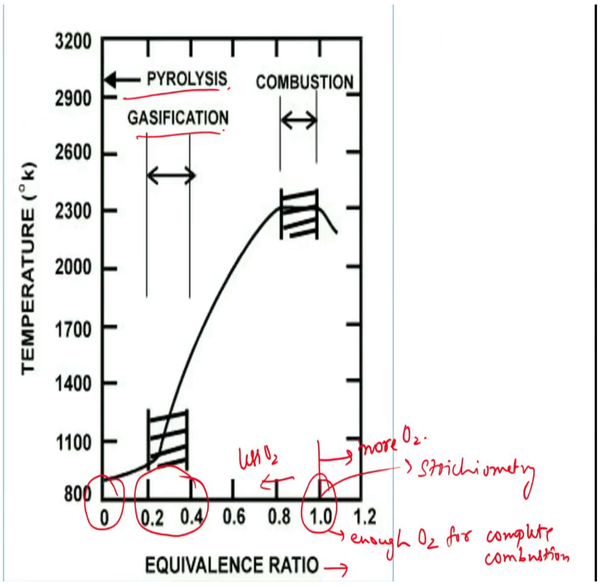

So, this is what we get in the gasification process a very simple process, and if we understand as we discussed in the last slide that is a sub stoichiometric process. So, now, if we look into this graph this x-axis is the equivalence ratio. And when we say equivalence ratio 1 means, it gives enough oxygen for complete combustion and that is what we mean by stoichiometry. So, this is the stoichiometry point where we have the enough oxygen and here it is less oxygen and beyond this point, we have more or excess oxygen.

So, when we are talking about the pyrolysis it happens without the presence of oxygen. So, 0 oxygen is there no oxygen or an absence of oxygen or just in the inert like nitrogen gas environment or something. But gasification, happens when we are supplying around 20 to 40 percent of the required oxygen amount.

And here we get finally, the carbon monoxide and a hydrogen as a product. And as we have seen in this particular slide this is not a single step, but a multiple step we have the pyrolysis, combustion and reduction all the three process happen together in a single reactor.

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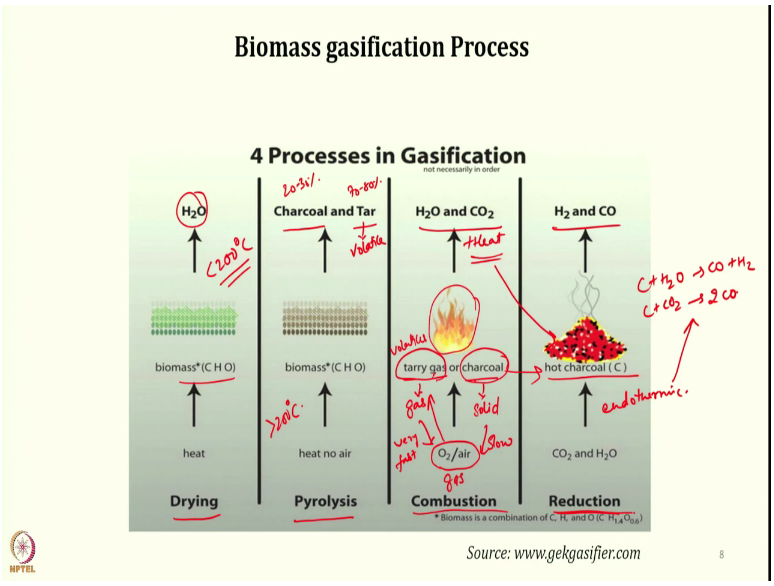

So, again to retreat physically how it happens, we first thing is that process the drying where we heat the biomass and remove the moisture. So, typically gasification process 20 to 30 percent of the moisture is allowed, because moisture removal is a very highly energy intensive process.

So, overall temperature gets reduced if you are putting very high amount of moisture, and typically many of the green biomass will have 40 to 50 percent of moisture and it will be difficult to process here. So, first we need to dry it and then this is happening below 200 degrees centigrade.

So, typically more than 200 degrees centigrade the organic molecules they start undergoing thermal decomposition or what we call as pyrolysis. So, below 200 degrees centigrade you will not see any of the of these molecules will undergo any molecular change or compound level nothing new will come out. But more than 200 degrees centigrade we will get, and what we get here is charcoal that we saw 20 to 30 percent by weight and the tar and this tar is 70 to 80 percent and this tar is nothing but the volatile.

So, this is nothing but the volatile only it is in literature you will find a different terminology for that. So, now when it undergoes combustion because we are passing oxygen in air. So, now, the question comes as we discussed we will allow only the volatiles to burn, but how to do it in a single reactor if we want how to achieve it in a single reactor with a selective combustion.

But, the beauty of the process is that chemistry itself take care of it, what happens if we supply oxygen in air, but this tarry gas this is gas and then it reacts with oxygen which is also in the gas phase. Gas phase reaction is very far, but this is solid; so, this is charcoal is present in a solid form; so, this fuel is solid. Solid gas reaction is very slow; so, this is very slow and this is very fast; not only few times, but more than 100 times faster than what is the solid gas reaction of carbon with oxygen.

So, what happens is most of the oxygen; most of the oxygen because the statistics and probability will favour the gas phase reaction and 99.9 percent of the oxygen will be consumed only by these volatiles. So, volatiles will consume most of the oxygen and this charcoal will just remain and go into the reduction zone.

So, but it raises its temperature because, it is present in the flame because this tarry gas it, now only not only undergoes combustion or oxidation, but also releases lot of heat. So, here CO_2, H_2O plus heat is produced and this heat drives are reduction reaction, because this process or this reaction is endothermic.

So, here we have $C + H_2O$ and $C + CO_2$ it gives $CO + H_2$ and this gives us two mole of CO. So, this is endothermic in nature both the reactions, but this hot environment that has been created by the combustion of the volatiles sustain this reaction with the charcoal which is now do not have any access to oxygen. But it has access to CO2 and H2O and it is happy to react and then it releases our H_2 and CO_2 as the product. So, that is the overall process of a biomass gasification and if we look into the reaction then combustion.

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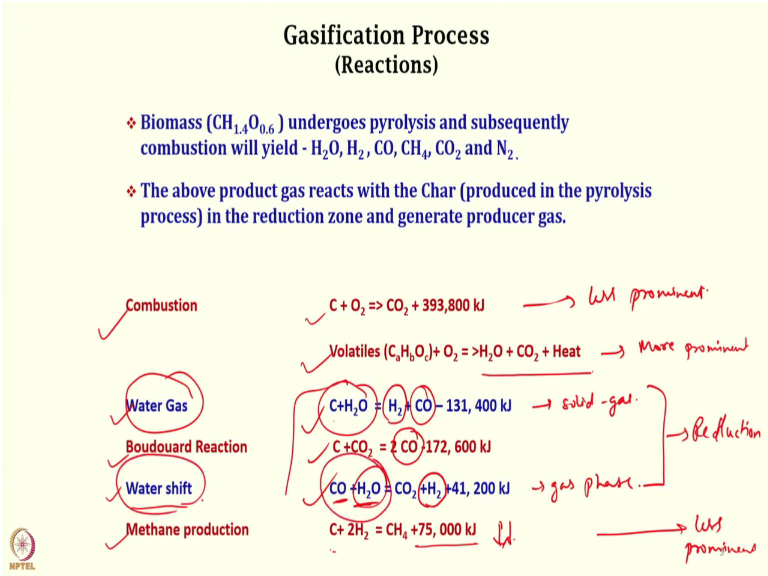

So, typically some part of the carbon will burn, but yeah very minor negligible amount. And then most of the oxygen will be consumed by volatiles when it reacts with oxygen and also it produces heat. And then the water gas reaction, C + H_2O and boudouard reaction these two are major producer of our fuel gas that is the hydrogen and the carbon monoxide.

Another reaction that I was talking about is the water shift reaction where carbon monoxide also reacts with H2O. If there is enough H2O present or if H2O is present in the system it will not only attack carbon, but also it will react with carbon monoxide. And carbon monoxide and H2O is now this is a gas phase reaction, again it is favoured more compared to this solid gas reaction.

So, here this also gives you extra hydrogen, and this is one of the thing that when we want to enhance the hydrogen production we can use this H_2O to enhance more and more hydrogen into it. And then we have a methane production and this is also slightly sort of exothermic, but the occurrence is quite low compared to these three reactions.

So, these three reactions that goes into the reduction zone are prominent and this is less prominent and this volatile oxidation is more prominent and this is less prominent. So, this is the overall chemistry of the gasification process.

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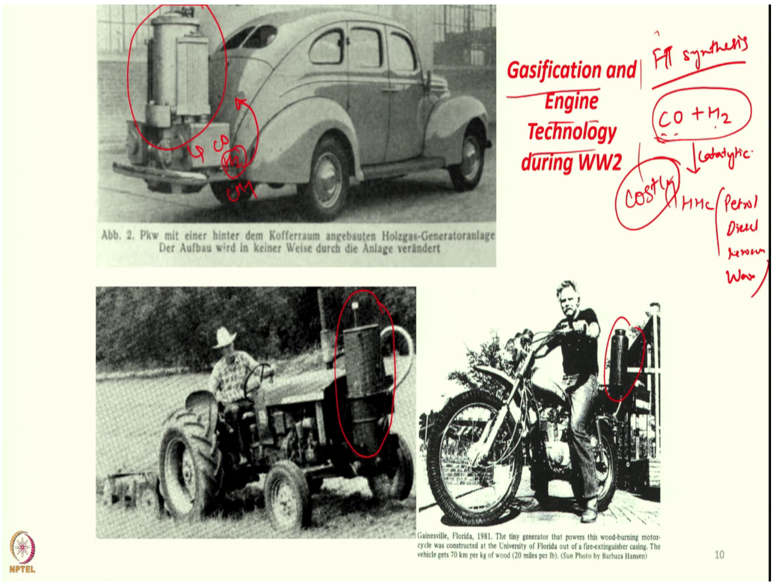

And now, when we look into the technology just to give a brief history of this gasification especially the biomass gasification process it is a very interesting history. It was the Second World War was going on and the US, UK and the allied forces, they found that blocking the supply of the petroleum may hamper the German forces.

Because, Europe as such Germany was almost holding the complete Europe, but Europe does not have much of a petroleum reserve they have lot of coal, but they do not have enough petroleum reserves in the Europe. So, and it was dependent on either gulf or the other countries in Africa for supply of the petroleum oil.

So, that was cut down and then general forces or the Hitler he was a little bit taken back, but then there was one scientist called Fischer Tropsch typically it is called the FT synthesis of Fischer and Tropsch. Fischer and Tropsch came up with the synthesis FT synthesis process where carbon monoxide plus H_2 it undergoes a catalytic conversion process where it gives you higher hydrocarbon.

This higher hydrocarbon can be petrol, diesel substitute or kerosene or even up to wax you can even create a wax. So, it creates a sort of it is a polymerization process where your carbon and hydrogen is here and oxygen is left out. So, oxygen is not part of this product it is left out the polymerization of carbon and hydrogen chain gives you higher hydrocarbons which can be equivalent in the properties to petrol and diesel which was required by the military.

So, Europe has a lot of coal reserve even the Germany itself had a huge coal reserve which was used to undergo gasification process similar to what is biomass gasification we will come to it after this module the coal gasification. So, this carbon monoxide and hydrogen was diverted here, but this process was costly.

So, the military application was only given the access to the liquid fuel and the normal population civilian population were not allowed to use petrol or diesel. So, it was completely banned the sale of petrol and diesel in the civilian areas were completely banned throughout the Europe. So, then the researchers came up with the biomass gasification and the engine technology.

So, what they do is rather than looking for coal or something can be, because this process of FT synthesis is costly not the gasification process and biomass is also available. So, rather than coal gasification they designed such reactors which were biomass gasifiers and which was producing gas. So, it was giving you carbon monoxide, hydrogen and the methane and this was going into the IC engine.

So, they developed the process technology which can fuel the conventional petrol or the diesel engine. So, diesel engine has to be converted to spark in a spark ignition mode because this fuel does not ignite by compression, compression ignition is not possible for this. But it easily ignites with the help of a spark plug and especially this hydrogen is a very good fuel in terms of its ignition properties hydrogen plays a very important role.

So, you can see that the even the in the tractor even in a two-wheeler. So, it was lot of things are produced there was a company in Poland which has retrofitted such gasification system like this and other in the trucks and buses and all they would have retrofitted more than 1 million vehicles. So, you can just imagine how popular it was during the World War II era, but once the World War was done away the petroleum supply in the Europe was very good very smooth supply was there.

And then the completely shifted back to the fossil fuel and this technology is slowly died down. But again, it picked up during the 80’s when there was again oil crashes, but that time it was not for the running the vehicles, but for power production but yeah. So, that was a very nice short history of this gasification which I thought that it will be interesting to share here. Now, again coming back to the gasification process.

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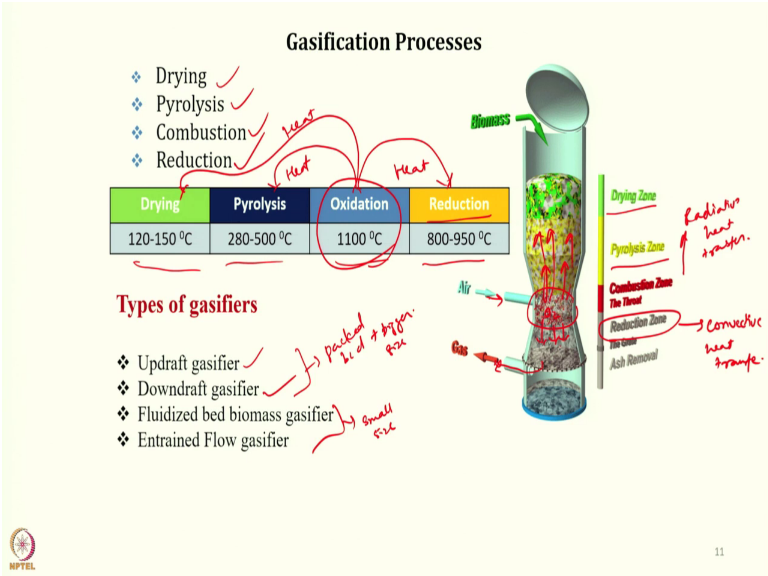

So, as we have discussed again, we will try to recap drying, pyrolysis, combustion and reduction. Drying happens typically in the temperature range of 120 to 150 degrees centigrade, pyrolysis more than 200 degrees centigrade and then oxidation zone goes very high temperature 1100 degrees centigrade.

And this then whatever the leftover charcoal and because of those reactions carbon with H2O and carbon with CO2 they are endothermic the temperature reduces to around 800 degrees centigrade or so. And this oxidation zone is supplying heat for this reduction process as well as it is supplying heat for this pyrolysis process as well as it is supplying heat for the drying process.

So, all the heat supplied is from this oxidation zone as you can see here is this is the oxidation zone in this downdraft reactor. So, this reactor is the downdraft reactor here and this through the radiation through the radiative heat transfer it supplies the heat to the pyrolysis zone and the drying zone. And then air is drawn from here and all the oxidation process happens and the hot gases passes through this reduction zone.

So, upper side the radiative heat transfers and in the reduction zone mostly the convective heat, because it is the hot gases which is carrying the heat. Comes to the charcoal and supplies the bulk amount of heat, because it requires lot of heat to convert the solid carbon into gases it is a slow process. So, a temperature has to be remained high pyrolysis can happen at 200-300 degrees centigrade its fine with it.

So, this is the typically process and when and then from the bottom we draw the gases; so, typically updraft gasifier will have a different configuration. So, these two are for termed as packed bed reactor and they take the bigger size of the biomass particle. And these two are the fluidized and the entrained flow which takes the small size particle and this takes the bigger size particle. So, we will not go into the detail, but yeah chemistry is important to understand from this part.

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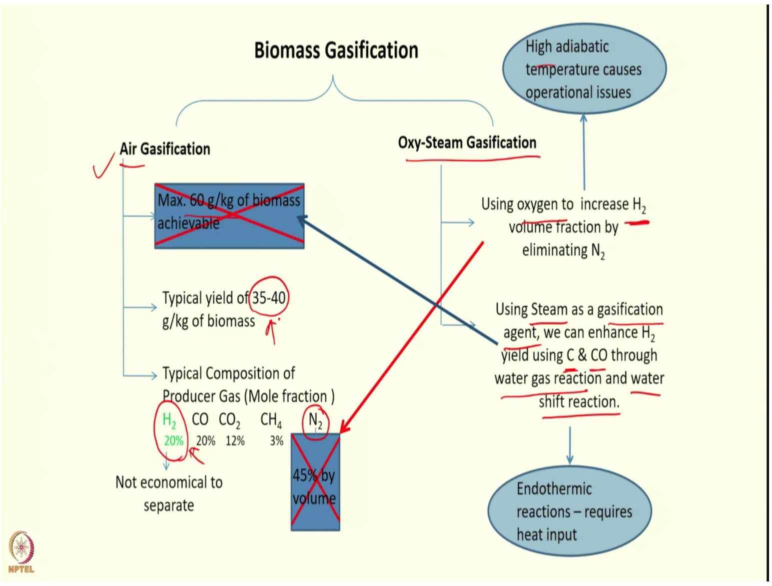

Now, coming to our main point we are looking for hydrogen, we have understood the gasification. I hope you have got the basic chemistry and overall reaction process in the reactor how in a single reactor itself we are able to produce gas and the basic chemistry also, but our intention is how to get the higher yield of hydrogen.

So, there is a limitation by the air gasification; so, in the air gasification what we have is we are just limited by around 60 grams of hydrogen in the biomass. Then typically only 35 to 45 grams of hydrogen per kg of biomass that is only achievable. And another issue is this nitrogen, which comes with the air because air 77 percent by volume is nitrogen. In the gas also we get around 45 percent by volume of nitrogen only and hydrogen is limited only around 20 percent.

So, then it becomes very costly or non-viable to separate it, once is this small amount of hydrogen in the yield as well as the low fraction; so, the separation also becomes a little bit costly. So, the process that can do away with this limitation is first is using the oxygen, to increase the hydrogen volume fraction by eliminating this nitrogen.

So, if you remove this automatically hydrogen volume fraction will go up approximately it will get double, but it will not increase the amount of or the mass of a hydrogen in the product gas. But that we can enhance by using steam, steam as a gasification agent. So, we have seen with the reaction with carbon and carbon monoxide through water gas reaction and water gas shift reaction; so, these two reaction.

So, again if we look into that; so, these two reaction; so, water gas reaction with carbon plus H2O and the water shift reaction that is carbon monoxide plus hydrogen. This gives us a high amount or excess amount of hydrogen through it and here we can get more than 100 grams of hydrogen by it. And this is highly endothermic and then this is the high adiabatic temperature causes operational issues.

So, if we use these two alone then we face problem, but if we combine these two through oxy steam gasification replacing nitrogen by steam. So, oxygen fraction will still be low it will not give us operational issues and steam fraction which participates mostly in the reaction in the reduction zone will give us high amount of hydrogen by reacting with carbon and carbon monoxide. So, these two combined together give us a very good stable operation of the reactor gasification system with the high amount of yield of hydrogen.

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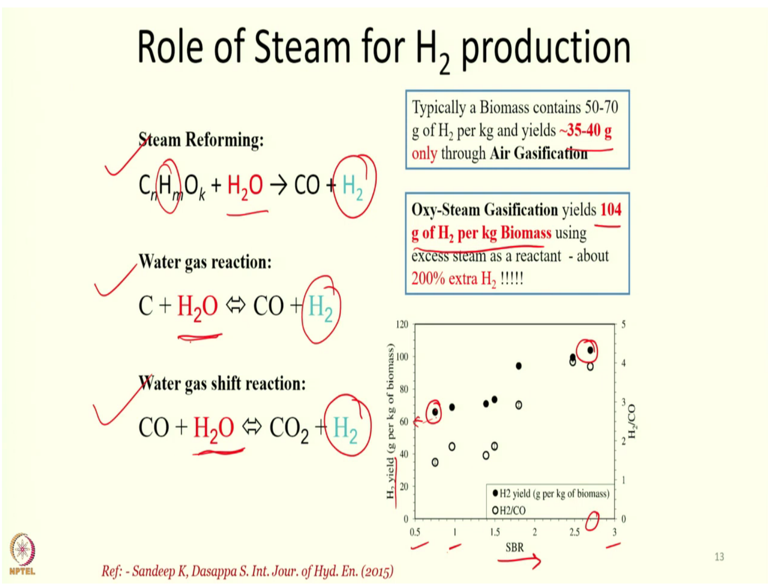

So, here again what is the role of steam here is one is the steam reforming, steam reforming then the water gas reaction and the water gas shift reaction. So, here we can see it is the steam which is giving us this hydrogen mostly. So, here hydrogen is coming from here that we have seen in the pyrolysis process also, but here in the water gas shift reaction H_2O is coming purely from steam in water gas reaction also hydrogen is coming purely from the steam.

So, typically biomass gasification air gasification which is limited by 35 to 40 grams here we can enhance it we have got around more than 100 grams of hydrogen per kg of the biomass. And that is almost 200 percent extra and this is the beauty of the system that we can use the carbon in the biomass to get the hydrogen.

So, and this is one of the results from the publication that as we increase the steam to biomass ratio. So, this is steam to biomass ratio as we increase from 0.5 to 2 to 3 and when our hydrogen yield is also increasing. So, y axis is hydrogen yield is around 66 grams, it goes more than 100 grams at the equivalence ratio for around 2.7; so, that is the beauty of this system of the oxy steam gasification.

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Oxy-Steam Gasification

H_2O/Biomass (mass basis)	0.4	0.75	1	1.4	1.8	2
H_2 yield (vol. fraction, %)	41.8	45.2	43.1	49.6	51.7	50.5
CO yield (vol. fraction, %)	27.6	24.9	26.5	17	12.8	13
H_2 yield (g/kg of biomass) – Experimental result	66	68	71	94	99	104
Percent of H_2 yield from steam (%) (65.5 g H_2 in biomass)	21.4	20.2	28	43.7	44.3	48.1
H_2/CO	1.5	1.8	1.6	2.9	4.0	3.9

Given Biomass contains 60 g H_2 per kg of Biomass. Process adds extra 44 g H_2 from steam to yield 104 g H_2 per kg Biomass

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So, this is the results as we increase the steam to biomass ratio our hydrogen yield is increasing from around 66 grams to 104 grams. And typically, the biomass gasification biomass contains around 60 grams and we are able to add 44 grams extra to get the 104 grams of hydrogen per kg of the pyrolysis.

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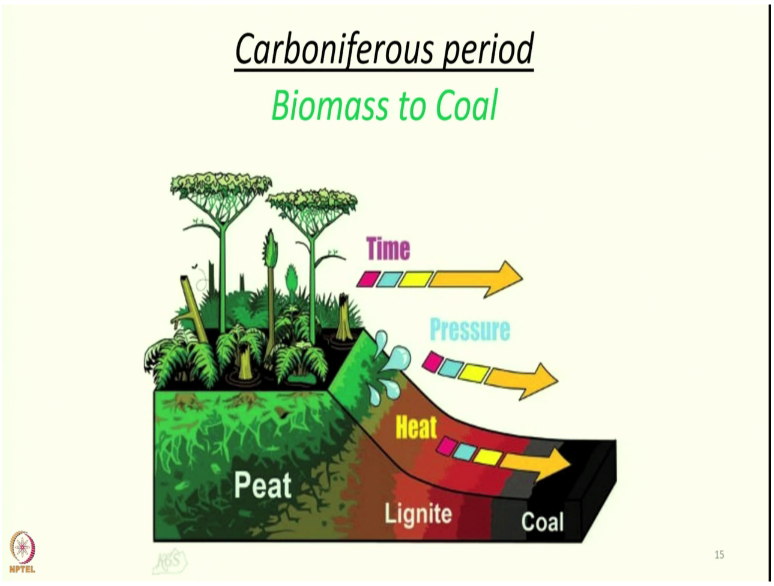

So, with this slide I would like to end or summarize this particular module. So, here in the starting we have looked into the chemistry of the pyrolysis process we are we are using the bio-oil reacting with a steam in a catalytic reactor to get more hydrogen. And then move to the gasification process where we try to understand the air gasification the chemistry behind it. How in a single reactor unlike the pyrolysis process where we have to go through two reactors, one for pyrolysis and one for pyrolysis bio-oil catalytic conversion to more hydrogen.

Here in the single reactor, we are able to get in the gasification process pyrolysis combustion of the volatiles and then the reduction of the CO_2 and H_2O by carbon. Now, that is a charcoal itself and then we and we use extra steam we can enhance the hydrogen production just like we did in the pyrolysis process, but in a single reactor. So, here we summarize the module for this pyrolysis and gasification part. And the biomass part in the next module we will discuss about the coal and the coal gasification and the hydrogen from the coal in the next module.

Thank you.