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Lecture - 18 Hydrogen Production from Coal

Hello. Welcome, everyone. So, we will be going through our last module, the module number 4 for this particular topic of hydrogen energy from biomass and the coal. In the past three modules we have looked into the biomass different technologies like pyrolysis and the gasification process.

How to maximize the hydrogen yield through that using hydrogen in the biomass as well through the steam as a reactant which reacts with carbon; so, using carbon in the biomass as well as the hydrogen present in the biomass to give you hydrogen. Now, we will discuss about the coal.

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So, when we look into the coal, first we have to identify or understand the fact that the coal is coming from your biomass. So, biomass is what has given us the coal. So, if you look into the time as we all know that there was era called carboniferous period which is actually attributed to bulk of the coal that we have now.

And, the reason being there is a very interesting story about that is that coal that has come through all the era or whatever plants are today what we have, will it give us the coal after millions of years to the future generation?

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Story of Evolution – Lignin-Coal-Fungus https://nautil.us/issue/94/evolving/why-birds-can-fly-overmount-everest-rp https://www.nationalgeographic.com/science/phenomena/20 16/01/07/the-fantastically-strange-origin-of-most-coal-onearth/

So, this is a very interesting story. And, I have given these two links; I would request all of you to go through these two links. It is a very interesting story. A very interesting story that it is the lignin, which has given us the majority of the coal that we have.

So, in the early era of the evolution most of the plants well means not most of the plant, but all the life evolved initially into the under the sea. Then from the sea it came to the ground. But, in the sea there was a unique thing that even if the plant grows tall like this tree, if it grows tall there will be a buoyancy force of the water that will keep it floated. It will not fall under its own weight.

But, when the plants start growing on the land, then the issue of how the tall trees can support itself. So, there was a million of years, millions of years the plant did not have this compound called lignin. So, and this is what you see the shrubs, the grasses and all which are very light in weight which will grow if it they grow tall, they will just bend down and will reach to a particular height on it. But, to compete specially in the thick forest to compete with the sunlight you have to grow tall and that is how the evolution happened.

But, after millions of years the evolution gave this magic chemical that is a lignin. So, this organic compound that is giving the strength, strength and the structural stability to the plants and the trees. So, even it will grow, it will not bend down the tree and even for the smaller plants or the shrubs it gives the structural stability to withstand the heavy wind or the animals or any impact as such.

So, this lignin become a very universal for most of the big plants and trees and all. But, there was a problem that still no microbes to decompose and that issue is still there, but not 100 percent. Just to give you a perspective, all of you would have noticed just imagine a coconut shell or a big tree trunk somewhere lying in the open.

If you have dry leaves, or fruit and all if you see it in the open, it will be just few days, a week or a month and it will completely get decomposed or some insect will come and eat it or microbes will decompose it completely to the sort of powder. But, a coconut shell if you keep throw it in the open, you come back next year that coconut shell still it will be there. You come after 2 years; you may still see it there. You will not see any animal which will eat it, because they do not digest.

You cannot digest the coconut shell. It is very high in lignin, very high in lignin. We do not have enzymes which can digest the lignin. Same thing is with the microbes. Majority of the microbes do not have any enzyme which can digest or decompose this lignin. So, it went again millions of years because, the evolution process is slow. It took again a million of year until a fungus which was found or which was evolved which could digest which could attack lignin and can digest it and decompose it.

But, this fungus came millions of years later and now right now also you can imagine if you are in dry places this fungus which needs high humidity to grow, you will not see this. But, if you are in a very wet area or during the monsoon then only you will see the fungus grows and it grows every anywhere. Even on your wooden table in a wooden shelf, it will grow because it can eat lignin, it can digest it, it can survive on that. And, most of the mushroom it grows on the tree trunk.

So, these are some of the evolution process which took some millions of years and that millions of years is called the carboniferous period. And, in this carboniferous period when the trees after their life they were dying out; every tree will have its own life, every plant will have its own life. Most of the other body parts except the lignin part except the trunk, the branches everything will get decomposed by microbes, animals, insects they will eat it up.

But, this lignin based trunk, the branches they still remained unconverted and they just piled up over the in the jungle and it was not few years, but millions of years. It was millions of years where it has covered the jungles in the forest in the with a pile of lignin. And, then through earthquake or through flood or through something it undergoes the under the ground. And, then under the ground within the thousand years it will decompose slowly, but this is thermal decomposition now.

So, in the lignin, if you give heat it can undergo pyrolysis. A decomposition will happen, but there also lignin is much more stable compared to a cellulose, hemicellulose which also makes a bulk of your plant. So, this peat and then further heat and pressure, high amount of pressure. So, it has heat plus pressure that moves more under the ground, more under the ground, high amount of pressure, high amount of heat; it converted it to lignite and the coal finally.

So, these are typically many people they identifying some literature, you will still find this lignite and peat classified at different category of coal. But, we do not need to go under that thing, but the thing is quality of the coal varies.

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And, how is the quality of the coal is varying is if we look into the fresh biomass. Fresh biomass which will have around 55 to 65 grams of hydrogen per kg of biomass; it has around 50 percent of oxygen in its molecular form. All organic molecules will have 50 percent of oxygen by weight, and roughly around 40 percent of carbon by weight. And, little bit amount of a hydrogen and some other in organics like iron, sodium, chlorine and all it will be there, potassium and all.

It has a calorific value of around 14 to 17 megajoule per kg. Now, when we look into the peat which has come after that it stayed inside the earth crust for around 10 to 15 thousand years. It is a long period, but still you have some 60 percent of organic matter still left. So, that is the you can see how slow the process was and how the slow the process is of the coal formation from the biomass. So, still after 10 to 15 thousand years 60 percent organic mass is there.

There is a very small increment in the calorific value. Then after 6 crore years or after 60 million years what you get is a lignite, which now has high amount of carbon and lot of oxygen has gone out as a moisture. Because, it will be oxygen will be embedded in that the dry carbon and the coal will have or the dry coal will have less amount of oxygen in it.

The calorific value also almost doubles, if you look into 14 to 17 megajoule in biomass and you have almost double the calorific value now. Then, again few more crore of years or more than 100 to 300 million years, now what you have got? The carbon content has now increased to 60 to 80 percent.

The decomposition is happening, hydrogen and oxygen is leaving the system, hydrogen and oxygen is leaving the system. Now, you have no organic molecules left. But, just see the time scale; 10 to 30 crore years, or 100 to 300 million years. That has been the time scale when the trace of the organic compound has left, still and the calorific value also improves in that.

And, the anthracite which is like one of the best quality of the coal, that you will get around 35 crore or 350 million years' old which has 80 to 95 percent of coal, negligible amount of moisture, very high calorific value. But, hydrogen content is very low, only around 20 grams' hydrogen per kg of coal. So, that is the overall evolution of your coal from the biomass. So, that is why I kept the these two together.

Now, we understand what the biomass and how much is the biomass having hydrogen. And, then and through this long duration of period and under the intense temperature and pressure inside the earth crust, then your biomass is converted to your coal of different categories, under the different timeline of the period. And, every type of coal will have different content of your hydrogen, but anthracite or bituminous will have very less amount of hydrogen in it.

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Now, this is some of the figures that is the 1st peat decay of the vegetative material, 2nd stage is the lignite, 3rd stage the bituminous coal. This you can see like a blackish which looks like coal and anthracite coal considered by some type of metamorphic rock. So, in the literature we will see the different definition of this coal. But, this is more having high amount of carbon in it, hydrogen is very low in it. Most of the hydrogen has been lost during the coal formation.



So, now looking into the coal gasification. So, this gasification overall chemistry is similar to what we have seen in the biomass gasification process. It is the early 19th century technology. Coal gas was used to light up the streets in many European cities. So, that is coal gas and this is nothing but your carbon monoxide plus hydrogen. So, this was used to light up streets. So, that was a street light system in the 19th century. So, you can just imagine how old and what could have been the gas which is carrying carbon monoxide in it is used for the street lighting; interesting it, is not it?

Now, going to the quality of the product gas depends on the quality of the coal used. If the coal has high amount of hydrogen, it will have a little higher amount of hydrogen, even though coal gasification it is the inherently the steam gasification. But, if the coal also is of poor quality, it will have high hydrogen, it will have high amount of hydrogen compared to high quality high grade coal will have less amount of hydrogen in your gas or the synthetic gas.

Because, steam gasification and 2 stage gasification plus shift reaction is used to enhance the hydrogen yield. So, this is the hydrogen yield, again the shift reactor that we have seen the reaction of carbon monoxide plus H_2O that gives you H_2 plus CO_2 . So, to enhance the and this is the 2nd stage or what we say the catalytic convergence state which is used for the coal gasification process for hydrogen yield.

H₂ production through Oxy Coal gasification Coal is gasified first followed by product gas passed though catalytic shift reactor with steam supply • Partial O₂ supply helps in exothermic oxidation and hence sustaining overall process. Boudouard reaction $C+CO_2 = 2CO - 172,600 \text{ kJ} \rightarrow$ Water gas shift reaction CO +H2O = CO2 +H2 +41, 200 kJ ()

Now, hydrogen production through coal gasification. So, coal is gasified first followed by the products gas pass through catalytic shift reactor with steam supply. Partial oxygen supply helps in exothermic oxidation and hence sustaining the overall process. So, this is similar. In the biomass gasification we have seen it is the volatile which was the gas reacting with oxygen and the exothermic reactions of volatile combustion was sustaining the endothermic reduction as well as endothermic pyrolysis and the drying process.

But, here the solid fuel that is the carbon itself is undergoing oxidation; the reaction will rates will be slow. But, if the temperature is maintained high, if you designed a reactor in such a way; reduce the size of the coal particles to very small you can get a very high reaction rates here as well and that is what is done.

Typically, the pulverized coal is what is used in the coal gasification systems. Very small micron size of coal particles is used which enhances the surface area and that is how it enhances the oxidation process of a coal for this exothermic reaction, which has sustained the overall process.

So, again the same Boudouard process which is endothermic, C plus CO_2 and the water gas shift reaction CO plus H2O which gives which is also mildly exothermic process which is prominently sort of present here. We are not looking into hydrogen based reaction because; hydrogen is not much into the system as such. So, this system and then this carbon monoxide can be used through shift reaction to enhance the hydrogen content. And, this is the carbon monoxide which can be used for further 2nd stage with the separate shift reactor, where we can have the hydrogen plus CO_2 giving you high amount of hydrogen. So, this is the simple chemistry. Unlike biomass gasification reactor, here the shift reaction is preferred to be in the separate 2nd stage as such.



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Now, looking into the coal gasification process. So, coal gasification process is one of the higher amount of hydrogen around 25 to 30 percent global hydrogen is coming through coal gasification. And, you can imagine there is a huge demand and then there is a huge requirement of big plants and all.

This is one of the very simple I mean it is not very simple complex, but very economical design. You use the underground or the earth itself as a for the supporting the reactor. So, here you can see this is your earth, inside it they have dig up the reactor part and they had made the reactor inside. The coal is supplied from here; you have an oxygen separation plant. Oxygen is separated from the air and is supplied here and then you get the gas from it and you sustain the overall process.

So, overall the very big reactor you can make it inside the earth itself. So, this is the very popular coal gasification system and it is a pulverized. So, the typically the coal particle size is of the 50 to 100 micron and typically the reactor type is pulverized coal in entrained flow or fluidized bed reactor. So, these are not preferred much into the fixed bed reactor like the

earlier gasification that example that we have seen in the figure that was the fixed bed, packed bed reactor, where bigger size of the biomass was used.

But, here the smaller, very fine size of particles are used because you have to enhance the solid gas reaction and that can be enhanced by increasing the surface area of the coal particles. And, that is done by pulverizing it, pulverized coal and the entrained flow or the fluidized bed reactors are preferred here.

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So, in the hydrogen production system what you have is, you have a crushed core that is pulverization happens here. You put it in the micron level size and the ash comes out the solid. Whatever the gas comes out you remove the particulate matter that is still some dust, some ash will be flowing with it. The solid particles you remove here, then you have a special requirement of sulphur removal.

In typically in biomass most of the biomass will not have much of a sulphur, that is problematic enough to remove it. But, in the coal the sulphur content is significantly high and this needs to be removed before you push it into the hydrogen separator. Because those reactors and also this water gas shift reactor, the catalyst use gets poisoned because of the sulphur present. So, that is how you need to remove the sulphur.

So, there is a sulphur removal unit and after that you remove the CO_2 and H_2O , H_2O easily gets removed by reducing the temperature below 100 degrees during by condensation. CO_2 is

removed typically by a mean solution or by high pressure water spray. And, then this particular carbon monoxide or hydrogen you can use for different chemical or the fuels like we have talked about for example, the FT synthesis; which will give you petrol or diesel.

But, if you are looking for hydrogen then you have to go through a 2nd stage reactor that is a water gas shift reactor. Because, it is the catalytic reactor for high amount of hydrogen to be produced, it cannot be clubbed here where there will be lot of sulphur present. In this particular reactor it will not be there. We need to remove the sulphur first and then feed it into the shift reactor and then by enhancing the hydrogen we get more hydrogen. So, this figure is talking about the fuel cell, but we can use the hydrogen for any purpose after separating it from the system.

So, this is how the thing is there. One of the very interesting sort of philosophy or the new thing that is getting prominence in research in India as well is the underground coal gasification. So, let me just spend few minutes here, quite an interesting thing. This is not again new technology; Russians have mastered almost 50-60 years back.

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So, what exactly it is, you like we have seen here in this particular reactor you design a reactor, but in the underground coal gasification; what you doing? You are using the mine itself as a reactor. Here what we have done is we have mined the coal and supplied here. This is coming from the mines. We supply it here, we pulverize it. We do the processing, transport, everything we do and then we push it into the reactor.

We are just saving on the cost of the construction of the reactor. But, here what philosophy is once you start getting this coal out of the cavities, you still have empty cavities in it. Why not use these cavities itself as a reactor? So, these cavities are itself of the coal which has high surface area, because it is a huge mine. All the surface exposed will be able to give you a reaction site.

So, all these things are here and in this cavity what you are doing is you have an injection well. Through injection well you push high temperature steam as well as some amount of oxygen.

And, then you push into this cavity, here it will react and it will give you. In the production well, you extract it up where you get carbon monoxide and hydrogen from the system. And, then after that you do the gas cleaning, because of the reactor everything you have got the gas cleaning then pass it through sulphur removal then water gas shift reactor, enhance the hydrogen content through it or whatever you want to do it.

But, the overall reactor is underground. So, this whole huge cavities, it will not be just big like a building, it will be kilometres long. So, these are the sort of a huge reaction sites that you can enhance, once you can have a control over it. But, yeah it is not as easy as it looks because, with the reaction and all this some of the walls it start collapsing, start collapsing and you need to have a control over that. Russians master it long back, but it is not a open technology from that, still I think one or two underground coal gasification mines are still operational in old part of Russia.

I think before the USSR, it was its in I think Kazakhstan or Uzbekistan. But, right now China is also investing a lot in this particular technology. And, here this carbon monoxide and hydrogen you can put it through and put up a methanol plant, put up a methanol plant. From it methanol the major feedstock is carbon monoxide and hydrogen and then you can get methanol through catalytic conversion process.

So, they are doing the coal to methanol projects China is doing that and then India is also looking for that the reason being reserve of coal and the energy independence. So, you do not know you never know like even in the current time or maybe couple of months back, we have seen the Russia and Ukraine conflict. You never know when the energy supply through natural gas or the petroleum will get interrupted. Every country, every sovereign country looks into energy independence. So, that we have enough of all type of energy requirement we can fulfil at our own. So, here in India we have a huge coal reserve. But, our coal one of the problem is our coal is not of a very good quality for the use in steel industry or the thermal power plant. Because of which the thermal power plant it is used, but the quality is bad. It has very high amount of ash, it cannot be used for steel production and all which requires a high quality, high percentage of carbon in it.

So, but these are very good for your gasification process. In gasification process once you master underground coal gasification, a huge plant running continuously for the years at a very low operational cost can give you a upper hand over getting the synthesis synthetic gas or the syn gas. And, you can convert it to liquid fuels, methanol, liquid fuels get hydrogen out of it and use that hydrogen.

So, energy independence is one of the things and underground coal gasification a cost effective gasification process can be one of the key for it. So, with this I just like to conclude this overall module. And, I hope all of you have understood and appreciated the role of biomass and coal for the hydrogen production, the different process and the chemistry behind it.

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And, yeah just with the thought; there is no better way to sequester carbon than preserving nature. Even if we are using biomass, let us use the agriculture waste or the municipal waste whatever the carbon is coming through the waste, let us react with steam and produce

hydrogen from it. So, with that note I would like to thank for taking up this course and going through this set of lectures.

Thank you.