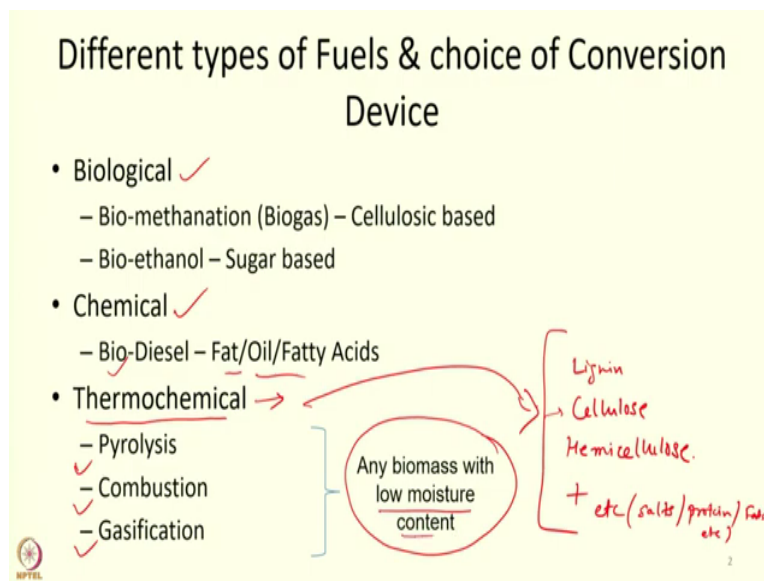


Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 16
Hydrogen Production from Biomass Part - 2

Hello, welcome everyone. Welcome again for our 2nd module.

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So, as you have seen in our last module so, we have discussed about the different type of fuels and then different type of fuel choice and conversion device. So, when we look into the biological pathway and we look into the biological pathway we have this bio methanation. So, bio methanation is nothing but the biogas generation and which we have seen it is mostly on the cellulosic based feedstock. So, if we have good cellulose in the waste then this technology is the most suitable one for that.

And, then when we look into the bio ethanol generation then we need something which is more on the sugar based side. So, biologically these two are the prominent technologies that convert our waste to energy. When we look into the chemical process so, chemical process we saw that biodiesel which requires mostly the fat, fatty oil and fatty acids.

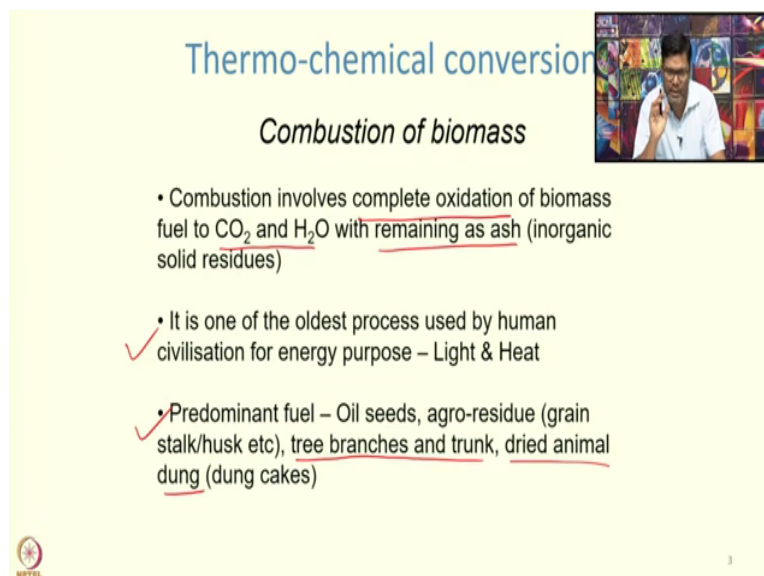
So, they are very much specific to a particular type of compounds or chemical species in the feedstock or organic species which they are selectively converting to the desired energy

carriers whether it is methane or ethanol or the biodiesel. So, but when we look into this thermochemical pathway which is focus of our study because this is process which is giving us the hydrogen. So, when we look into the thermo chemical pathway we have this pyrolysis, combustion and gasification. These three are the prominent technologies which are classified under thermo chemical conversion.

So, here we have the flexibility that any biomass with low moisture content can be converted. So, we have seen that mostly the three compositions are lignin, cellulose and the hemicellulose. So, these three are major component plus we have something like salts, something we have protein and then we have fats etc. So, these are mostly the less component in the biomass waste and especially if we are looking into the something organic waste which is coming from the plant based species.

So, it is agro residue or even the cellulose makes the major compound for the animal excreta. So, these are three makes the bulk of your thing. And, thermochemical conversion it does not have any distinction or preference for this thing; only thing it needs to have a low moisture content. So, we will see what exactly this thermochemical conversion process is and combustion is something which all of us know. So, we will start with that.

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Thermo-chemical conversion

Combustion of biomass

- Combustion involves complete oxidation of biomass fuel to CO_2 and H_2O with remaining as ash (inorganic solid residues)
- ✓ It is one of the oldest process used by human civilisation for energy purpose - Light & Heat
- ✓ Predominant fuel - Oil seeds, agro-residue (grain stalk/husk etc), tree branches and trunk, dried animal dung (dung cakes)

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So, thermo chemical conversion, combustion of biomass: so, combustion of biomass is one of the oldest process or the technology that human civilization has invented controlled fire. Control fire was one of the major or one of the I would say the most important finding of the

human civilization for the light and heat and keeping the animal away from them. So, this was one of the most significant invention or the discovery by a human civilization.

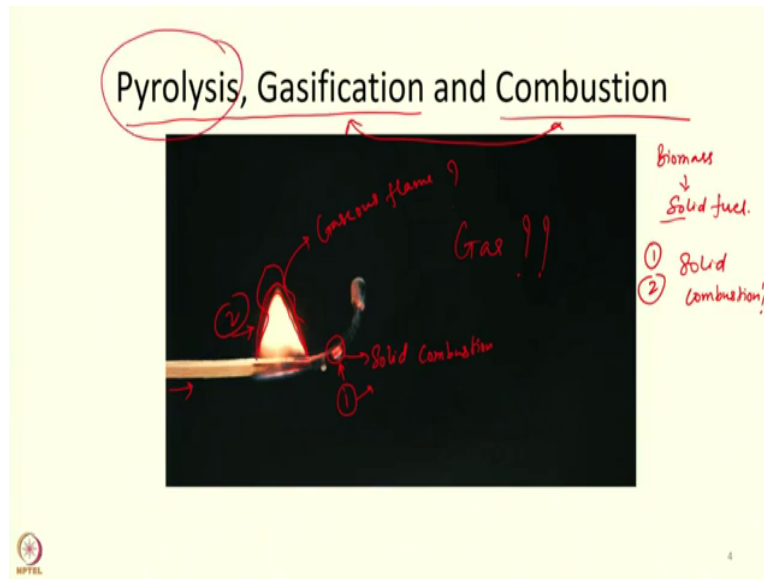
So, what exactly combustion is technically speaking? We all know what combustion is. Something burning, yes, so, technically which involves the complete oxidation. So, combustion which involves the complete oxidation or the stoichiometry combustion which we call complete oxidation of biomass fuel to CO_2 and H_2O with remaining coming as ash. So, that we classify or technically as combustion.

So, our predominant fuel that we have been using for centuries it is oil seeds, agro residue, the grain stalk and husk. So, agro residue is not something new that we are trying to use it to get rid of the problem of paddy straw burning; agro residue burning in the fields that is one of the burning issues of the today generation, but it is something which has been in use for centuries.

So, these agro residues have been used as a fuel for cooking as well as a fodder for the animal stock for the cows and buffaloes. So, plus there have been tradition of collecting the tree branches and the broken trunk and broken tree branches, collection of firewood; collection of firewood from the nearby jungle or from the villages which have been the key cooking fuel for centuries or for thousands of years probably.

So, then another is the dried animal dungs. So, animal dung and dry cakes which is quite common still now in our villages and specifically this is one of the very good process to get rid of the animal waste especially in the rural areas. So, this is basically the combustion process technically speaking.

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Now, when we talk about the pyrolysis and the gasification, so, these two seems to be a new term how it is different from this combustion. So, this pyrolysis, gasification and combustion so, these are not something which are very much different, but here we will see the combustion involves this pyrolysis and gasification. So, these are quite interlinked. So, I would like to explain it with an example of a this burning match stick.

So, this burning match stick all of us have seen, have used, have burned it and we know whatever you are seeing here it is very much familiar to everyone one of us. So, when we look into this particular thing this flame that you are seeing this yellow luminous flame – this is something which we classify or identify as a combustion process as a oxidation process, and then we have this red charcoal burning.

So, these red charcoal burning and then this is a luminous flame. Both of them are oxidation. Both of them are combustion technically in both the part the combustion is going on. So, then the question comes what is the difference between these two. If I ask you a question you have biomass is a solid fuel; and then we are seeing these two flames or these two oxidation zone or combustion zone. I would say combustion zone we are seeing this one and this two.

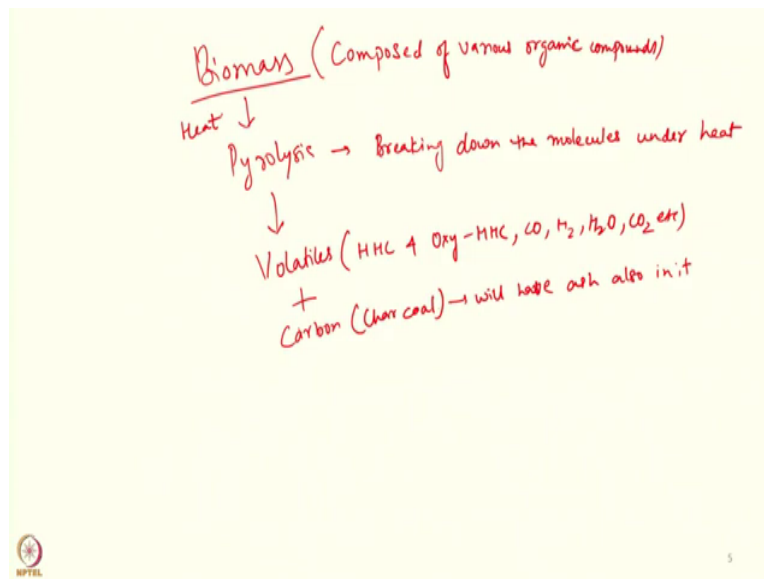
So, 1 and 2 which one is a solid combustion? So, that is a question. So, just take a pause of 10 seconds, think. Think that this red charcoal burning is a solid combustion yes or no, and this flame luminous flame; yellow luminous flame is it a solid combustion or a gaseous combustion. So, just give it a thought.

So, once you look into that just by common sense that how do we see we do not need to go into the detail of technical definition of solid combustion and gaseous combustion. Common sense says that some gases if it is burning if we it will be not restricted to one place if we blow it with air you will see a moving flame. So, it will move. So, this particular flame will move.

It is not something solid that is fixed at one place; it is something fluid which is flowing. So, it is either liquid or it is a gas. So, our 1, this is your solid combustion. If you blow it this charcoal is not going anywhere and this charcoal the carbon in this charcoal is getting oxidized which is in the solid form. So, this is classified as solid combustion.

Now, what this is a gaseous flame? Now, the question comes from where does this gas comes? Now, that is the process called pyrolysis. So, in pyrolysis what happens?

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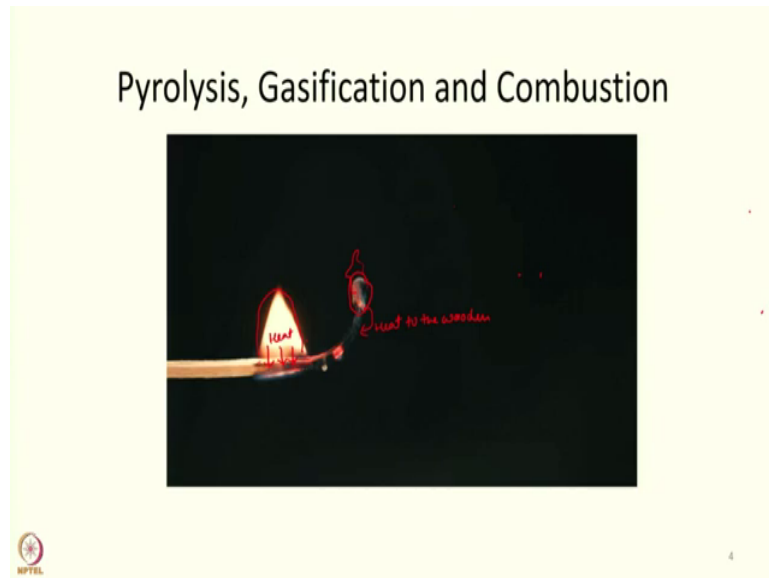


In pyrolysis what we do is whenever we have a biomass; biomass it is nothing but composed of various organic compounds. So, when you supply heat, what happens it undergoes pyrolysis. So, pyrolysis means pyro means heat and lysis means breaking down. So, pyrolysis means breaking down the molecules or the organic compounds under heat.

So, you are supplying the heat or the energy basically if you want to break a bond you need to give some energy to it and that energy is actually supplied in the form of heat. So, you are

supplying the heat and then it is getting broken down and then you can recall that how does your overall combustion process of this thing.

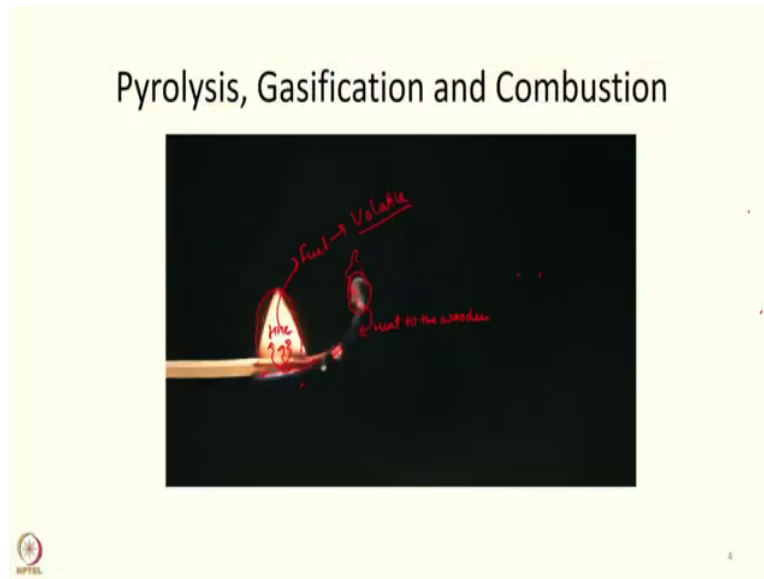
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So, now you can identify this as some chemical which you rub on the match stick side and then it will catch fire. It will catch fire and what it does? It supplies heat to the wooden stick and then this is what happening here. So, this flame is not only supplying heat in the surrounding, but also it is supplying heat in the bottom side to this wooden piece of the match stick.

So, and you can see that here your some of the portion some of the portion is has gone blackish; that means, it has it is undergoing the thermal breakdown. Organic compounds which are essentially the higher hydrocarbon, oxygenated hydrocarbon, so, they are undergoing series of thermal crackdown. It is undergoing a thermal crackdown and releasing the lighter compounds into the atmosphere.

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So, lighter compounds when it undergoes it comes out here and this is nothing, but your fuel your higher hydrocarbon is actually coming as fuel and this is called volatile. So, what does this pyrolysis process produce? It produces volatiles and volatiles is nothing but higher hydrocarbon. So, short form for that HHC higher hydrocarbon and oxygenated higher hydrocarbon and plus it also has carbon monoxide, hydrogen, H_2O , CO_2 .

So, there is lot of more than typically if you do a pyrolysis of a biomass you will see that there are more than 200 species different chemical compounds that comes out of the biomass during the process of pyrolysis. So, this is what is happening, but is it the only thing that you get from this pyrolysis? No, what you are seeing here is you are also seeing the left over this.

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Pyrolysis, Gasification and Combustion



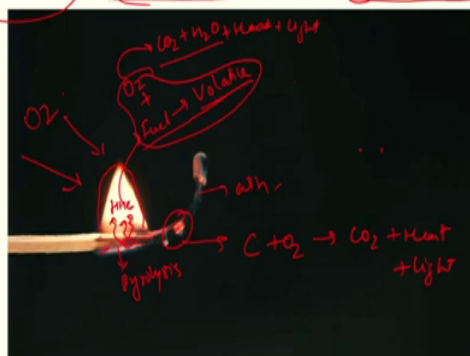
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So, this is what is coming as another product of the carbon in the form of charcoal. So, typical language we call it charcoal and this will have ash also in it because ash those inorganic compounds sodium, potassium all those things will not undergo means will not get oxidized nitrogen and all compounds.

So, they will remain in the solid form in different whether it is oxidized or different other form but it will remain in the solid phase and will be embedded in your charcoal and finally, if the charcoal will get burned.

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Pyrolysis, Gasification and Combustion



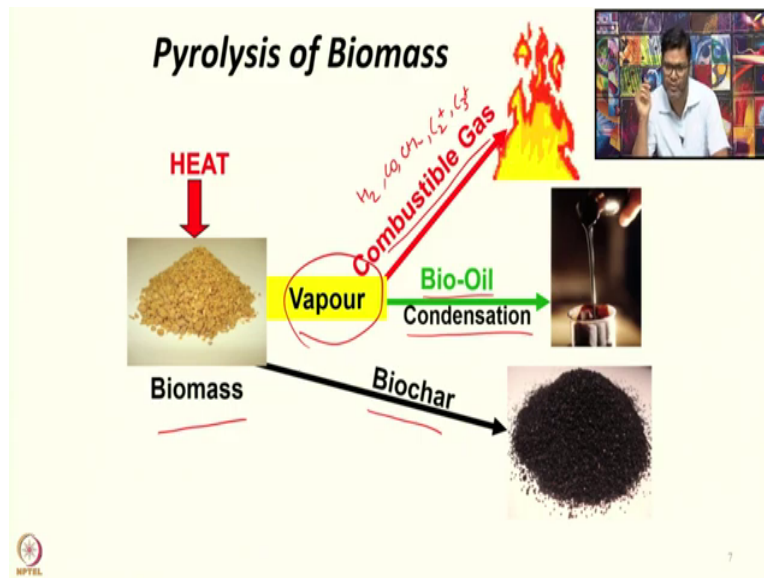
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So, when charcoal gets burnt what you get is if your charcoal gets burned finally, you will get ash and then all the combination of all this process is called the combustion. So, here what is happening is, you are doing a pyrolysis here then you are generating fuel that is volatile. And then you are getting oxygen from the surrounding air and this is reacting with oxygen to give you $\text{CO}_2 + \text{H}_2\text{O} + \text{heat} + \text{light}$. So, here we are seeing light also as energy and heat also coming out.

So, heat and light, but this CO_2 and H_2O is released when you are having this oxidation of this volatile and plus here what you are seeing is carbon is getting reacted with oxygen to give you $\text{CO}_2 + \text{heat} + \text{light}$, if you want to get this light from this small red hot burning charcoal. So, this is what is we identify as combustion is nothing but combination of your pyrolysis and we will see that where does this gasification comes into picture.

So, in gasification it is something where pyrolysis combustion is both are actually happening. So, we will take this gasification a little later in the next module. What we will do is we will continue with the pyrolysis process.

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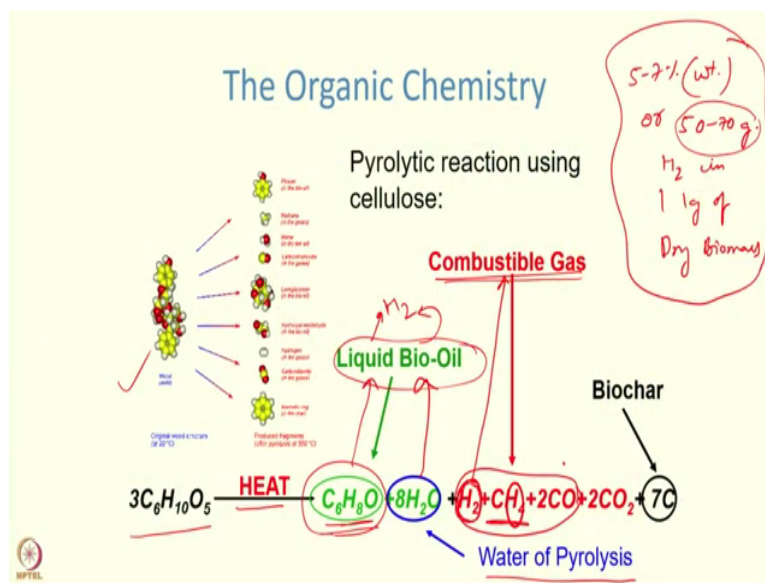


So, pyrolysis, I hope you understood that whenever we are breaking down the biomass by supplying heat pyrolysis happens and in the pyrolysis this biomass is getting converted into something called as vapour. Because it is at high temperature everything you will see it is coming out as a vapour, but if you bring down at the room temperature, then you will see that you will get some as condensate which is technically called as bio oil which is higher

hydrocarbon compound which remains at liquid at the room temperature. So, this is what happens in this case.

And, combustible gases which are essentially the lighter compounds like you will get hydrogen, CO, then methane, then your C₂+ compound, C₃+ compound. So, they will remain in the gaseous phase under the ambient condition. So, they are combustible gases and then condensate bio-oil and then solid residue of the pyrolysis we have seen in the previous slide we get the charcoal. So, this charcoal is also part of that.

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So, now when we look into the organic chemistry of this so, typically this is one of the example of your glucose. So, this is simple glucose where your glucose molecule when you supply heat breaks down into liquid bio-oil. So, this is C₆ compound which will remain in the liquid state once you bring down it to room temperature and then methane, hydrogen, carbon monoxide.

They are combustible gases and plus you are getting bio char carbon as a residue and then also you are getting as the water of pyrolysis. So, this is water, this will also come in the solution with the bio oil, you have to separate it. So, that is one of the challenge and one of the process that you have to separate this water of pyrolysis if you want to use the liquid bio oil. And, what is the use for liquid bio oil that we will see in the next slide.

So, here we have seen that our hydrogen is coming out as one of the product in the combustible gas and here in this particular course we are interested in this hydrogen. But, also we will see that this liquid oil will also give us hydrogen and that is how it gives us so, let us see.

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Different Pyrolysis pathways → $> 725^{\circ}\text{C}$
↓
 $\sim 900^{\circ}\text{C}$

| Mode | Conditions | Liquid | Char | Gas |
|----------------|--|--------|------|-----|
| Fast pyrolysis | Moderate temperature, short residence time | 75% | 12% | 13% |
| Slow Pyrolysis | Low temperature, very long residence time | 30% | 35% | 35% |
| Gas production | High temperature, long residence time. | 5% | 10% | 85% |

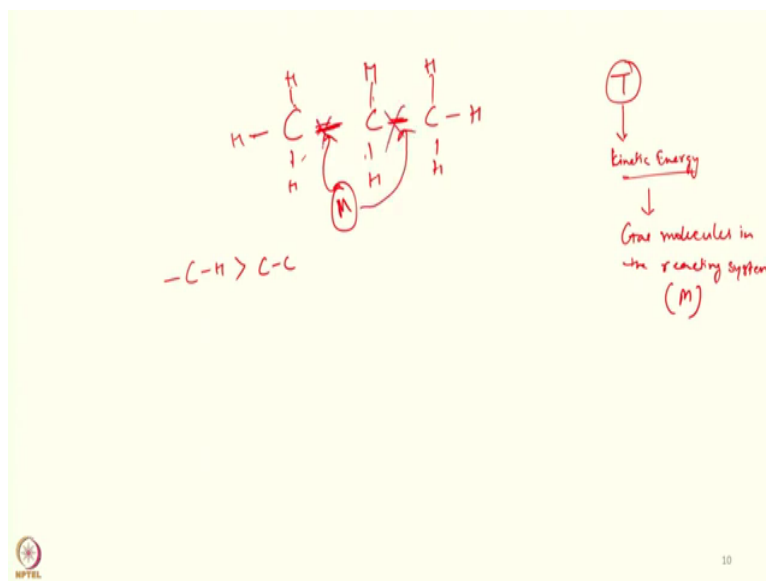
Product yields (dry feed basis) for pyrolysis of wood.

$\text{H}_2 \uparrow$

So, before going into the chemistry of getting hydrogen from the bio oil or the liquid condensate, different pyrolysis pathway depending on what is the temperature and what type of product do we get. So, these three are the major broad classification of the pyrolysis. So, first is the fast pyrolysis where we do it at moderate temperature and short residence time; and then slow pyrolysis where we do it at low temperature and very long residence time. And then gas production where we look for high temperature and long residence time.

So, these three and here we are seeing that when it is short residence time moderate temperature than what we are getting? We are getting high amount of liquid. When we are doing slow pyrolysis we are getting high amount of solid char and when we are doing looking for gas production high temperature and long residence time we are getting this high amount of gas. So, to understand this we have to understand the very basic chemistry of how this pyrolysis is happening and what is the role of temperature and the residence time.

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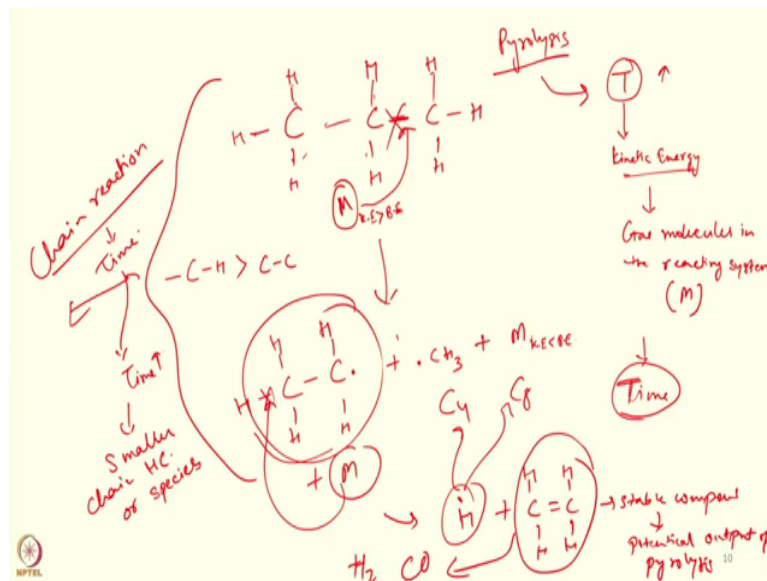


So, if we look into the any higher hydrocarbon we will not take very long just take the example of your C_3 compound. So, this is nothing but your C_3H_8 . Now, your temperature signifies kinetic energy of the molecules. So, temperature is measure of the root mean scale the average out velocity or kinetic energy of the gas molecules and when we say high temperature means we are giving the high kinetic energy.

And, high kinetic energy and this could be the gas molecules in the reacting system and what does it do? Just take this could be M . This M could be oxygen, M could be nitrogen, M could be argon or M could be even this propane or this C_3H_8 molecule also which has reached to a high velocity or the high kinetic energy it possesses. And, why this is required high temperature for initiating any set of reaction? Because you need to break down any of these bonds.

So, typically what happens is these carbon hydrogen bonds are more stronger or stronger than your carbon – carbon bonds. So, this carbon – carbon bonds here are weaker. So, at low temperature when this M hits here or hits here it will get broken down. So, just imagine that this will get broken down.

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So, what you will get when you reach increase the temperature? When you are increasing the temperature means we are doing the pyrolysis. We are doing the pyrolysis increasing the temperature and then some of the molecules will come and hit this at high velocity and will break the bond. So, you will get C₂ compound and plus CH₃ here. So, these are still radical if we write down it like this. So, we are getting this two radical compounds and now this is happening.

Now, reaction also needs time, reaction is not instantaneously. All these M molecules when this happens this M which had kinetic energy greater than the bond energy in that time or was at high temperature it will come down with kinetic energy less than the bond energy because it has transferred its energy for breaking down the bond. So, here the M has slowed down or the kinetic energy of the system has reduced.

So, it is not that instantaneously when you do or increase the temperature then everything will get broken down at the instant. Also because in one set you are getting this C₂ and C₃ then again some M will come and hit here with high kinetic energy and you will get hydrogen will come out and plus you will get C double bond H - H - H - H which is a stable compound.

Stable compound potential output of your pyrolysis. This is just an example we are biomass is not having this propane as such, but we are getting this C₂H₄ which is a stable compound because at the end of any reaction you will get the species which are stable compounds. They are not radicals or ions or something which they will be stable compounds.

Now, this H is radical and very reactive. It will go and hit something else which will be say C4 compound, there will be some C8 compound, there will be carbohydrates, cellulose, hemicelluloses, lignin. There are variety of things having different bond energy having different chemical structure. Everywhere you will see that they are getting broken down. So, it all these things initiate a chain reaction.

So, whenever we say chain reaction it also involves time and with increase in time if you give more and more time you will get smaller out smaller chain compound; smaller chain hydrocarbon or species or the chemical species will be of shorter chain. So, if you give it a time this C2 compound will also yield this and this can also get converted to CO, H2 and something else.

So, if you give C5, C6, C8 you will see that ultimately everything will come down to C3, C2 and all those things, but you need to give time. So, that is what is happening here and we see in this particular slide, if you give short residence time and moderate temperature. So, moderate temperature what happens is at the moderate temperature your overall kinetic energy of the reaction system is low. You do not have enough energy to break some of the tough or stronger bonds.

Not all the bonds in this thing will have the same energy level in typically this pyrolysis happens it starts at around more than 175 degrees centigrade and it continues up to 900 degrees centigrade. Some of the tough thermally very stable compound thermally stable they are very strong bonds and they are lignin's. Lignin's, the cellulose and hemicellulose start disintegrating or start breaking down at the lower temperature starts with the hemicelluloses.

Hemicellulose, some of the bond energy is low. It is you will see that 175-180 degrees they will start breaking down, but lignin will not start breaking down below 450 degrees or so. So, every different compound have a different number of bonds and every bond will have it is own bond energy. So, if you have moderate temperature then many of the compounds you will not be able to target. And, another thing is short residence time whatever you have disintegrated it will mostly be still be the large hydrocarbon compound which will be in the liquid state at the ambient temperature.

So, you will get very less amount of gaseous product in it, but then the same thing if we go for long residence time and increase the temperature also little bit, then you will see that whatever this liquid compound was it will also start getting converted to smaller hydrocarbon

that will be in gaseous state. And, also you will see that some of the char which still has lot of organic molecules still unconverted. This charcoal and this charcoal does not mean that it is only carbon still they will have some hydrogen and oxygen in it.

And this particular thing you will see that it is getting reduced and you will get converted to this liquid and then liquid will get converted to gas. So, a charcoal output is also coming down. And, then when we look into a low temperature, but very long residence time low temperature many of the organic molecule will not be able to specially the lignin and some of the cellulose which also get disintegrate or cracked down at the high temperature which charcoal yield will be still very high ok.

And because you are giving the long residence time your liquid thing will come down and your gaseous output will increase and this liquid thing will reduce. So, this is the effect of the long residence time and your charcoal still is high because you have given very low temperature. So, depending on what type of output you want you go for different pathway.

And, here what we are looking for? We are looking for more of the combustible gases because this hydrogen is in the combustible gases. The more the gas you have you will have more amount of hydrogen in it. So, for high amount of hydrogen production we go for the high temperature long residence time of the pyrolysis process. So, this is about basic of the pyrolysis.

We will go further after pyrolysis also can we do something with this liquid whatever this liquid is what we discussed in the previous slide that how we get the liquid bio oil also to the hydrogen. So, we are just looking into whatever hydrogen is there in the biomass and typically it is around 5 to 7 weight percentage by the weight or 50 to 70 gram of elemental hydrogen in 1 kg of dry biomass.

So, this is something present there and something we can get it from the combustible gas you get it in the gaseous state hydrogen, but still there will be something which will be in the embedded in CH_4 which will be in the liquid bio oil and that how we get it. So, that we will take up in the next module and we will discuss on this which is actually the more industrial way or the effective way of harvesting the hydrogen or at least we want to go up to 50 to 70 gram whatever is the hydrogen there we want to extract that and can we extract more than this also.

Can we get more this we will try to understand in the next module. So, in this module we will stop here.

Thank you again for your patience and giving time.