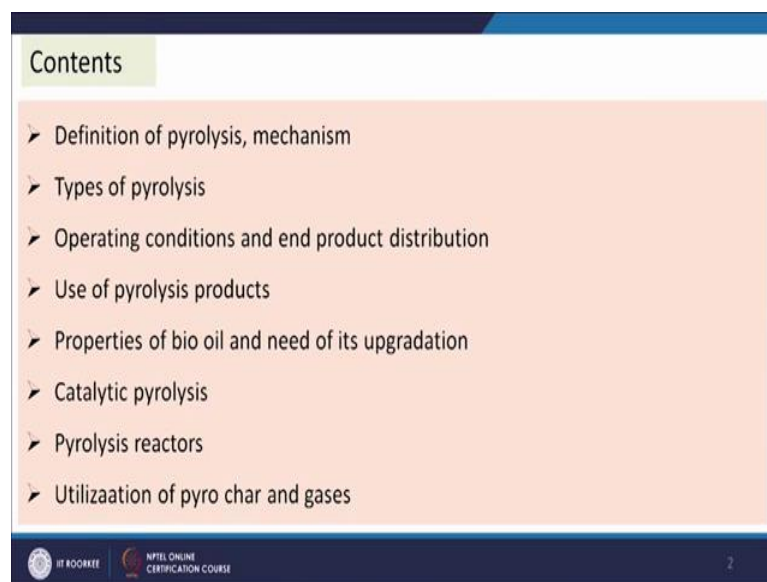


Waste to energy conversion
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Lecture – 14
Energy production from wastes through pyrolysis-1

Good morning everyone. In the last modules we have discussed on incineration and gasification two important route thermal route for the conversion of waste to energy in this module we will discuss on pyrolysis which is another route that is thermal route for the production of energy from waste and biomass.

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Contents
➤ Definition of pyrolysis, mechanism
➤ Types of pyrolysis
➤ Operating conditions and end product distribution
➤ Use of pyrolysis products
➤ Properties of bio oil and need of its upgradation
➤ Catalytic pyrolysis
➤ Pyrolysis reactors
➤ Utilizaation of pyro char and gases

We have discussed that incineration is mostly used for the conversion of biomass and waste to energy followed by gasification and then pyrolysis. So, this pyrolysis process is not widely used in commercial scale, but extensive research is going on for the development on this and. So, in future we may get commercial scale in applications of pyrolysis.

In incineration we used excess amount of oxygen in gasification we use controlled amount of oxygen and in pyrolysis we use no oxygen theoretically, but some amount of oxygen may be allowed and some new research is going on. So, pyrolysis in presence of less amount of oxygen in this module we will discuss on the definition of pyrolysis its mechanism type of pyrolysis operating conditions and end product distribution use of

pyrolysis products properties of bio oil and need of its up gradation catalytic pyrolysis pyrolysis reactors and utilization of pyro char and gases.

We will divide the discussion into two parts in the first part we will discuss from definition to the catalytic pyrolysis and in the second part we will discuss on pyrolysis reactors and utilization of pyro char and gasses.

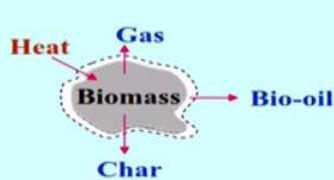
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Pyrolysis



Definition of pyrolysis

- Pyrolysis = pyro (fire) + lysis (cutting)
- Thermal decomposition of carbonaceous material by the heat in absence of oxygen

Biomass/waste $\xrightarrow{\text{Heat}}$ Char + Bio-oil + H_2O + Gas (CO_2 , CO, CH_4 , H_2)

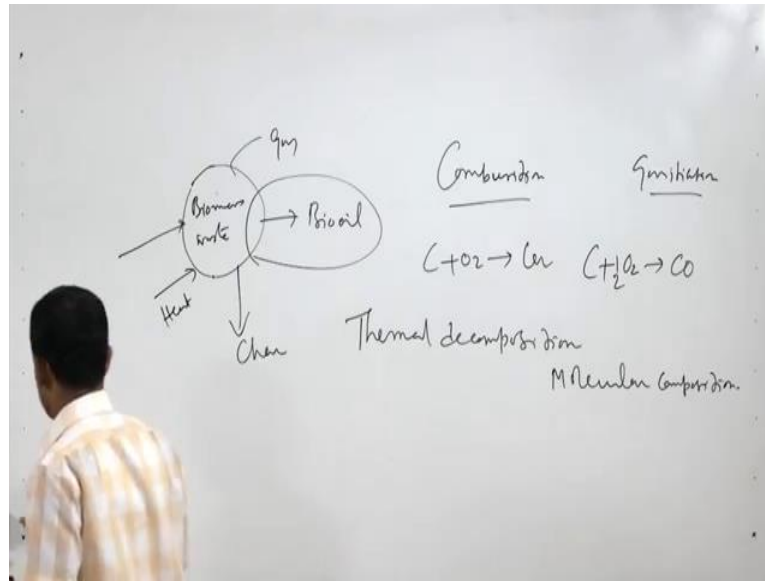


- It is the first step of gasification and combustion process
- It is the only thermochemical process which converts different types of biomass and organic wastes into solid, liquid and gaseous fuel

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Pyrolysis the word itself gives some idea about it. So, pyro means fire, lysis means cutting. So, this is the process that is thermal decomposition process which decomposes carbonaceous material by the application of heat in absence of oxygen.

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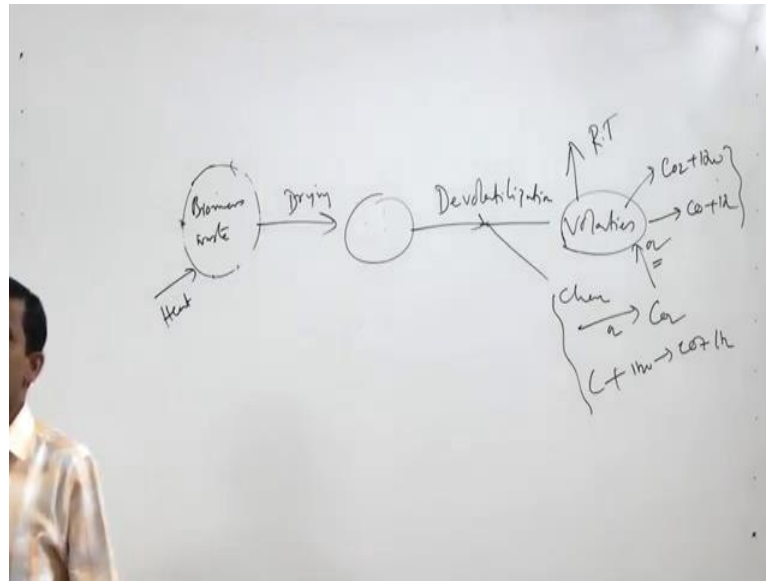


So, if we have some biomass and waste or any carbonaceous feedstock just simply we will apply heat in the combustion and in the gasification, we had to put some other medium that is oxygen for combustion and O₂ and H₂O in case of gasification, but in this case we do not (Refer Time: 03:25) to only heat and that heat will give us char that will give us gas and that will give us bio oil.

This is very simple to explain this phenomena graphically, but. In fact, this thing bio oil production and char and gas productions is not. So, very simple process number of simultaneous reactions is going on when we apply heat on to the biomass and waste if we think about a combustion process or a gasification process it is very easy to explain these things there C is reacting elemental carbon of the material is reacting with oxygen and it is carbon into CO₂ here we can say C it is reacting with oxygen and it is produce in CO, but here there is no media for conversion only heat. So, thermal decomposition is going on thermal decomposition is going on.

So, the thermal decomposition what is the kinetics what is the rate and how this is happening what will be the molecular composition that is not easy to predict this pyrolysis is also the part of the incineration and gasification. So, this is the first step of the incineration and gasification find some waste comes in contact with heat at first the moisture vaporize is and then devolatilization takes place. So, devolatilization takes place.

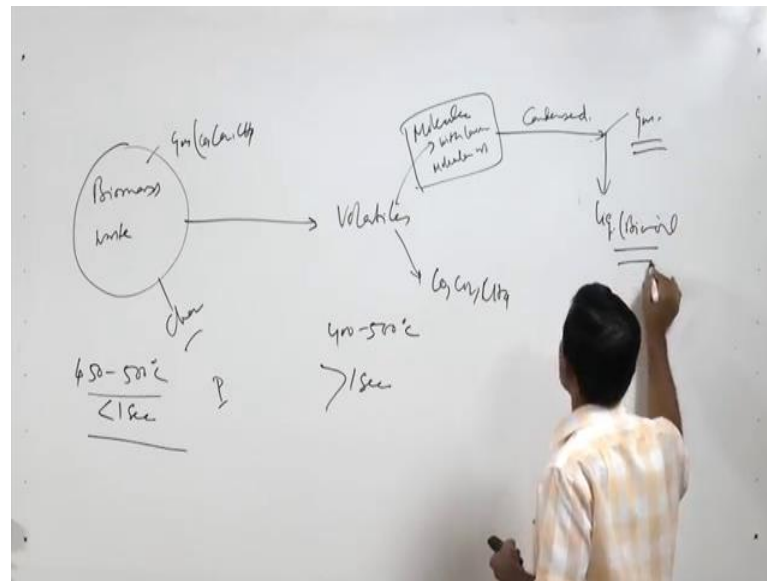
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In case of combustion, the volatile first drawing then it is coming to de volatilization that we will give us volatiles and char.

This volatiles will contain many compounds all aldehyde alcohol acid many thing. So, when we put oxygen CO_2 plus H_2O when we give controlled the amount of oxygen it will give COS_2 and then char is also oxidized CO_2 in case of oxygen again this char is converted to CO plus H_2 in gasification they are for gasification this is for combustion, but in case of pyrolysis nothing happens here, so this volatiles will be going off from the system or if we keep it for a longer time for longer retention time. So, that volatiles will further we broken down into smaller compounds and those smaller compounds will also be combined together and through different chemical reactions and we will produce number of products or components.

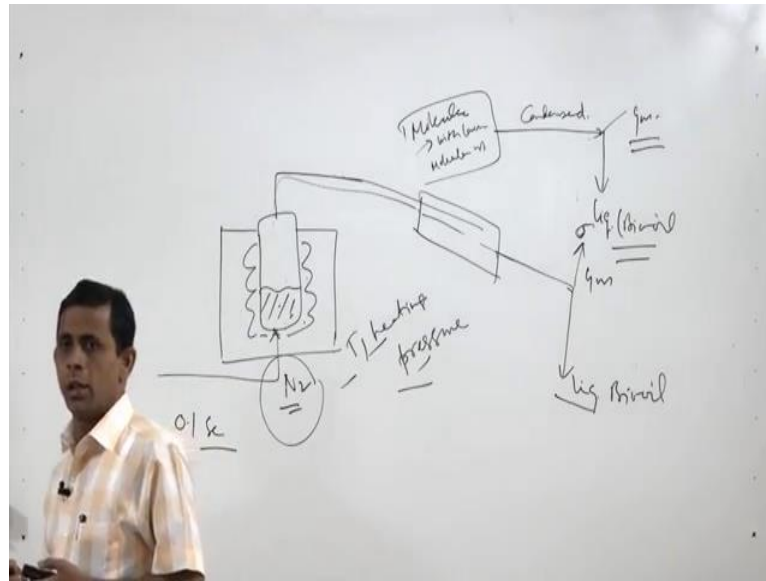
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So, here thus pyrolysis mechanism is shown in the slide where the biomass and waste is taken waste is taken and heated then it gives volatiles char and also gas. So, this gas maybe CO may be CO₂ or CH₄, but here what are the temperature 450 to 500 degree centigrade very small time very small times say 1 second less than one second if the material is heated then we will get these things. Now we will increase the time. So, when we will increase the time, greater than 1 second. So, 400 to say 500 degree centigrade; so this volatiles will further we broken down. So, this will give some gas molecules like similar CO CO₂ CH₄ or it will give some other molecules that is with lower molecular weight.

So, this is this volatile in vapor phase material is further condensed after condensation we will get liquid that is called bio oil and other part we will get gas. So, this is the mechanic path for the production of gas liquid and chars. Now number of reactions are going on and depending upon the residence time depending upon the temperature depending upon the pressure on this reactor the distributions of these products will be varying. So, this is one batch scale reactor for the pyrolysis of biomass and waste.

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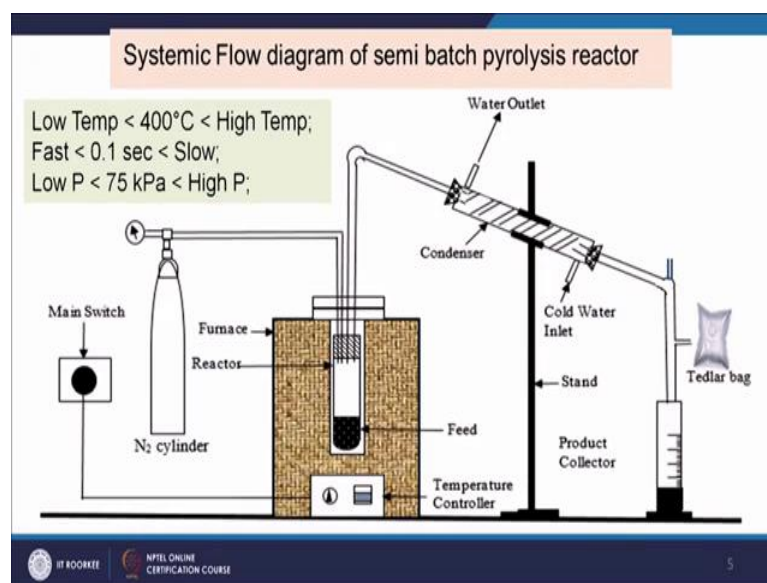


We will get some important information in this figure we have one pyrolysis chamber very small one inside a furnace. So, this furnace will apply heat we will put some material here and where putting here we are heating by coil permitting the material we have put it and then disconnected.

So, when we will raise the temperature. So, that vapor will go char will remain inside vapor and gas will go, so will condense it in the condenser. So, we will get the liquid from this and we will get gas from the top bio oil one interesting thing is how the gases will go we need to provide some carrier gas that is basically nitrogen inert. So, in carrier gas we need to supply that is now necessary in case of other 2 processes thermal processes that is incineration or combustion and gasification. So, this is the characteristics of the pyrolysis process where we need to provide nitrogen or we may put some blower here and create very small vacuum.

So, that the gas generated may go through this and liquid can be produced now the few questions are what will be the rate of heating.

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What will be the temperature what will be the pressure to maintain a certain products because the product distributions depend upon the temperature heating rate pressure depending on the basis of this variation of these temperature heating rate and pressure number of pyrolysis methods have been developed and identified. So, in some cases we use high pressure in some cases we use low pressure, but high pressure and low pressure this does not mean a very high value of the pressure you see here the low pressure means pressure less than seventy 5 kilo pascal anybody is greater than this. So, there is high pressure.

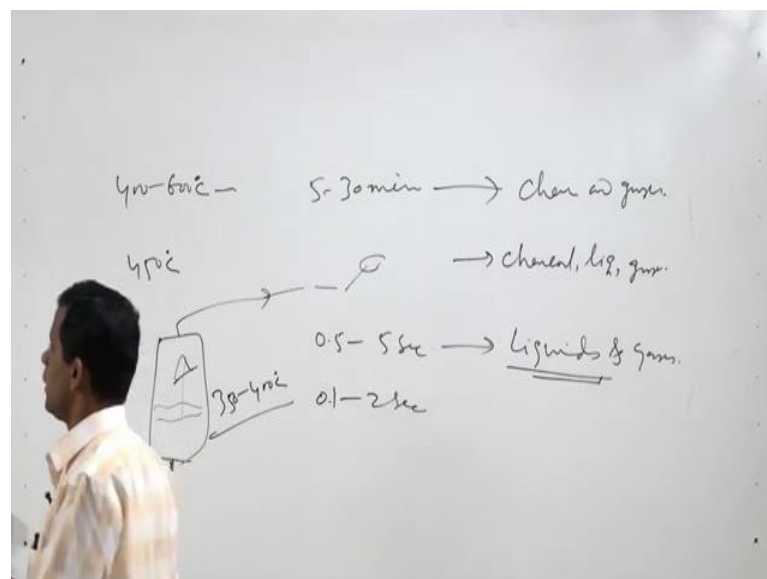
So, pyrolysis process reacts under atmospheric pressure or below atmospheric pressure also for vacuum pyrolysis and low temperature means less than 400 degree centigrade and first means residence time less than 0.1 second and slow means this is greater than this. So, these are some characteristics are some important parameters which are maintained in pyrolysis reactor.

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Typical biomass pyrolysis technologies, conditions, and major products				
Technology	Temperature Range (° C)	Heating rate	Residence time	Main Products
Carbonization	350-500	Very low	Hours to days	Charcoal
Slow pyrolysis	400-600	Medium	5 to 30 min	Char and gases
	~ 450	Low	Hours	Charcoal, liquid and gases
Fast Pyrolysis	400-650	High	0.5 to 5 seconds	Liquids and gases

Now, depending upon this the value of these are temperature the heating rate and residence time we can get different type of pyrolysis like say carbonization the primitive one in this case very slow heating rate is applied for a longer period and 350 to 500 degree centigrade is maintained. So, by this method we will get charcoal basically then the slope pyrolysis came.

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So, for slope pyrolysis, the heating rate maybe medium or maybe low, so temperature is 400 to 600 degree centigrade, so where the medium heating rate if we give and 5 to 30

minutes of residence time that we will give us char and gases that we will give us char and gases, but if it is say 450 degree centigrade, but low heating rate and then residence time is in hours then it will give us charcoal liquid and gases now first pyrolysis uses the temperature of 500 to 650 degree centigrade and high heating rate is used and residence time is also less the resistance time is only 0.5 to 5 second and it gives us liquids and gases the uniqueness of this process with comparison to incineration and gasification is that it can give three products gas liquid fuel and char and desirable more desirable product is liquid.

So, the first pyrolysis produces liquids in as a major product and getting more interest in recent years.

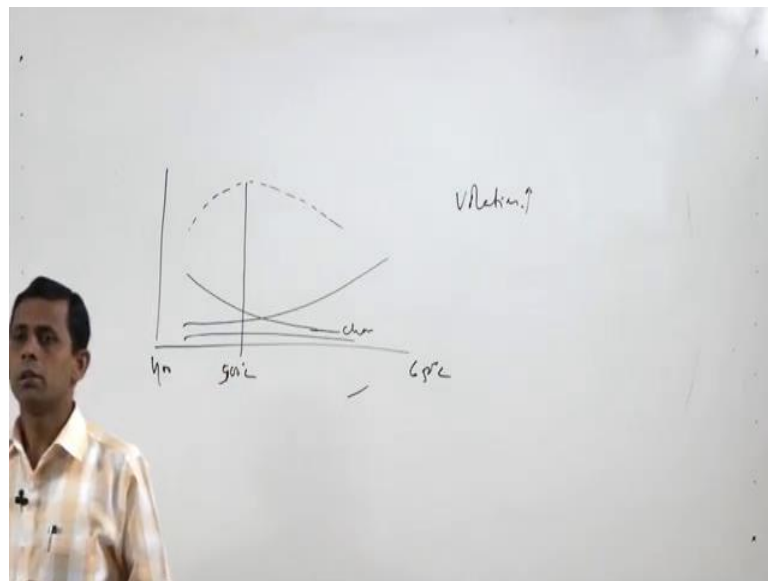
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Technology	Temperature Range (° C)	Heating rate	Residence time	Main Products
Flash Pyrolysis	400-650	High	0.1 to 2 seconds	Liquids and gases
	650-900	High	<1 second	Liquids and gases
Ultra Pyrolysis	1000	Very high	<0.5 seconds	Chemicals and gases
Vacuum Pyrolysis	350-400	Medium	2-30 seconds	Liquids
Hydrolysis	<500	High	<10 seconds	Liquids
Methanopyrolysis	>700	High	<10 seconds	Liquids

Further development in the in this pyrolysis process is flash pyrolysis in this case temperature is say 400 to 650 degree centigrade high heating rate 0.122 second residence time and it gives liquid and gases similarly ultra pyrolysis very high temperature and one thousand degree centigrade and very high heating rate and very less residence time less than 0.5 second, it gives us chemicals and gasses. So, vacuum pyrolysis just to a discussing that find there will be no nitrogen, but there will be kept some adding some blower at this end some vacuum can be generated. So, when vacuum is generated. So, more volatiles will come up into the vapor phase and we it will give us more liquids.

So, that is why more liquids we get using vacuum pyrolysis. So, 350 to 400 degree centigrade is required here temperature requirement is also relatively less with respect to other pyrolysis and here we get 2 to 30 second residence time media making heating rate is required the hydrolysis and methanopyrolysis are to other processes which have been reported recently and the conditions on provided here for all these pyrolysis processes the product distribution varies with increase in temperature if we increase the temperature than the product distribution varies.

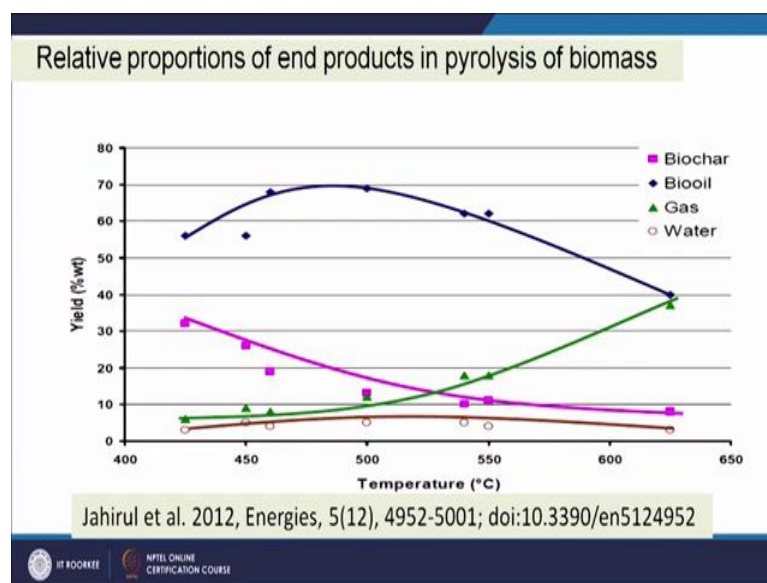
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If you go for lower to higher temperature say 400 to 650 degree centigrade the bio oil initially increases and then it decreases.

After attaining a certain value it decreases. So, there are say 450 to 500 degree centigrade this decreases; obviously, this is specific to certain biomass.

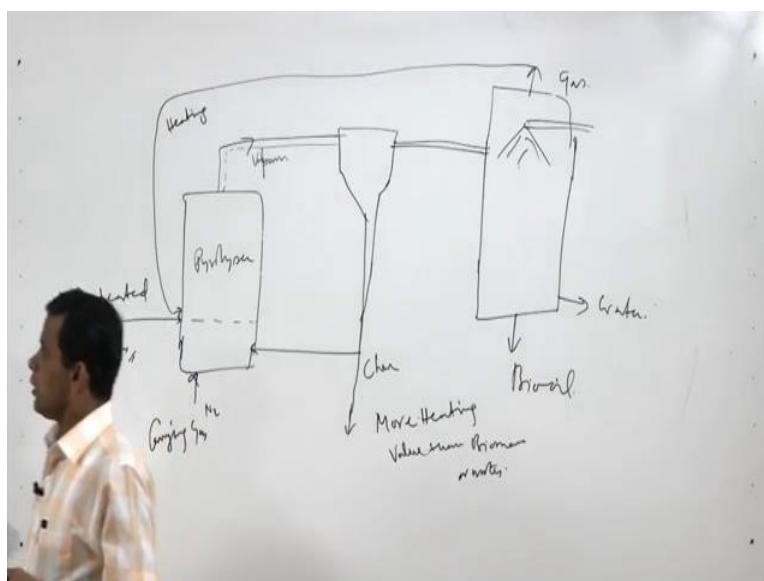
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And then bio char decreases with increase in temperature. So, bio char decreases with increase in temperature and moisture content there is no much change there is no much change in moisture content and gas content increases with increase in temperature gas contents increase with increase in temperature we can explain this phenomena on the basis of the mechanism of pyrolysis we have seen that there are there are primary degradation then further secondary cracking of the of the volatiles.

So, more temperature gives more gases more gasses. So, liquid decreases and more temperature will also produce more gases and liquids. So, char decreases with increase in temperature and gas increases because secondary reactions are going on the volatiles. So, that more smaller molecules of the gasses are produced.

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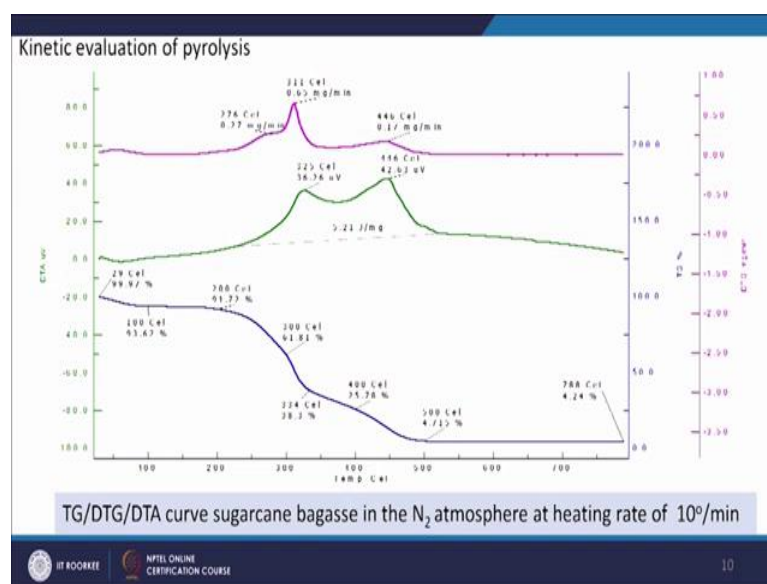
Now, we will see the process flow sheets of the pyrolyzer unit. So, one pyrolyzer we will put biomass and waste that biomass and waste must be pretreated because this will be able to handle certain biomass only. So, that pretreatment is required just like segregations and homogenization etcetera.

So, that pretreated biomass that has to be used and we need carrying gas nitrogen inert gas normally used. So, this may be fixed bed type or maybe fluidized bed type if fluidized bed type then we have to add sand here. So, it sand will be fluidized and biomass will also be fluidized with the sand and heat transfer take place and pyrolysis will take place. So, when these vapors will goes up along with the particles some particles will also go and then it will enter into some separation unit. So, this separation unit we will give us char this separation unit will us char part of the char can be recycled here then this gas is going from this collector you need to cooling unit. So, here the gas is cooled either by direct quenching or indirect cooling.

So, here some example is given as direct quenching, so here will be spraying. So, gas will be cooled and that will be collected and from the bottom you will get water that will be having some impurities and treatment is required for this and from the bottom we will be getting bio oil the gas which we are getting that can be sent here for heating purpose this can be used for heating purpose now char which we are getting in this case and biomass and waste which we are getting here will be having different heating value the

char will be having more heating value than that of heating value then biomass or waste or any other feed stocks. So, this is the flow sheet of the pyrolysis process to understand the kinetics of the complex pyrolysis process people use the help of TCATC and DTA data.

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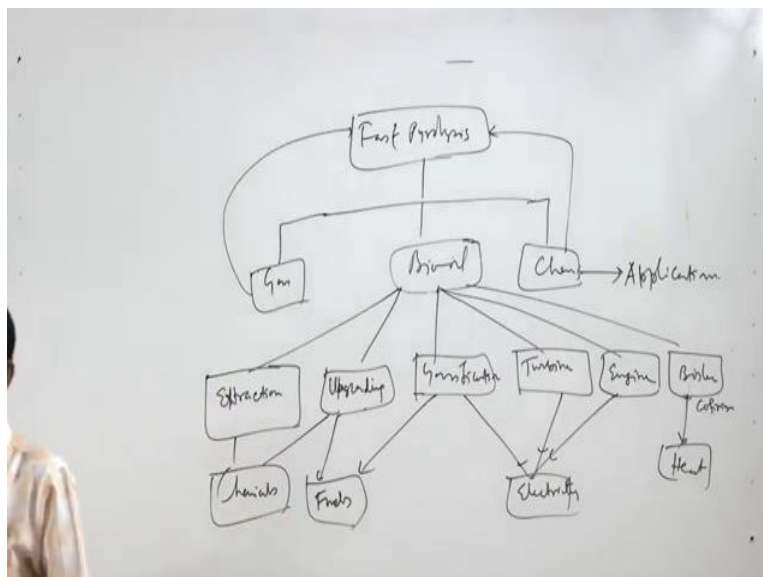


So, on thermal gravimetric analysis the data generated like this. So, in this graph the TG data it is evident that up to 200 only 8; around 8 percent mass loss is there, but when the temperature is increased to three hundred. So, 38 percent mass is remaining; that means, it is 60-62 percent mass is lost. So, here after 5 degree centigrade only 4.716 percent mass is remaining. So, after increasing the temperature above 500 no for no significant loss of mass we achieve here. So, by DT and DTG, DTA and TG; this TG data; it is clear to us that for this particular biomass that is sugarcane bagasse we do not need to heat above 500 degree centigrade.

Similarly, from this graph we are getting here the rate of change of mass is different with respect to time. So, this is maximum 0.65 mg per unit at this 311 degree centigrade temperature and here also 446 degree centigrade, we are getting 0.17 mg per unit. So, we are getting the 276 to 446, this temperature is more critical or more suitable for the pyrolysis of this biomass it is these data are used also to determine the kinetics of the reaction and the order of the reaction I am not going to explain in detail all those

procedure, but extensive research is going on to determine the kinetic parameters for different types of biomass and wastes.

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Now, we will see the application of pyrolysis products. So, say first pyrolysis say. So, it will basically give us three product one inch gas bio oil char. So, this has will be used here for the heating of this because this requires heat. So, that heat can be produced from the gas now this char some char can also be used and burnt hot side this pyrolysis reactor and can be heated other applications of char there are some other applications of the char and bio oil can be used into different routes through different routes this can be used for the separation of the compounds present in it, it has large number of organic compounds including acids, aldehydes, phenols, ketones, etcetera. So, those valuable chemicals can be extracted.

So, extraction can be done. So, it can give us valuable chemicals this bio oil can be upgraded its quality is not very good. So, directly bio oil may not be used in engines. So, we need to upgrade it. So, by up gradation by upgrading we can get fuels we can fuels we can get chemicals also we can also use this bio oil for gasification we can use this for turbine we can use it for engines we can use it for boiler and co firing and co firing. So, boiler and co firing will give us heat engine and turbine will give us electricity. So, gasification turbine and engine will give us electricity gasification will also give us fuel.

So, from bio oil we can get different chemicals different fuels and it can be used for electricity and heat production here.

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Various chemicals and fuels from pyrolysis bio-oil	
Some chemicals fuels form pyrolysis bio oil are:	
Chemicals	Fuels
Resins	Hydrogen
Fertilizer	Upgraded HDO
Flavours	Fuel via syngas
Adhesives	
Acetic acid	
Industries feedstocks	

We will see some important chemicals which can be produced from the bio oil there is some resins fertilizer flavors adhesives acetic acid and industries feed stocks and some fuels we can get from hydrogen through gasification hydrogen upgraded hydro deoxygenated fuels.

The hydro deoxygenate it oxygen present in the bio oil is in higher amount which is not desirable and reduces the quality of the fuel that is why this de oxygenation is required that is called up gradation. So, that fuel can be used and once the gasification we are using we can get other FT synthesis also. So, we can get other fuels there are some properties of the pyrolysis bio oil we will now discuss some important properties and responsible for this properties for example, this oils is having some appearance that is dark red brown to dark green appearance. So, this appearance is because of micro carbon and chemical composition in oil.

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Some properties of pyrolysis bio-oil and their reasons		
Properties		Reasons
Appearance	Dark red-brown to dark green	Micro-carbon and chemical composition in oil
Odor	Distinctive odor an acrid smoky smell	Lower molecular weight aldehydes and acids
Density	Very high compared to fossil fuel Pyrolysis bio-oil: 1.2 kg/liter Fossil oil: 0.85 kg/liter	High moisture and heavy molecule contamination
Viscosity	Can vary from as low as 25 centistokes (cSt) to as high as 1000 cSt	Wide range of feedstock, water content and the amount of light ends collected
Heating value	Significantly lower than fossil oil	High oxygen content

Another property is its odor. So, distinguishing this distinctive odor and acid smoke is smell is available that is due to the presence of different types of aldehydes and acids we have density of this is more than the fossil oil and it is given here and this is because of high moisture and heavy molecular contamination and viscosity and heating value is also not similar to the transportation fuels.

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Some properties of pyrolysis bio-oil and their reasons		
Properties		Reasons
Aging	Viscosity increase, Volatility decrease, Phase separation and Deposition of gum occur with time	Complex structure with acids, aldehydes, alcohols, sugars, furfural and furans etc. due to the degradation of cellulose and hemicellulose ; phenols, guaiacols, syringols, vanilline, various aromatic compounds and high molecular weight water insoluble compounds from lignin degradation
Miscibility	Miscible with polar solvent but totally immiscible with petroleum fuel	Polar in nature

Another important difficult with his edging means with time is viscosity increases volatility decreases phase separation takes place this is because of the presence of

different molecules which are generated through the degradation of cellulose and hemicelluloses as well as the lignin as mentioned here different types of acids aldehydes alcohols sugars phenols etcetera are responsible for this phase separations and other degradations in the quality.

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Comparison of typical bio-oil and diesel characteristics			
Physical Property	Bio-oil	Diesel	Comments
Water content (wt.%)	15-30	0.05	Due to original moisture in feedstock; dehydration reaction; and storage Water reduces the heating value and viscosity
Oxygen content (wt.%)	35-40	0	It leads to the lower energy density and immiscibility with hydrocarbon fuels
Low pH	2.5	-	Large amounts of carboxylic acids, such as acetic and formic acids
Viscosity (@ 50°C) cP	40-100	4	Important for fuel injection system and combustion properties of fuel
HHV (MJ/kg)	16-19	45	Low HHV due to high oxygen content
Ash content (wt.%)	0-0.2	0.01	Alkali metals in ash can causes corrosion problem

This here we see the comparison of some properties between diesel and biodiesel we see here the moisture content and oxygen content is very high with respect to diesel which are not desirable and reduces the quality fuel quality of this and low pH that is 2.5 due to the presence of carboxylic acids and acidic and formic acid etcetera which are also not desirable.

The heating value is also less in this case and that is due to the presence of high oxygen content there are some advantages of this process that is we can use the waste we can use the we can get the liquid product came.

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Advantages and disadvantages of Bio oil

Advantages

- Carbon neutrality
- Utilizes otherwise waste biomass
- Possibility of utilization in small-scale power generation systems as well as use in large power stations
- Storability and transportability of liquid fuel
- High-energy density compared to biomass gasification fuel
- Potential of using pyrolysis liquid in existing power plants

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But it has some disadvantages also the oxygen containing in the liquid fuel is not desirable it is not stable for a longer time. So, there are number of disadvantage as mentioned here. So, to remove this disadvantage the up gradation of biodiesel, bio oil is required and physical methods and chemical methods are used for the up gradation of the bio oil.

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Pyrolysis bio oil upgradation

Physical methods	Chemical Methods
<ul style="list-style-type: none">• Filtration for char removal• Emulsification with hydrocarbons• Solvent addition	<ul style="list-style-type: none">• Reaction with alcohols• Catalytic deoxygenation<ul style="list-style-type: none">➤ Hydrotreating➤ Catalytic (zeolite) vapor cracking

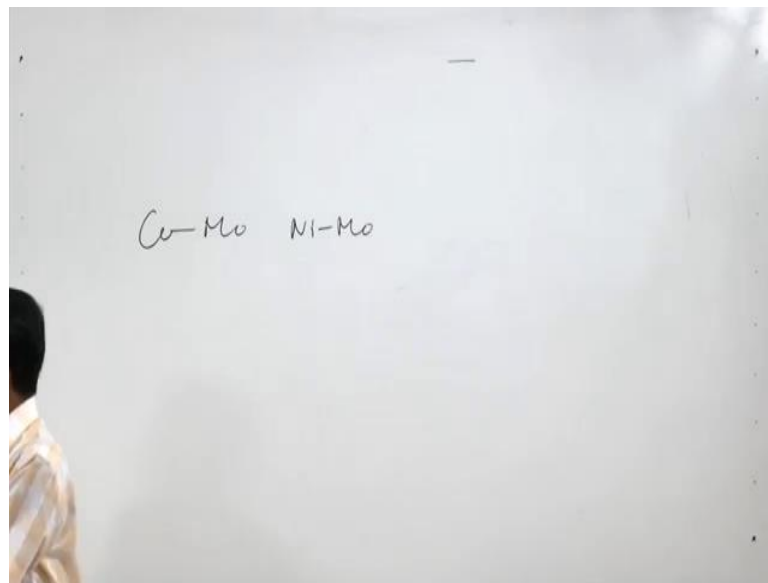
- Bio-oil contains heavy compounds with long carbon chain, low H/C ratio and high O/C ratio.
- Upgrading is done to remove oxygenated compounds responsible for reducing the quality of the bio- oil either through hydrotreating or catalytic cracking.
- Hydrotreating is performed at a temperature of around 350°C, under high pressure of hydrogen, in presence of heterogeneous Co-Mo, Ni-Mo based cat.

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The physical method is filtration for char removal emulsification with hydrocarbons and solved degradation for the chemicals methods reaction with alcohols and catalytic deoxygenation.

So, the catalyst deoxygenation can be done either by hydro treating or by application of some other catalytic vapor cracking. So, this hydro treating is performed at a temperature of around 350 degree centigrade with some catalyst that is cobalt molybdenum and your nickel molybdenum.

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So, using this catalyst the hydro treating is possible. So, another approach is going on either we produce bio oil and upgrade it in place of these the people are trying to use catalyst during the production of the bio oil; that means, in the pyrolysis process and different catalyst have been introduced in the pyrolyzers and the quality have been improved in terms of the its reduced acidity viscosity and oxygen content. So, here some catalysts used for this purpose are mentioned.

So, after this in this module and we will discuss in the next module about different pyrolysis reactors.

Thank you very much for your patience.