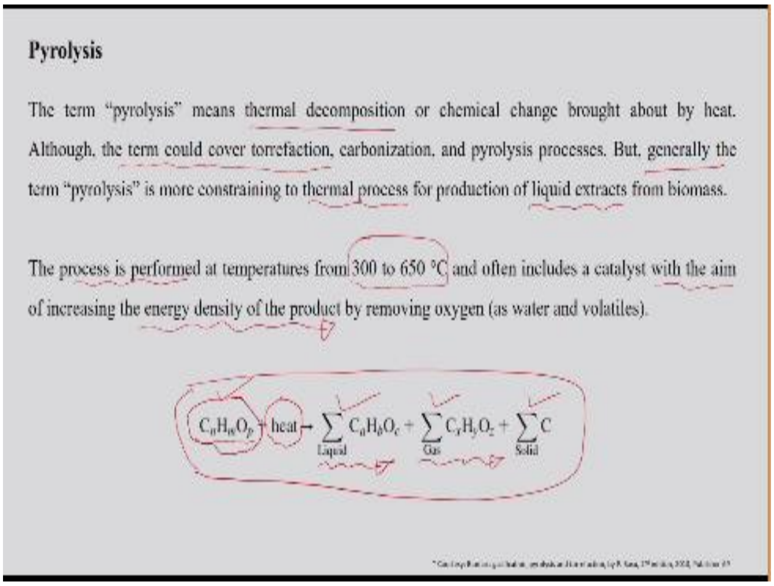
Renewable Energy Engineering: Solar, Wind and Biomass Energy Systems
Prof. Vaibhav V. Goud and Dr. R. Anandalakshmi
Department of Chemical Engineering
Indian Institute of Technology – Guwahati

Lecture - 29
Thermo-Chemical Conversion Processes Pyrolysis, Liquefaction and Conversion Processes

Good morning everyone. Welcome to part 3 of lecture 2 under the module 8. So, in this lecture, we will discuss about the thermo-chemical conversion processes that is pyrolysis, liquefaction followed by the chemical conversion processes. So, let us begin with the pyrolysis.

(Refer Slide Time: 00:46)



The term pyrolysis means the thermal decomposition or chemical change brought about by heat. The term pyrolysis could cover the torrefaction, carbonization and the pyrolysis process as well. If you recall our discussion about torrefaction and the carbonization process, so, torrefaction process is also carried out in absence of oxygen, but in a very narrow temperature range.

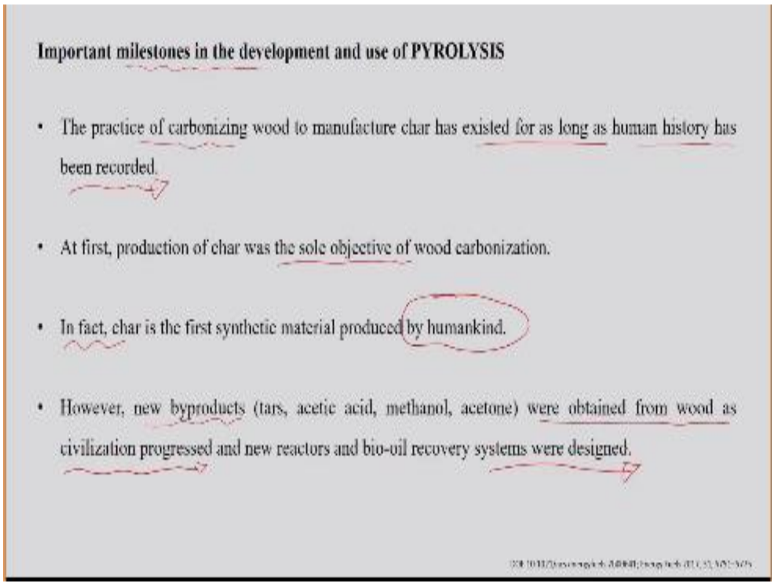
Whereas, in case of carbonization the partial oxygen is allowed to carry out the conversión, so that it can provide the heat which is required for the process. And similarly, in pyrolysis process also, it carries out in absence of oxygen or sometimes partial oxygen is allowed to provide the thermal energy which is required for the process. And that is why the term pyrolysis could also cover torrefaction, carbonization in the pyrolysis processes.

But generally, the term pyrolysis is more constraining to thermal processes for production of the liquid extract from the biomass. And that is the main objective of the pyrolysis process to obtain the liquid product from the biomasss. Apart from that also, it leads to the production of char and the gas as the product. The process is performed at a temperature range of say, 300 to 650 degree C and it often includes a catalyst.

Because in this case, the aim is of increasing the energy density by removing the oxygen from the biomass so that it can lead to the production of high energy dense fuel in the form of liquid product. Generally, the pyrolysis process mainly provides liquid, gas and char as a product that is also called as a solid char as the product by thermally decomposing the biomass into a specific temperature range as we have discussed earlier.

And it breaks down the large molecular weight hydrocarbon compound in the biomass to a low molecular weight compound that is mainly a condensable gases, which can be condensed to produce the liquid as a product which is also termed as a bio-oil. Along with that it also releases certain fraction of the gases and solid char as the product. And this is how the thermal decomposition of the biomass, which we have represented here in the form of carbon, hydrogen and oxygen is carried out by hitting the sample under specific condition.

(Refer Slide Time: 03:07)

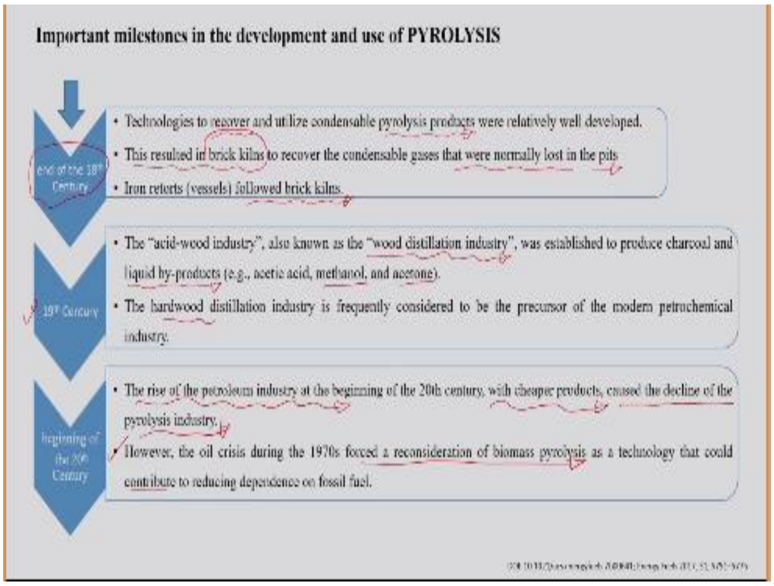


So now, once we understand the pyrolysis process, let us try to understand the important milestones in the development and the use of pyrolysis process. The practice of carbonising wood to manufacture the char has existed for as long as the human history has been recorded.

And at first, the production of char was the sole objective of the wood carbonization process. And in fact, the char is the first synthetic material produced by the human kind.

However, the new products like tar, acetic acid, acetone, methanol, were also produced from the wood as civilization progressed. And new reactors and bio-oil recovery systems were designed accordingly to obtain this kind of byproduct in the form of acetic acid, acetone, methanol and tar as the product.

(Refer Slide Time: 04:13)



Now, if you look at the history of the development of the pyrolysis process in the science and technology, so at the beginning of the 18th century, the technologies to recover and utilize the condensable gases in the form of the pyrolysis products were relatively well developed. And this resulted in the brick kilns to recover the condensable gases that were normally lost in the pits.

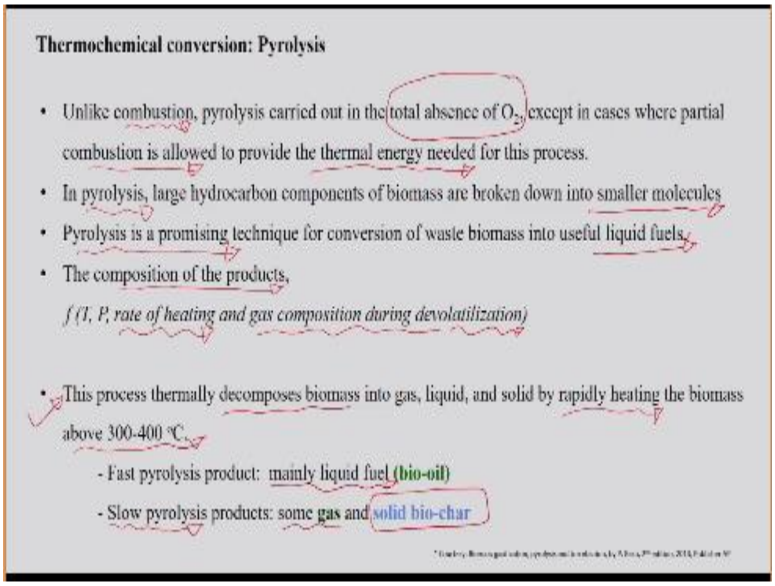
And after that the iron retort followed the brick kilns. And this is how the pyrolysis process and the development of the pyrolysis reactors occurs in the science and technology. In the 19th century, the acid-wood industry also known as the wood distillation industry, was established to produce the charcoal and the liquid by product in the form of acetic acid, methanol and acetone.

As we already discussed in the previous slide, these are the important milestones in the development of the pyrolysis process in the science and technology. And the hardwood distillation industry is frequently considered to be the precursor of the petrochemical industry. And because of that the rise of the petroleum industry has happened at the beginning of the 20th century.

And with the availability of the cheaper product because of the rise in the petrochemical industry in the 20th century, it caused the decline of the pyrolysis industry. However, the oil crisis during 1970s forced reconsideration of the biomass pyrolysis process as a technology that could contribute to reducing dependence on the fossil fuels. And this is how the development of the pyrolysis process happens in the science and technology.

So, now, once we understand the history of the pyrolysis process, let us talk about the analysis process in more detail.

(Refer Slide Time: 05:47)



Unlike combustión process, the pyrolysis process it is carried out in total absence of oxygen. Except in some cases, where partial combustion is allowed to provide the thermal energy which is required for the process. So, by partially combusting the char and the gas during the pyrolysis process, it can provide the thermal energy which is required for the process, because the pyrolysis process is a endothermic reaction.

Hence, it requires external heat source, which can be fulfilled by partially combusting the char and the gases and then that particular heat produced during the process can be supplied to the thermal energy which is required for the specific pyrolysis operation. In the pyrolysis, large hydrocarbon component of the biomass are broken down into the smaller molecules. That is what is the advantage of the pyrolysis process is like.

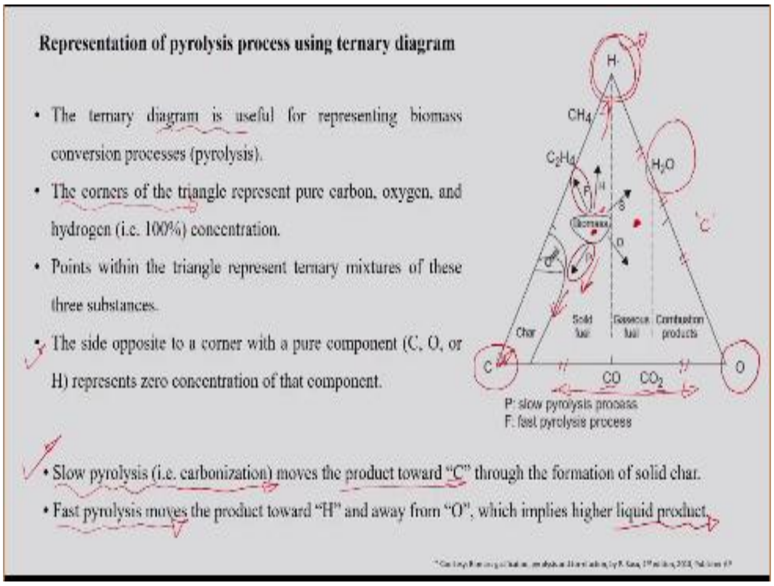
It undergoes the thermal decomposition and also the chemical changes are also brought by the thermal effect. And the pyrolysis is a promising technique for the conversion of waste biomass into a useful liquid fuel as a product. The composition of the product obtained during the pyrolysis process, it mainly a function of the temperature, pressure and the rate of heating of the biomass in the pyrolyzer.

Apart from that, the gas composition during the devolatilization of the biomass is also one of the parameters which need to be considered effectively to obtain the final product of the interest. This process thermally decomposes the biomass to produce solid, liquid and gas as the product by rapidly heating the biomass above 300 to 400 degree C and based on this particular heating rate, the pyrolysis process are also classified into the fast pyrolysis process and the slow pyrolysis process.

And the product of the fast pyrolysis process are mainly liquid fuel with small fraction of gas and tar as the product. Whereas the process carried out using the slow pyrolysis process mainly leads to the formation of some gases and solid bio-char as the major product. And that is what is the difference between the slow and the fast pyrolysis process. And it mainly depends on the rate of heating of the samples in the pyrolyzer, whether it is a rapid heating or whether it is a slow heating.

Based on that the product of interest can be obtained using the pyrolysis process. Now, based on the heating rate, the pyrolysis process also can be represented using the ternary diagram.

(Refer Slide Time: 08:17)



And the ternary diagram here, it is useful for representing the biomass conversion processes. And here our focus of interest is on the pyrolysis process. So the ternary diagram which is shown here, it mainly discusses about the pyrolysis process. Apart from that, the ternary diagram can also be used to represent the other biomass conversion processes that is the gasification as well as the combustión.

The corner of the triangle here in the ternary diagram, it represents the carbón, hydrogen and the oxygen content in the biomass sample.And the point within the triangle represent the ternary mixture of this component. The side which is opposite to a corner,say for example, this is the side which is opposite to the corner compound that is C here, it represents the zero concentration of that component.

That means, if you see here in this case, the side which is opposite to the C is this particular side and it represents the zero concentration of C component on this particular side. Similarly, if we talk about the other corner in a ternary diagram that is a suppose edge, so side opposite to the edge is, suppose this is particular side which is opposite to the C, it represent the zero concentration of H in this particular side.

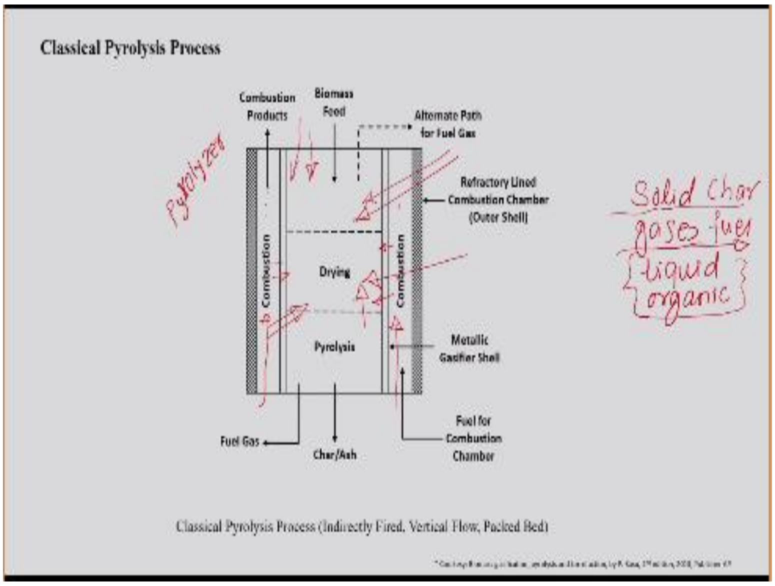
So, it can be easily visualised in this particular ternary diagram, because here it mainly produces CO and CO 2 as a product, but it does not contain any edge. Similarly, the side opposite to corner C, it contains H 2 O as a product where it does not have any C component in its composition. So this is how the ternary diagram is useful for representing the biomass conversion process.

Now, let us consider a small example of biomass here. Here the biomass represent the composition in the form of C, H and O. So, biomass it undergoes thermal decomposition process so, it leads to the production of different product. If the process is carried out using the slow pyrolysis operation that is a carbonization, then it moves the product toward C to the formation of solid char as a product.

And that is what we have discussed in the previous slide even though slow pyrolysis process, it mainly gives solid char as a product. And that is the reason here if you see the slow pyrolysis process, it moves toward the product C that is char through the formation of char as a product. Similarly, if you talk about the fast pyrolysis process here, then it moves the product toward edge which is represented here in the form of say H.

So, it moves the product toward the edge and away from the oxygen which implies the higher liquid product. And this is what we have discussed again in the previous slide that the fast pyrolysis process it leads to the production of the liquid as the major product along with the traces of the product that is gas and the char. So, this is how the ternary diagram can be used to represent the biomass conversion process.

(Refer Slide Time: 11:29)



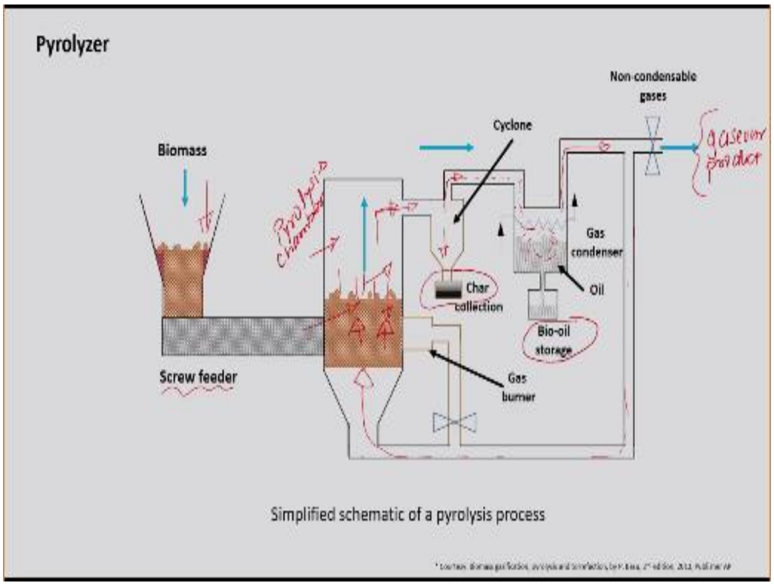
So, once we understand the ternary diagram and the biomass conversion process, let us try to take the simple example of the classical pyrolysis operation in a pyrolyzer reactor. So, in the pyrolysis process, a carbonaceous material which is fed from the top inside the reactor undergoes the thermal cracking and it decomposes to form solid char, gaseous fuel and liquid organic compound as a product.

Currently, the thermal decomposition process in which the heat energy which is required for the pyrolysis process is supplied by partial combustion of the char and the volatile gases and is being termed as the pyrolysis process. So, because of that the combustion operation which you see here, it allows the combustion of the char and the volatile gases and the heat of the combustion produced in this particular chamber here can be transferred to the pyrolysis chamber to allow the pyrolysis operation to takes place.

The carbonaceous material in the form of solid carbon or the gases or the liquid organic compounds can be cracked down or pyrolysed inside the pyrolyzer to produce the product of the interest. So, as I mentioned, the pyrolysis process is an endothermic reaction and hence, it requires external heat as a source to carry out the pyrolysis operation. And the char as well as the volatile gases produced during the pyrolysis operation can partially be combusted to provide the thermal energy which is required for the pyrolysis operation.

So, this is how the classical pyrolysis operation takes place inside the pyrolyzer. Now, if you just look at the another schematic here, which discusses about the fluidized bed pyrolyzer.

(Refer Slide Time: 13:08)



In case of fluidized bed pyrolyzer the biomass is fed using a screw feeder inside the pyrolysis chamber containing hot solids. So, the heat from the particular hot solid is transferred to the biomass which is coming in contact with the hot solid inside the pyrolysis chamber and it leads to the pyrolysis temperature and after that the thermal cracking of the biomass takes place.

So, the condensable and the non condensable gases released from the biomass leaves the chamber here and the solid char partly remain inside the chamber and it partly leaves along with the gas can be collected inside this particular chamber here. And it cooled down in the downstream reactor. The condensable gases along with the non condensable gases are also passed through this particular zone here.

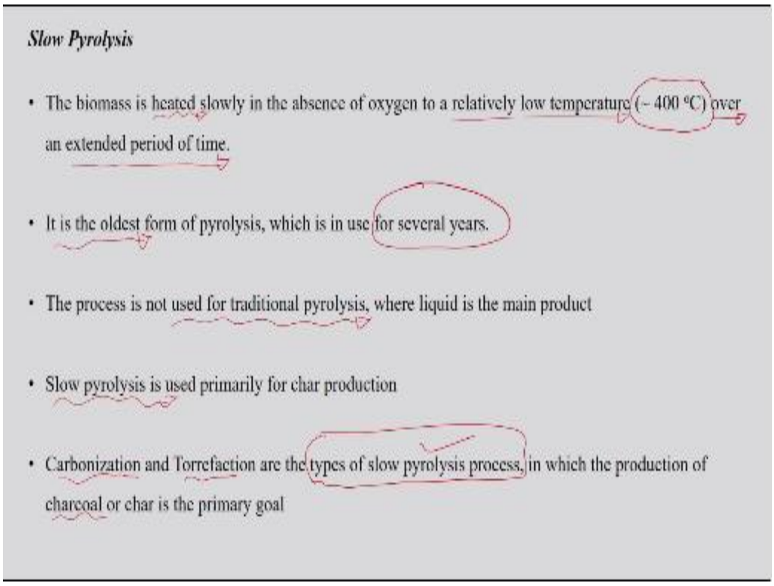
And it allows the condensation of the condensable gases in the form of the liquid bio-oil as a product and the non condensable gases can be released from this particular end here as a gaseous product. The char which is obtained during this process is also considered as a commercial product. Apart from that, the partial combustion of the char is also allowed to provide the thermal energy which is required for the process.

Apart from that, the product gas which is obtained from the pyrolyzer which is a mainly a non condensable gases, which is free of the oxygen. So, the part of the gas can also be supplied as a heat source or a fuel rising medium inside the pyrolysis chamber to allow the pyrolysis operation to takes place, as well as to provide the thermal energy which is required for the process.

And this is how the fluidized bed operation of the pyrolysis process takes place inside the reactor. Once we understand the fluidized bed as well as the simple classical pyrolysis operation, now, let us discuss about the types of the pyrolysis processes. So, here the pyrolysis process are generally classified into the four categories based on the heating rate and it is classified as slow pyrolysis, fast pyrolysis, flash pyrolysis and the isothermal pyrolysis operation.

Also based on the environment or the medium which is used during the pyrolysis process, it is also classified into the 2 sub classification that is high-pressure pyrolysis and the hydrous pyrolysis. So, let us discuss about the types of the pyrolysis one by one.

(Refer Slide Time: 15:48)

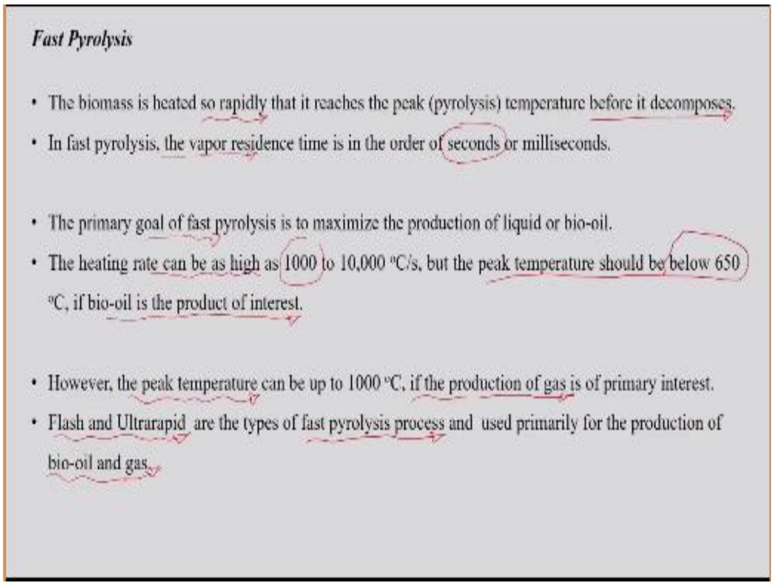


Now, the slow pyrolysis process. In case of the slow pyrolysis process, the biomass is heated slowly in the absence of oxygen to a relatively low temperatura. And in this case the temperature is relatively low over an extended period of time. Because, as we already discussed earlier, the product of interest in the slow pyrolysis process is the char. So, as a result, it allows the heating over extended period of time.

As well as if you see here, the low temperature heating is preferred in the slow pyrolysis process. And it is the oldest form of the pyrolysis which is in use for several years. And this process is not in use for traditional pyrolysis, where liquid is the main product. And the slow pyrolysis process, it is also used primarily for the char production. Because, if the product of interest is a char only, then the slow pyrolysis process is preferred.

Carbonization and the torrefaction are the types of slow pyrolysis process as we have discussed in the first slide itself and I also described like how this carbonization and the torrefaction are the types of slow pyrolysis process in which the production of charcoal or the char is the primary goal. And this is how the slow pyrolysis of the biomass is carried out if the product of interest is only the char.

(Refer Slide Time: 17:14)

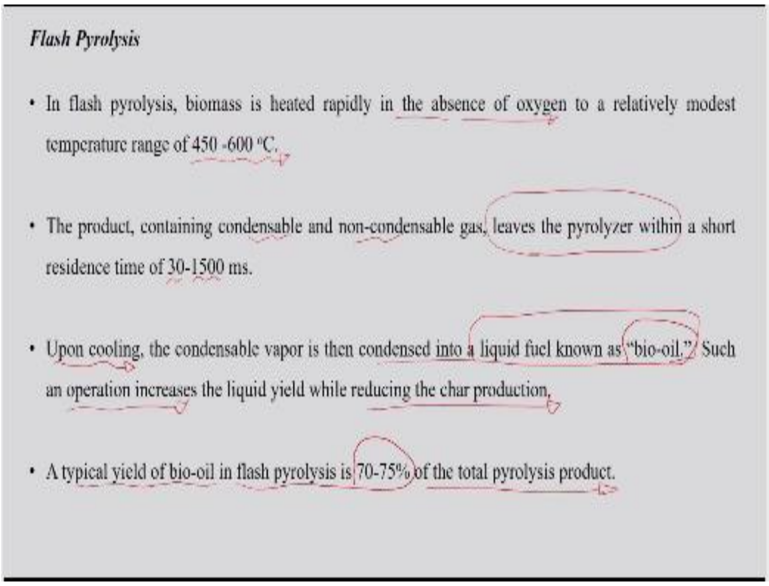


Apart from that, in case of fast pyrolysis, the biomass is heated, so rapidly that it reaches the peak temperature before it decomposes. And in fast pyrolysis, the vapour residence time is in the order of seconds or milliseconds. The primary goal of fast pyrolysis process is to maximise the production of the liquid fuel as a product. And the heating rate can be as high as around like even 1000 to even like 10,000 degrees C per second.

But the peak temperature it should be below 650 degree C if the bio-oil is the product of interest. And this is how the fast pyrolysis process is operated. If the bio-oil is of the product of interest, then the fast pyrolysis process operation is preferred to obtain the liquid fuel as a product. However, the peak temperature of about 1000 degree C is also preferred, if the production of the gas is primary objective.

And the flash and the ultra rapid pyrolysis are considered as the types of the fast pyrolysis process and used primarily for the production of bio-oil and gas as a product. So, now, let us discuss about this flash pyrolysis process in more detail.

(Refer Slide Time: 18:34)



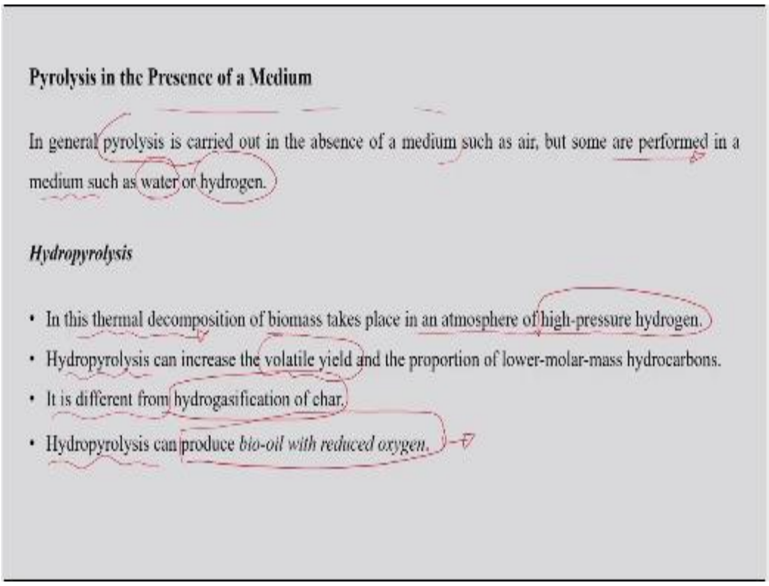
In case of flash pyrolysis the biomass is also heated rapidly in absence of oxygen, but to relatively a modest temperature around like 450 to 600 degree C only. The product containing condensable, non condensable gases leaves the pyrolyzer within a short residence time of around 30 to your 1500 milliseconds. So, in this case, the gases are not allowed to stay for a longer period of time inside the reactor.

However, if it is preferred it can be escaped out as quickly as possible and can be condensed outside in the downstream reactor to collect liquid as a product. Upon cooling, the condensable vapour is then cooled into the liquid phase which is known as a bio-oil as I mentioned. Because of the short residence time of the vapour inside the reactor so, most of the vapours are escaped out from the reactor as quickly as posible.

And can be condensed outside in the downstream reactor to produce liquid fuel which is known as bio-oil as a product. And such an operation increases the liquid yield while reducing the char production during the operation. And that is what is the advantage of the flash pyrolysis process. Here we can maximise the liquid yield and we can reduce or minimise the char production during the process.

A typical oil yield in the flash policies process is around 70 to 75%, which is a maximum of the total pyrolysis product. And that is what is the advantage of the flash and the fast pyrolysis process to maximise the liquid fuel as a product. So, now, after understanding the flash pyrolysis process, let us discuss about the pyrolysis processes which are carried out in presence of the medium.

(Refer Slide Time: 18:34)



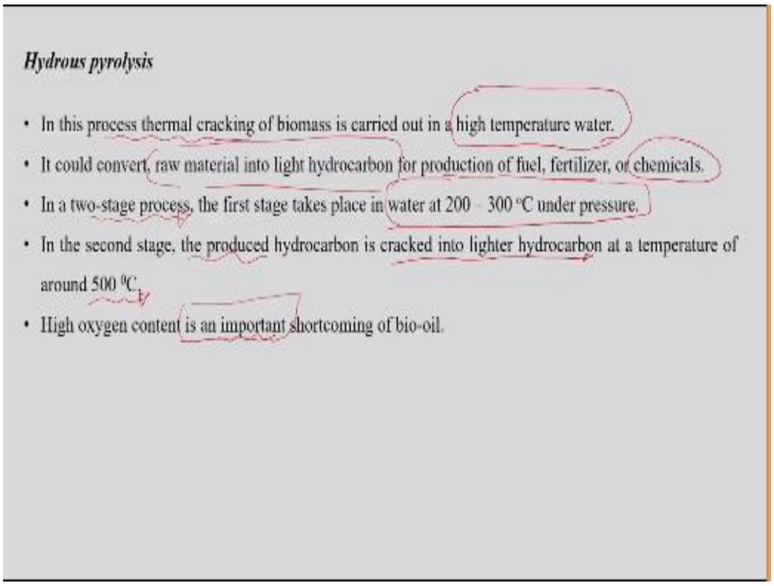
So, as I mentioned, in general the pyrolysis process is carried out in absence of any medium such as air, but, some operations are preferred in presence of some mediums such as water or hydrogen. And according to that this particular process are classified as a hydropyrolysis or the hydrous pyrolysis. Now, let us discuss about the hydropyrolysis first.

In case of hydropyrolysis, the thermal decomposition of the biomass, it takes place in an atmosphere of high-pressure hydrogen and that is why it is termed as a hydropyrolysis, because here the atmosphere of the medium is a high-pressure hydrogen. And the hydropyrolysis process, it can increase the volatile yield and the proportion of low molar mass hydrocarbon.

That is the advantage of the hydropyrolysis process and it is different from the hydrogasification of the char. As we are discussing the biomass gasification also, this particular process is different from that of the hydrogasification of the char. Hydropyrolysis process can produce the bio-oil with reduced oxygen. This is one of the most important advantage of the hydropyrolysis process, because it produce the bio-oil with reduced oxygen in its composition.

And hence, it can be effectively upgraded using the hydro processing technique to produce high quality fuel.

(Refer Slide Time: 18:34)

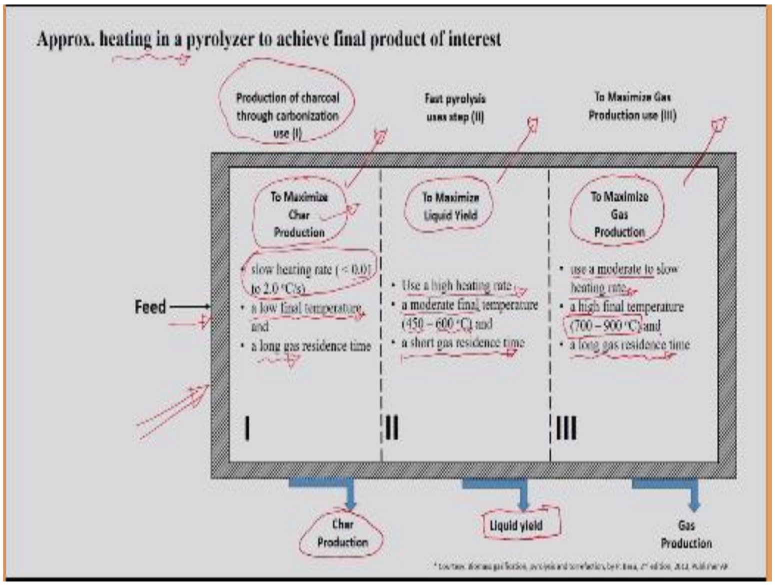


Whereas, in case of the hydrous pyrolysis, the thermal cracking of the biomass is carried out in a high temperature water. So, here the medium is high temperature water whereas, in the previous case, the process is carried out using a hydrogen as a medium. So, it could convert a raw material into the light hydrocarbon for the production of the fuel as well as fertiliser and chemical as a product.

In this particular process, it is a 2 stage operation in the first stage, it is carried out in water at around 200 to 300 degree C under pressure. And the hydrocarbons which are produced in the first stage is cracked into the lighter hydrocarbon at a temperature range of around like 500 degree C. The high oxygen content is an important shortcoming of the bio-oil produced using the hydrous pyrolysis process.

And that is how is the difference between the hydropyrolysis and hydrous pyrolysis in case of the hydrocarbons is the oxygen content is relatively low. Whereas, in case of the hydrous pyrolysis, the high oxygen content is one of the main important shortcoming of the hydrous pyrolysis process.

(Refer Slide Time: 23:02)



After learning the types of pyrolysis operation in the pyrolyzer, the pyrolysis of the carbonaceous material is carried out using a specific operating condition to meet the requirement of the final product of the interest. So, here one schematic has been shown, which is represented in the form of different stages that is stage one, stage 2 and the stage three.

So, now, let us consider this schematic as a one pyrolyzer and each individual unit in this schematic, it represents the independent pyrolyzer as well. So, now, based on the product of interest, which is required at the end of the operation, the pyrolysis operation can be carried out to meet the requirement of the final product of the interest. Say, for example, here the biomass is fed inside the pyrolyzer.

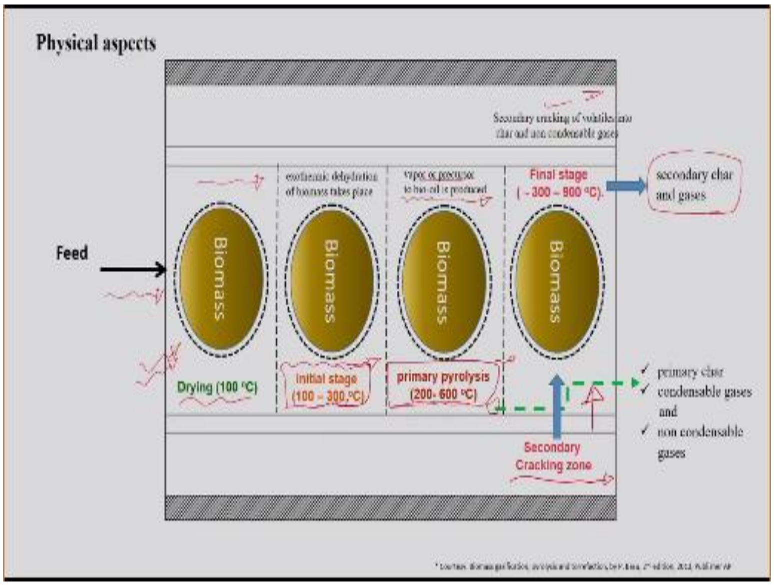
And if the objective is to maximise the char production in the pyrolysis operation, then use slow heating rate in the range of .01 to 2 degrees C per second and a low final temperature is allowed inside this particular process and also provide a long residence time inside the reactor. So, that the final product of the interest that is a char can be obtained at the end of the pyrolysis process. That is termed as a slow pyrolysis operation.

If the objective of the operation is to maximise the liquid yield as a product, then use a high heating rate as we have discussed earlier that is a fast pyrolysis process and a moderate final temperature in the range of around 450 to 600 degree C and short gas residence time. As a result it will lead to a liquid oil as a product and that is the maximum oil yield which can be achieved using the fast pyrolysis process because of the short residence time of gas inside the reactor.

If the objective is to achieve maximum gas production, then use moderate to slow hitting rate inside the pyrolyzer. And a final temperature can be in the range of around 700 to 900 degree C and also provide a long residence time to the vapours inside the reactor to achieve maximum gas production from the pyrolyzer. And this is how the pyrolysis operation is carried out to adjust the operating parameter inside the pyrolyzer and to meet the requirement of final product of the interest.

Now, after understanding the pyrolysis operation and how to achieve the final product of the interest in the form of char, liquid and gas as a product.

(Refer Slide Time: 25:29)



So, let us consider the physical aspect of the pyrolysis process inside the pyrolyzer. So, from the thermal standpoint, it is divided into the four chamber. For example, drying operation, the initial stage, primary stage and the secondary cracking zone inside the pyrolyzer. So, in the drying operation, which is carried out in the range of 100 degree C, it mostly released the free moisture and the loosely bound water inside the biomass.

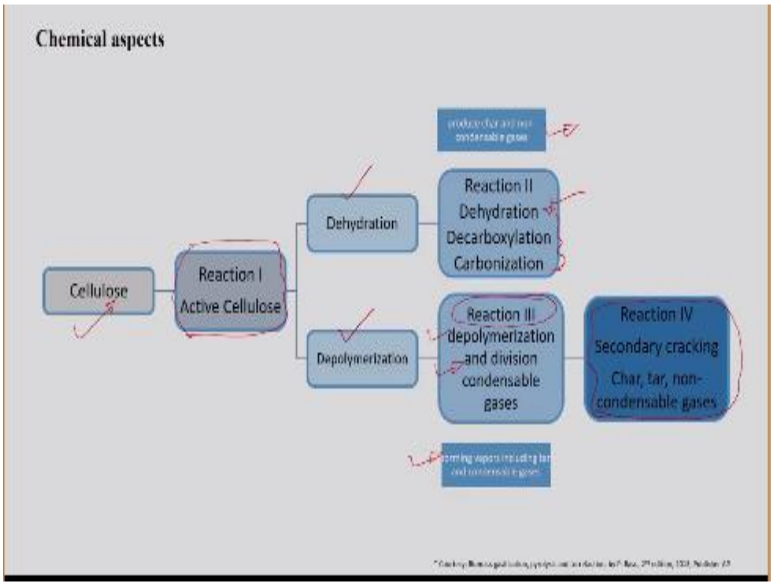
In the second stage, which is called as the initial stage, which is carried out in the temperature range of 100 to 300 degree C, so, exothermic reaction of the biomass takes place and releases some non condensable gases in the form of CO and the CO 2. So, the third stage which is a primary pyrolysis of the product producing the initial stage, which is carried out in the temperature and range of 200 to 600 degrees C.

And it mainly produced vapour or precursor to bio-oil in this particular stage. And if the vapour produced during this particular stage is allowed to escape out as quickly as possible, then it can be condensed outside in a downstream reactor to produce bio-oil as a product. On the other hand, if the vapours are allowed to stay for a long residence time inside the reactor, then in that case, the condensable gases in the form of long hydrocarbon compounds are thermally cracked to produce the additional char.

And that is what happens in the secondary cracking zone and it mainly reduces the liquid product during the pyrolysis process. And in case of the secondary process, it mainly gives secondary char and gas as a product which are mainly a non condensable gases. As we have mentioned here, the secondary cracking of the volatile which are present in the reactor are break down into a char and the non condensable gases.

And eventually it reduces the bio-oil yield during the process. Now, once you understand the physical aspect of the pyrolysis process, let us discuss about the chemical aspect of the pyrolysis process.

(Refer Slide Time: 27:26)

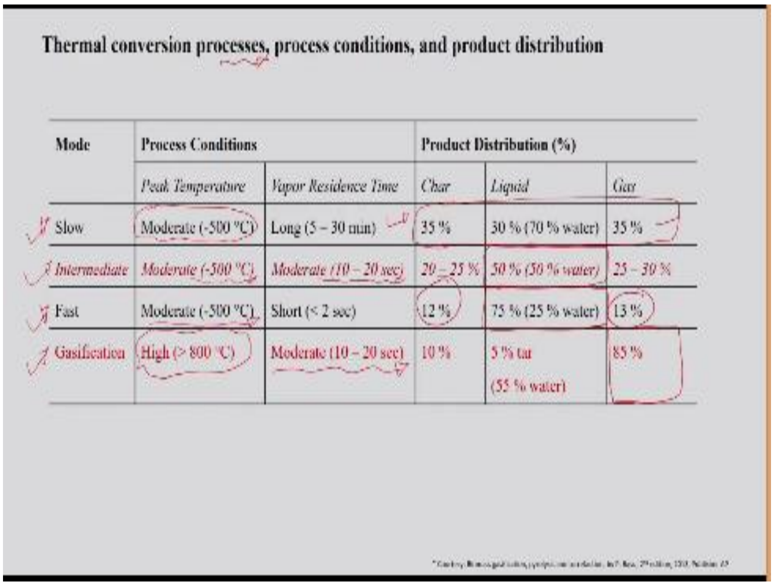


So, for the understanding purpose, here we have considered the cellulose as a component of the biomass. So, in this case the pre pyrolysis operation is carried out in the reaction I followed by 2 competing reaction that is dehydration and the depolymerization reaction. So, in the reaction II if you see here, its mainly a dehydration, decarboxylation and carbonization reaction and it mainly produces char and a non condensable gases as the product.

Whereas, in the reaction III, if you see here it is mainly depolymerization and it divides the condensable gases and forms vapours including tar and the condensable gases as the product. And the condensable vapours produced during this process is allowed to escape out as quickly as possible, then it can be condensed as a liquid bio-oil as a product. On the other hand, if the vapours are allowed to stay inside that reactor for a long residence time, then the secondary cracking of the vapours takes place.

And then it forms char, tar and the non condensable gases as a product. This is how it is important to remove the vapours as early as possible inside the pyrolyzer to improve the and to maximise the liquid yield as a product.

(Refer Slide Time: 28:47)



Thermal conversion processes, process conditions, and product distribution

Mode	Process Conditions		Product Distribution (%)		
	Peak Temperature	Vapor Residence Time	Char	Liquid	Gas
Slow	Moderate (~500 °C)	Long (5 – 30 min)	35 %	30 % (70 % water)	35 %
Intermediate	Moderate (~500 °C)	Moderate (10 – 20 sec)	20 – 25 %	50 % (50 % water)	25 – 30 %
Fast	Moderate (~500 °C)	Short (< 2 sec)	12 %	75 % (25 % water)	13 %
Gasification	High (> 800 °C)	Moderate (10 – 20 sec)	10 %	5 % tar (55 % water)	85 %

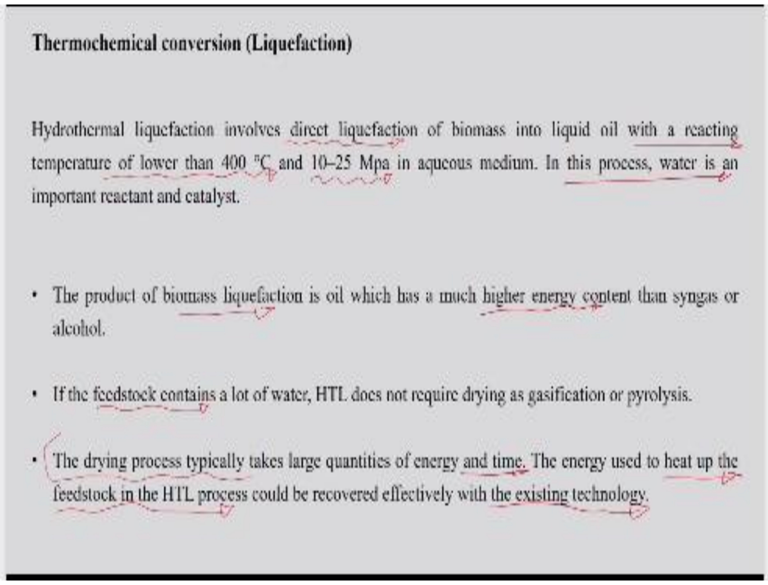
So, after understanding the physical and the chemical aspect of the pyrolysis process, let us try to compare the thermo-chemical conversion processes based on their process condition and the product distribution. So, in this case, let us discuss about the slow pyrolysis process first. In case of slow pyrolysis if you see, the peak temperature is moderate in the range of say 450 to 500 degree C.

And the residence time is relatively long in case of slow pyrolysis process, because the product of interest is a char. So, in this case, it gives wide distribution of the product in the form of 35% char, 30% liquid and 35% gases. So, this is how the distribution of the product takes place inside the slow pyrolysis process. If it is a intermediate mode of operation, in this case even the temperature is almost same, but the residence time is relatively less compared to the slow pyrolysis process.

And as a result, it leads to maximise the liquid product which is a product of the interest. Similarly, if we talk about the fast pyrolysis process, here also the peak temperature which is moderate and the residence time is relatively short which is less than your 2 seconds here and it gives maximum liquid as a product along with the traces of gas and char as a product.

Now, if you compare these processes with the gasification where the product of interest is only the gas, then in that case the peak temperature is relatively high that is greater than 800 degrees C and the residence time of the vapours inside the gasifier is around like 10 to 20 second and it maximise the gas as a product instead of liquid and the char. That is how this particular process can be carried out effectively to produce the product of interest either the liquid, gas or char as a product by just varying the operating condition inside the reactor.

(Refer Slide Time: 30:41)

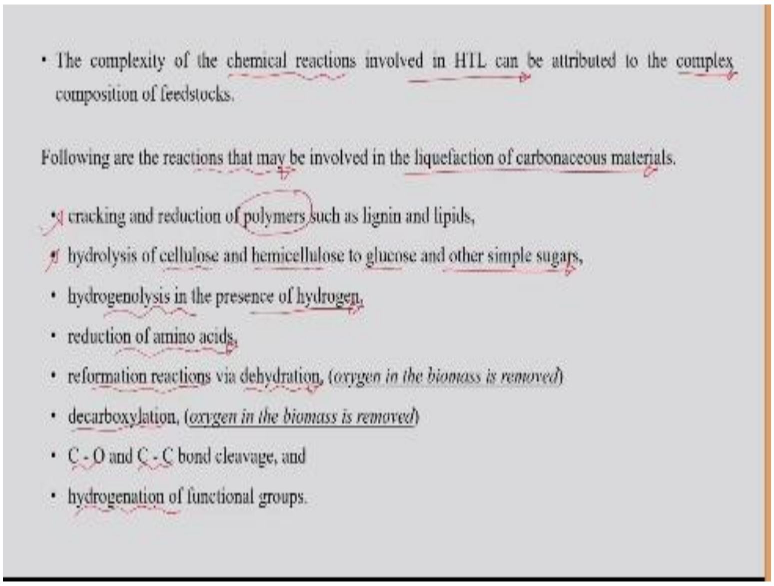


Now, once you understand the pyrolysis process, so, let us discuss about the another thermo-chemical conversion operation that is a liquefaction process. So, hydrothermal liquefaction process, it involves the direct liquefaction of the biomass into the liquid oil with a reacting temperature have even lower than 400 degrees C. But in this particular operation, it requires a significant pressure to keep the reaction mixture in the aqueous médium.

And in this process, the water is an important reactant and even the catalyst. And that is what is the role of the water in the hydrothermal liquefaction. It plays as the role of reactant as well as the catalyst. And the product of the biomass liquefaction is oil which has much higher energy content than that of the syngas and coal produced using the biochemical conversion process. If the feedstock contains a lot of water, HTL does not require the drying as gasification and the pyrolysis does.

The drying process typically, it takes large quantities of energy and time and the energy used to heat up the feedstock in the HTL process could be recovered effectively using the existing technology. And that is what is the advantage of the hydrothermal liquefaction technology is like the heat which is required to heat up the feedstock inside the reactor can be recovered effectively using this existing technology.

(Refer Slide Time: 32:04)



The hydrothermal liquefaction is a very complex reaction and the complexity of the chemical reaction involved in the hydrothermal liquefaction can be attributed to the complex composition of the feedstock. And following are the main reactions which are involved in the liquefaction of the carbonaceous material. So, if you look at the reactions here, it mainly involves the cracking and reduction of the polymers such as lignin and lipids followed by the hydrolysis of the cellulose and hemicellulose to glucose and other simple sugars.

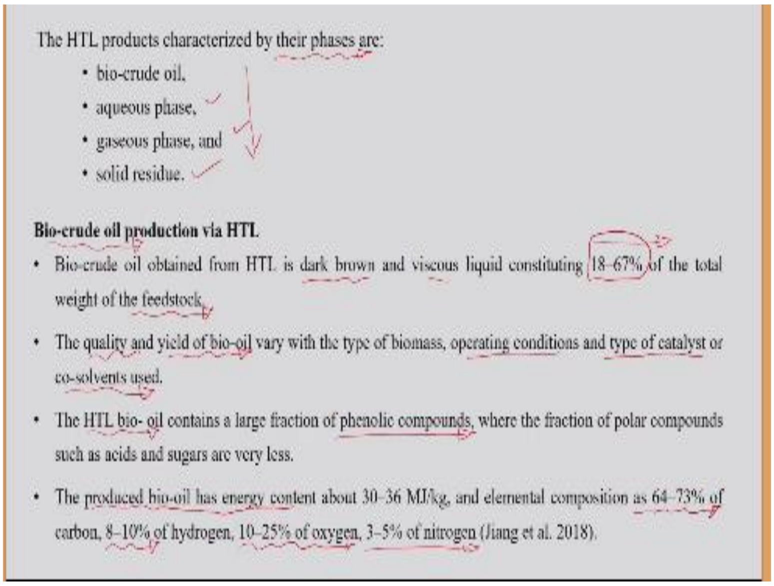
This is one of the major reaction which takes place in the hydrothermal liquefaction process followed by the hydrogenolysis in the presence of the hydrogen produced during the hydrothermal liquefaction process and reduction of the amino acid at the biomass feedstock.

It mainly consists of protein, lipids, fats and carbonaceous material. So, the protein contained in the biomass is reduced into the amino acid during the hydrothermal liquefaction process and the reformation reaction via dehydration and the decarboxylation reaction.

If you remember our discussion in the gasification and even the combustion processes. So, the dehydration process, it mainly removes the oxygen in the biomass in the form of H 2 O, whereas decarboxylation process it removes oxygen in the biomass in the form of the C O 2. And these particular reactions are also takes place in the hydrothermal liquefaction process and by which it removes the oxygen present in the biomass.

And C-O and the C-C bond cleavage reaction followed by the hydrogenation of the functional groups and these all are the number of reactions which takes place in the hydrothermal liquefaction of the biomass.

(Refer Slide Time: 33:44)

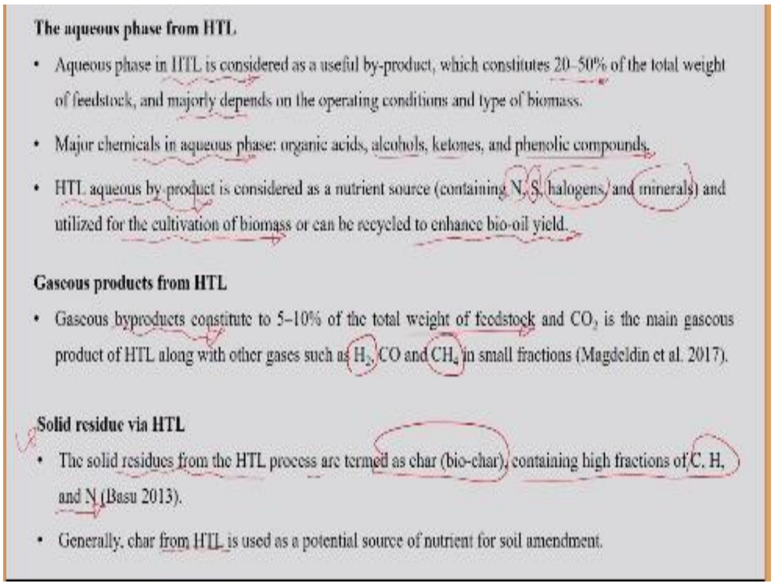


So, the hydrothermal liquefaction of the biomass and the product produced from the hydrothermal liquefaction of biomass are categorised based on their phases. That is the bio-crude oil phase, aqueous phase, gaseous phase and solid residue as the product. So, the bio-crude oil which is obtained from the HTL process is a dark brown and the viscous liquid consisting around 18 to 67 % of the total weight of the feedstock.

And that is what is the advantage of the HTL process because, it leads to maximise the liquid product and it is in the range of 18 to 67 % of the total weight of the feedstock. The quality and the yield of bio-oil it varies and it depends on the type of biomass which is used during the hydrothermal liquefaction process. And the operating condition as well as the type of catalysts or the co- solvents used during the process also plays a major role in improving the quality of the product in the HTL process.

The HTL bio-oil, it contains a large fraction of the phenolic compound, whereas, the fraction of polar compounds such as glucose and acids are very less in the bio-oil produced in the HTL process. And the produced bio-oil, it has high energy content in the range of about 30 to 36 mega joule per kg and also has elemental composition in the form of 64 to 73 % is carbon content, 18 to 10% of hydrogen, 10 to 20% of oxygen and 3 to 5% of the nitrogen.

(Refer Slide Time: 35:14)



So, now, if you discuss about the aqueous phase which is obtained from the hydrothermal liquefaction of the biomass. So, the aqueous phase in the HTL is considered as a useful byproduct and which constitutes around 20 to 50% of the total weight of the feedstock. And it majorly depends on the operating condition even on the type of biomass.

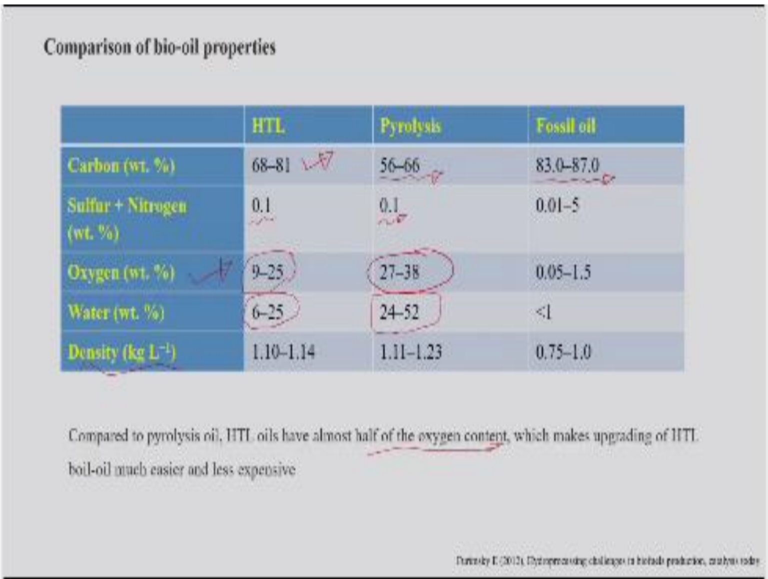
Similarly, as we have discussed the type of biomass as well as the opening condition of the HTL process are mainly responsible to produce the organic phase, aqueous phase, solid phase and the gas phase in during the hydrothermal liquefaction process. And the major chemicals in the aqueous phase are organic acids, alcohol, ketones and the phenolic compounds. And the HTL aqueous byproduct is also considered as a nutrient source because it contains nitrogen, sulphur, sub halogens and minerals as well.

And it can be utilised for the cultivation of biomass or also can be recycled to enhance the bio-oil yield in the operation. That is what is the advantage of the particular process as well. And that is what I mentioned in the previous slide that the energy which is required to heat up the feedstock in the hydrothermal liquefaction process can also be recovered effectively using this existing technology.

And the gaseous product obtained during the particular HTL process, it costituted around 5 to 10 % only of the total weight of the feedstock and it mainly consists of C O 2 as a gas in its composition along with the other gases such as hydrogen, carbon monoxide and methane but these are in very small fraction. Whereas, if we talk about the solid residues, which is obtained using the HTL process.

So, the solid residues from the HTL process are termed as a char that is also called as a biochar. And it contains high fraction of carbon, hydrogen and the nitrogen. And generally, the chart from the HTL is used as a potential source of nutrient for the soil amendment or also act as a soil enhancer.

(Refer Slide Time: 37:16)



So, now, let us compare the bio-oil obtained using the pyrolysis as well as using the HTL process. If you see here, the carbon content in the bio-oil produced using the HTL process is relatively high, which is equivalent to even the fossil oil carbon content. But the carbon content of the bio-oil produced using the pyrolysis process is relatively less as compared to the HTL process.

And also contains a small fraction of sulphur and the nitrogen in its composition and it is more or less same in the bio-oil produced in the HTL and the pyrolysis process and the oxygen content if you see in case of the HTL process, it is just almost half of the oxygen content of the pyrolysis produced by oil. And that is what is a one of the major advantage of the bio-oil produced using the HTL process.

As the oxygen content in the bio-oil produced using the hydrothermal liquefaction process is almost half of the oxygen content of the bio-oil produced using the pyrolysis process. And water content also it is significantly less in the bio-oil produced using the hydrothermal liquefaction process. Whereas, in case of the bio-oil produced using the pyrolysis process, as significant amount of the wáter.

And density is more or less same from the bio-oil produced either using the steam process or the pyrolysis process. And this is how is the comparison of the bio-oil produced using the hydrothermal and the pyrolysis process. The bio-oil produced from the pyrolysis process as well as from the hydrothermal the creation process also has certain limitations.So, the undesirable characteristics of the bio-oil it restricts its use as a fuel.

(Refer Slide Time: 38:50)

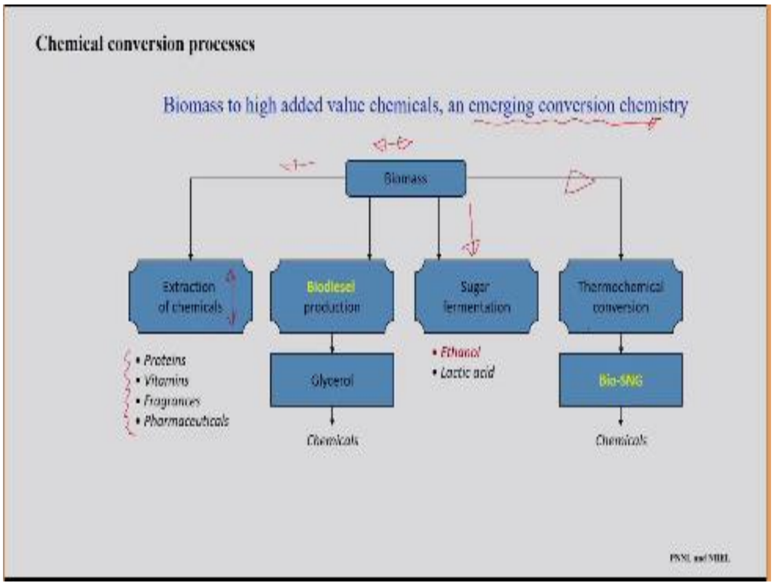
So, the low pH value is one of the issue of the bio-oil and its effect is mainly a corrosión problem. Secondly is the high viscosity. It cause, handling and the pumping problem as well during the operation. Instability and the temperature sensitivity is another undesirable characteristics of the bio-oil produced during this particular process. And it leads to the storage problema, phase separation, decomposition and the gum formation during the storage condition.

And it leads to increase the viscosity of the bio-oil also if it is stored for a prolonged period of time. Char and the solid content in the bio-oill produced using these processes, it leads to the issue of the combustion during the operation, equipment blockage and the erosion. Similarly, the presence of the alkali metals in the bio-oil produced leads to the deposition of the solids in boilers, engine and the turbines during the operation.

And the water content in the bio-oil it leads to reduce the heating value of the bio-oil. Also the oxygen content in the bio-oil also reduces the heating value and as a result the bio-oil produced using these processes can be upgraded using a hydro processing technique. Systems can be upgraded using a hydroprocessing technique and which can be used to deoxygenate the oil.

So, the excess oxygen which is present in the bio-oil can be removed using the hydroprocessing technique, which can be used to deoxygenate the oil and subsequently improve the properties of the bio-oil. So, that the high quality fuel which is obtained during this hydro deoxygenation reaction can be used as a fuel.

(Refer Slide Time: 40:22)



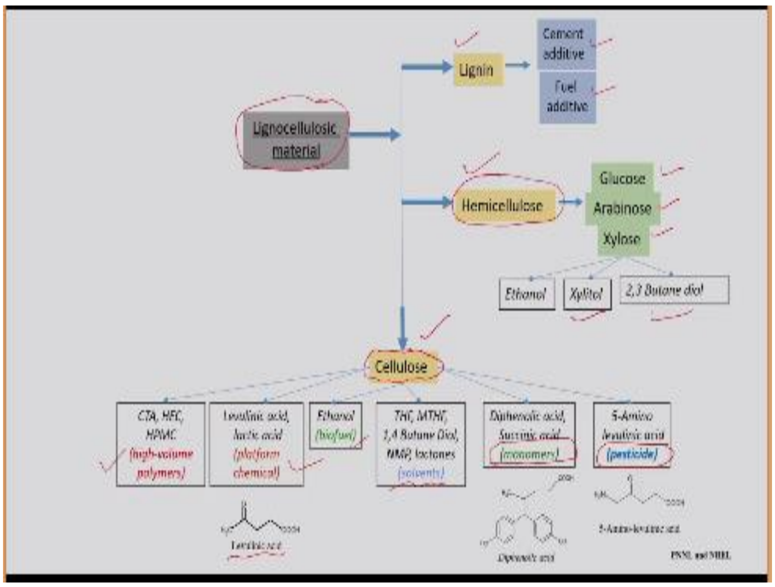
So, now, after understanding the thermo-chemical conversion processes such as pyrolysis and the liquefaction process, let us discuss about the chemical conversion processes. So, the lignocellular biomass, it consists of cellulose, hemicellulose and lignin. And these 3 are the main component in the lignocellulosic biomass. So, effective utilisation of these lignocellulosic material can lead to the production of the value added chemicals by using a emerging conversion process chemistry.

So, the lignocellulosic biomass can be effectively utilised to convert it into a suitable chemicals. So, the specific class of biomass it can be used to extract proteins, vitamins, fragments and pharmaceutical grade chemical from the specific grade of biomass using the suitable extraction technique. Similarly, the other type of biomass such as the oil seeds can be effectively utilised to produce the oil.

And the oil produced from the oil seeds can be subsequently transesterified using the chemical process to produce the biodiesel and the diesel or as a product. So, the glycerol which is act as a byproduct during the process can also be processed further using the hydrogenolysis process to produce the propanediol as a chemical. So, this is how the oil seeds can also be effectively utilised to produce the fuel as well as the chemical using a suitable conversion technique.

Apart from that, the reducing sugar which are obtained from the hydrolysis of the biomass can also be fermented to produce the ethanol and lactic acid as a product and can also be thermo-chemically converted to produce the bioSNG. And the bio syngas produced from the thermo-chemical processes can also be converted into a chemical using a suitable catalytic conversion technique.

(Refer Slide Time: 42:08)

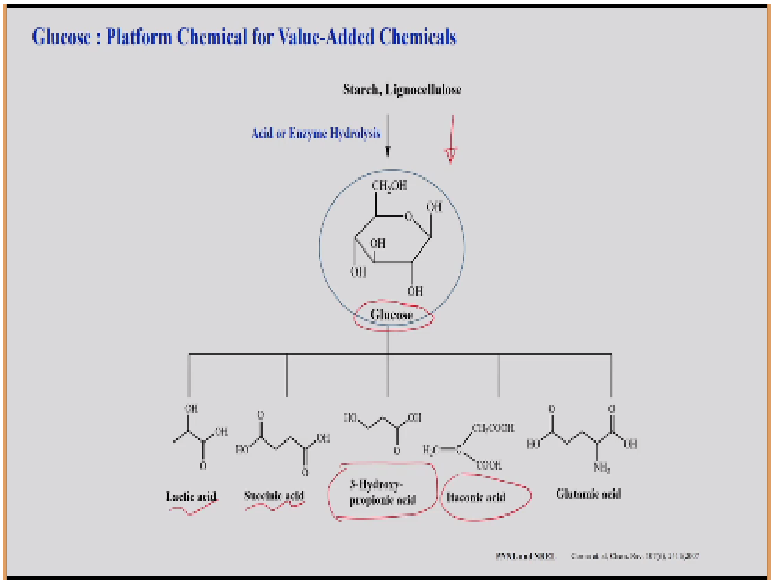


Apart from that, if you see the particular chart here, the lignocellulosic biomass as I mentioned, it mainly consists of lignin, hemicellulose and cellulose as a main component. So, the lignin can be processed individually to produce cement additives and the fuel additives as a product in the form of the chemical. And the hemicellulose fraction of the biomass can be hydrolyzed using the acid hydrolysis process to produce glucose, arabinose and xylose as the chemical.

And these are the platform chemicals to produce ethanol, xylitol and the butanediol as a product. Apart from that, the cellulose which is the major component of the lignocellulosic biomass can also be converted effectively into the range of value added chemicals in the form of high value polymers that form chemicals that is a levulinic acid, biofuels that is in the form of ethanol, solvents, monomers that is diphenolic acid example which is given here is a diphenolic acids and the pesticide in the form of 5-aminolevulinic acid.

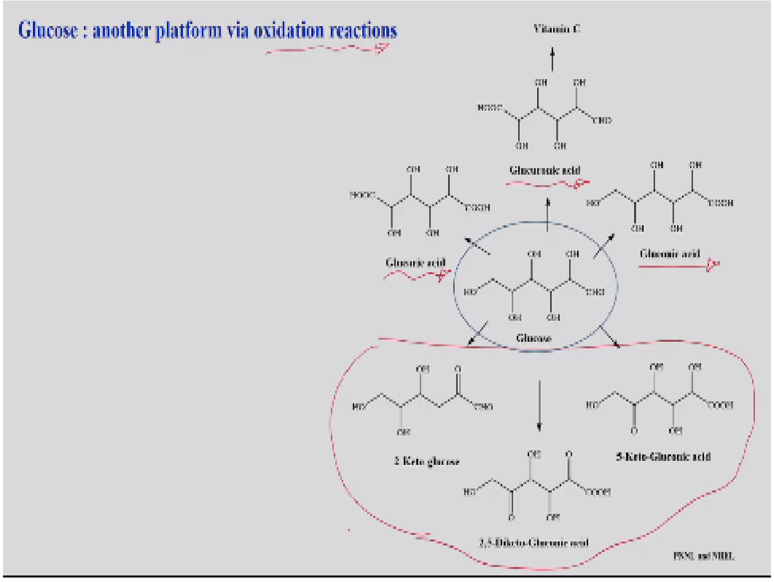
So, likewise, the lignocellulosic biomass can also be utilised effectively to produce the range of the chemicals. So, if you see here, another platform chemical that is a glucose can also be effective utilised to produce the value added chemical.

(Refer Slide Time: 43:22)



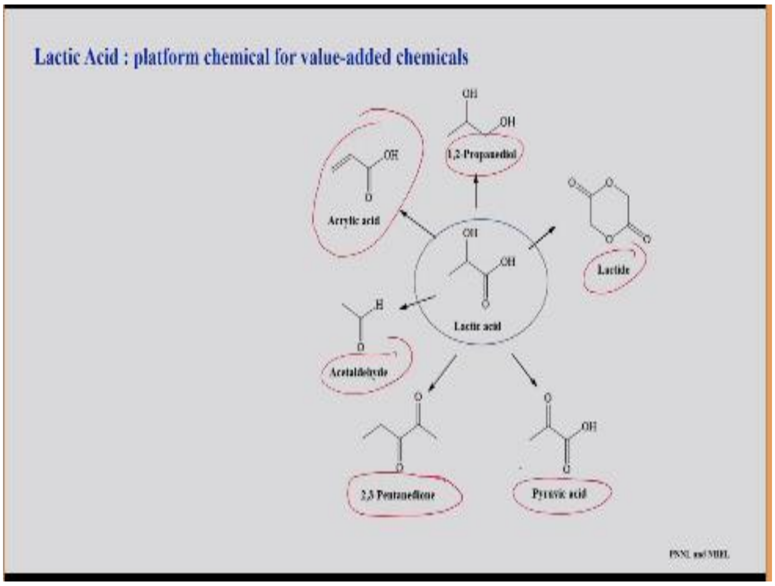
So, the glucose can be obtained effectively from the hydrolysis process that is the hydrolysis of the lignocellulosic biomass can be used to the production of the glucose and the glucose which is produced during this process can effectively be converted into the lactic acid succinic acid, 3 hydroxy propionic acid, itaconic acid and the glutamic acid. So the range of chemicals can also be obtained using the glucose as a platform chemical.

(Refer Slide Time: 43:50)



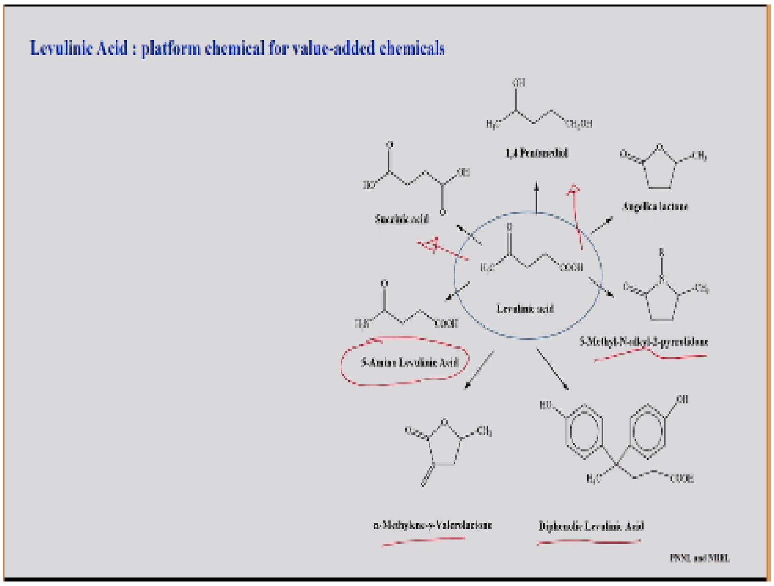
Apart from that, the glucose can also be used as a platform chemical and via oxidation reaction, it can also leads to the range of the chemicals in the form of gluconic acid glucuronic acid, glucaric acid and a range of other chemicals as well. So this is how the particular glucose can also be utilised as a suitable platform to produce different kinds of value added chemical.

(Refer Slide Time: 44:21)



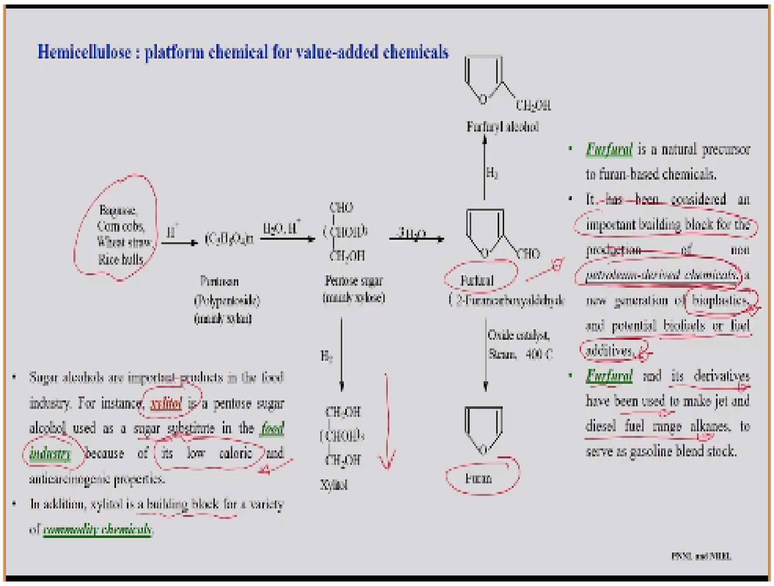
So this lactic acid produced from the glucose can also be effectively utilised to produce a range of the value added chemicals that is in the form of acid, aldehyde, lactide and propanediol. So this kind of chemicals can also be obtained from the platform chemical that is a lactic acid.Apart from that it also used to produce the 2 3 pentanedione and the pyruvic acid.

(Refer Slide Time: 44:46)



Now once you understand about the lactic acid, so another chemical which is a levulinic acid will also act as one of the platform chemical to produce value added chemical. And the levulinic acid can leads to the production of 1,4 pentanediol, succinic acid and 5 amino levulinic acid, which also act as a pesticide. So, likewise, range of the chemicals can also be obtained using levulonic acid as a platform chemical and it can lead to the production of the value added chemical from the lignocellulosic biomass.

(Refer Slide Time: 45:21)



Apart from that, if you see here, there is a one more platform chemical which can effectively utilise to produce the range of the chemicals that is a hemicellulose. So, the hemicellulose fraction of the lignocellulosic biomass can be effectively utilised to produce the value added chemical. So, the hemicellulose fraction of the lignocellulosic biomass can be hydrolyzed using the acid hydrolysis technique to produce the pentose sugar.

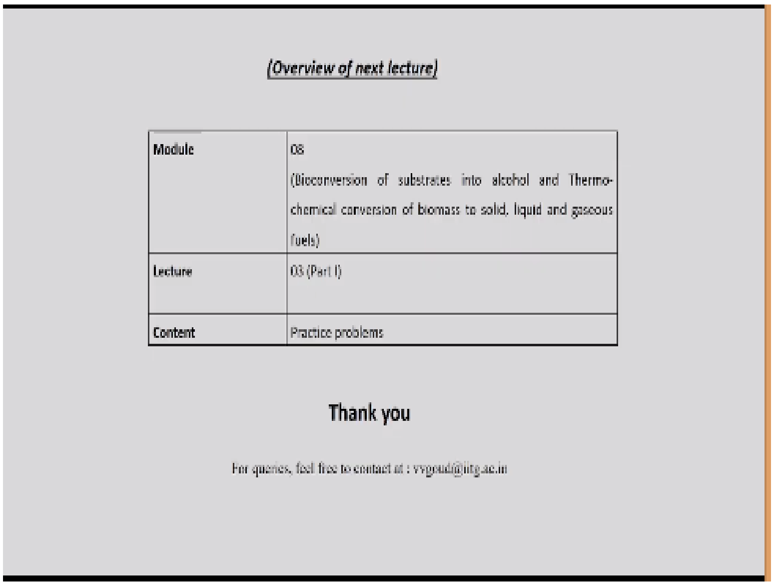
And the pentose sugar in the form of xylose, obtained during the hydrolysis of the hemicellulose can further be converted into the xilitol, furfural and the produced furfural cannot further be converted into the furfural alcohol and furan. So, the xylitol which is a pentose sugar alcohol, it is used as a sugar substitute in the food industry, because of the its low calorific value and anti carcinogenic effect.

So, that is what is the importance of the xylitol in the food industry. Apart from that, the xylitol is also act as a building block for the variety of the commodity chemicals. And the furfural produced from the pentose sugar is also been considered as an important building block for the production of non petroleum based derived chemicals that is the new generation of the bioplastics and the potential bio-fuel or the fuel additives.

Apart from that the furfural and its derivatives have also been used to make jet and the diesel fuel range alkanes to serve as a gasoline blend stock. So, range of these particular chemicals can be produced using lignocellulosic biomass as a feedstock. And this all talks about the conversion of the lignocellulosic biomass to produce a range of chemicals using a emerging process conversion chemistry.

So with this, we will end our lecture which discusses about the pyrolysis, liquefaction and the chemical conversion processes.

(Refer Slide Time: 47:23)



So in the next lecture, we will practice few examples from the thermo-chemical conversion processes that is gasification and the combustión. Regarding this lecture, if you have any doubt, feel free to contact me at vvgoud@iitg.ac.in. Thank you.