Biomass Conversion and Biorefinery

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Module 08
Lecture-22
Biooil and Biochar Production Reactors

Good morning students. This is lecture 1 under module 8. In this lecture, we will be discussing about biooil and biochar production, then the factors affecting biooil and biochar production and about the reactors. So, let us begin.

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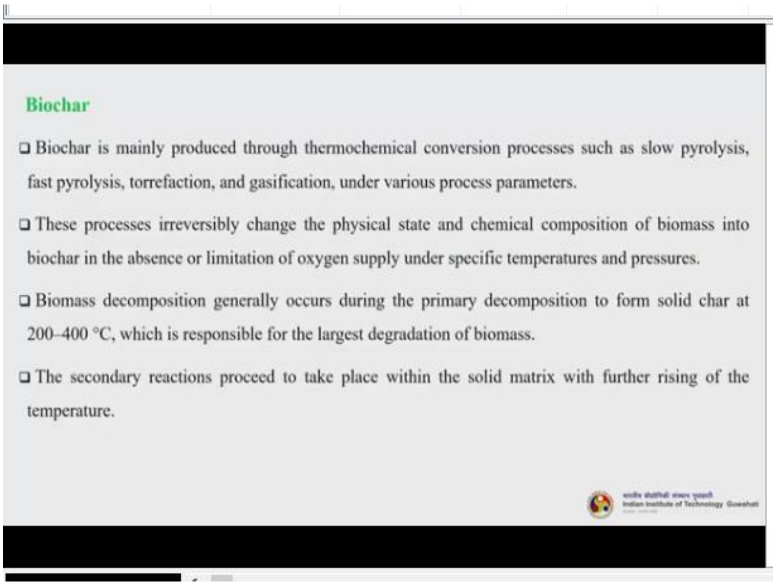

Biochar

- Biochar is mainly produced through thermochemical conversion processes such as slow pyrolysis, fast pyrolysis, torrefaction, and gasification, under various process parameters.
- These processes irreversibly change the physical state and chemical composition of biomass into biochar in the absence or limitation of oxygen supply under specific temperatures and pressures.
- Biomass decomposition generally occurs during the primary decomposition to form solid char at 200–400 °C, which is responsible for the largest degradation of biomass.
- The secondary reactions proceed to take place within the solid matrix with further rising of the temperature.

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Biomass decomposition generally occurs during the primary decomposition to form solid char at 200 to 400 degrees centigrade, which is responsible for the largest degradation of biomass; the secondary reactions proceed to take place within the solid matrix with further rising of the temperature. As you know that in our earlier class also we have discussed that biooil and biochar are the 2 most valuable and important products of the thermochemical conversion.

So, there are various types of processes that can be used or techniques that can be used starting from gasification, pyrolysis, torrefaction, hydrothermal liquefaction, there are many thermochemical conversion processes, which we have already discussed. Now, it has always been seen that whenever you eye apply for a higher biooil production, then the process and the reactor process parameters will be a little different than when you are eying the biochar as the main product and that we are going to discuss today also.

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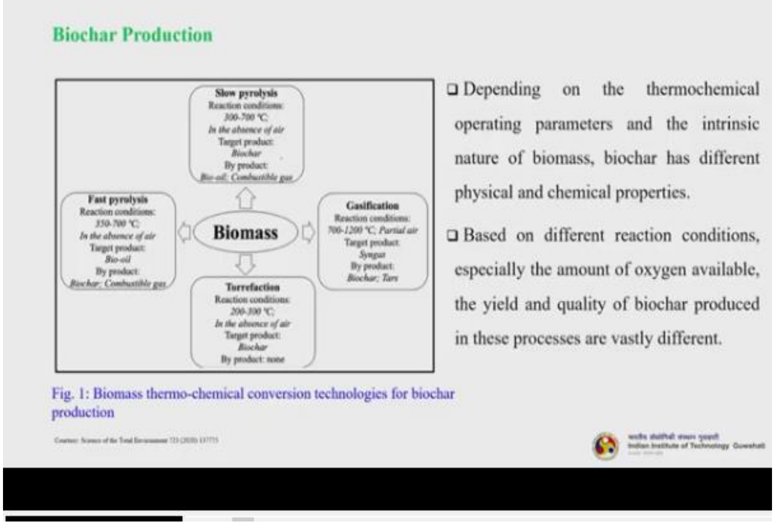

Biochar Production

Slow pyrolysis
Reaction conditions:
300-700 °C
In the absence of air
Target product:
Biochar
By product:
Bio-oil; Combustible gas

Fast pyrolysis
Reaction conditions:
350-700 °C
In the absence of air
Target product:
Bio-oil
By product:
Biochar; Combustible gas

Biomass

Gasification
Reaction conditions:
700-1200 °C; Partial air
Target product:
Syngas
By product:
Biochar; Tars

Torrefaction
Reaction conditions:
200-300 °C
In the absence of air
Target product:
Biochar
By product: none

Fig. 1: Biomass thermo-chemical conversion technologies for biochar production

- ❑ Depending on the thermochemical operating parameters and the intrinsic nature of biomass, biochar has different physical and chemical properties.
- ❑ Based on different reaction conditions, especially the amount of oxygen available, the yield and quality of biochar produced in these processes are vastly different.

If you look at biochar production from biomass using the thermochemical conversion technologies - so, we can have 4 different classes of processes. The first let us begin with the fast pyrolysis; so, this particular slide will make you understand that what are the process conditions that is required to produce biochar and of course, even biooil also. So, in fast pyrolysis the reaction conditions are little different. So, it is around 350 to 700 degrees centigrade in the absence of air and target is actually biooil. So, fast pyrolysis is always used to produce biooil. The biochar that you get, the quality is not so good. So, the byproducts are biochar and combustibles.

So, then, slow pyrolysis. In slow pyrolysis, the reaction conditions are again 300 to 700 degrees centigrade, the temperature is almost more or less the same in the absence of air, but the target product here is majorly the biochar. Apart from that, you may get some biooil and combustible gases.

Now, the next is gasification. Here the reaction conditions are a little different. So, around 700 to 1200 degrees centigrade, partial air is there - we have discussed about gasification in detail earlier. Here the target product is of course, syngas, byproduct is by biochar and tars. Now, here the biochar whatever we are getting is okay, moderately quality is fine or moderate we can say.

Then torrefaction, here the reaction conditions and temperatures are very less compared to other processes around 200 to 300 degrees centigrade in the absence of air, but the major product is biochar and we get no byproducts from this torrefaction process.

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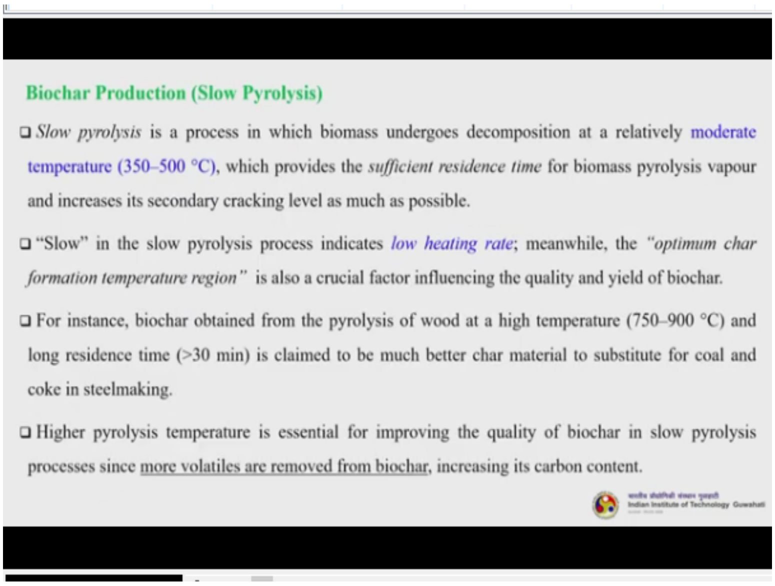

Biochar Production (Slow Pyrolysis)

- ❑ *Slow pyrolysis* is a process in which biomass undergoes decomposition at a relatively moderate temperature (350–500 °C), which provides the *sufficient residence time* for biomass pyrolysis vapour and increases its secondary cracking level as much as possible.
- ❑ "Slow" in the slow pyrolysis process indicates *low heating rate*; meanwhile, the *"optimum char formation temperature region"* is also a crucial factor influencing the quality and yield of biochar.
- ❑ For instance, biochar obtained from the pyrolysis of wood at a high temperature (750–900 °C) and long residence time (>30 min) is claimed to be much better char material to substitute for coal and coke in steelmaking.
- ❑ Higher pyrolysis temperature is essential for improving the quality of biochar in slow pyrolysis processes since more volatiles are removed from biochar, increasing its carbon content.

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So, let us understand one by one all the processes. So, first is the slow pyrolysis. So, slow pyrolysis is a process in which biomass undergoes decomposition at a relatively moderate temperature 350 to 500 degrees centigrade, which provides the sufficient residence time for biomass pyrolysis vapour and increases its secondary cracking level as much as possible. "Slow" in the slow pyrolysis process indicates low heating rate and meanwhile, the optimum char formation temperature region is also a crucial factor influencing the quality and yield of biochar.

For instance, biochar obtained from the pyrolysis of wood at a higher temperature 750 to 900 degrees centigrade and long residence time greater than 30 minutes is claimed to be much better char material to substitute for coal and coke in steelmaking. Higher pyrolysis temperature is essential for improving the quality of biochar in slow pyrolysis processes since more volatiles are removed from biochar increasing its carbon content.

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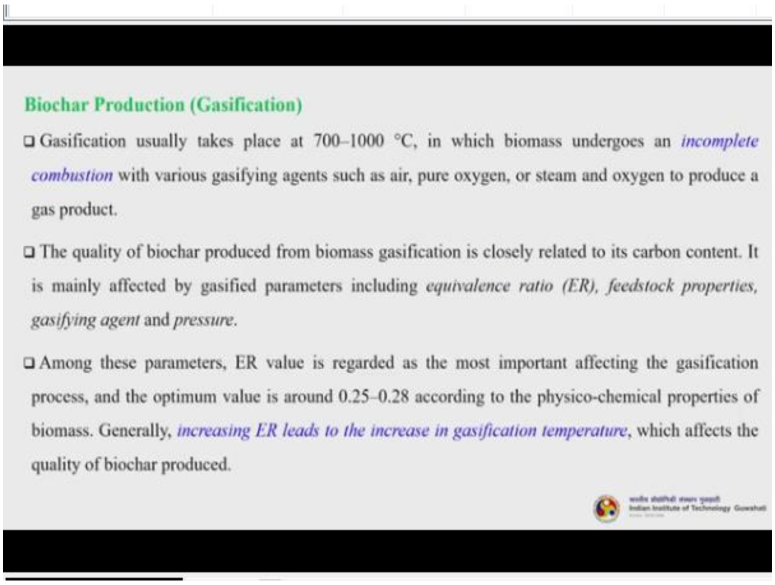

Biochar Production (Gasification)

- Gasification usually takes place at 700–1000 °C, in which biomass undergoes an *incomplete combustion* with various gasifying agents such as air, pure oxygen, or steam and oxygen to produce a gas product.
- The quality of biochar produced from biomass gasification is closely related to its carbon content. It is mainly affected by gasified parameters including *equivalence ratio (ER), feedstock properties, gasifying agent* and *pressure.*
- Among these parameters, ER value is regarded as the most important affecting the gasification process, and the optimum value is around 0.25–0.28 according to the physico-chemical properties of biomass. Generally, *increasing ER leads to the increase in gasification temperature*, which affects the quality of biochar produced.

Then gasification: Gasification usually takes place at 700 to 1000 degrees centigrade, in which biomass undergoes an incomplete combustion with various gasifying agents, such as air, pure oxygen or steam and oxygen to produce a gaseous product. The quality of biochar produced from biomass gasification is closely related to its carbon content. It is mainly affected by the gasified parameters which increase the equivalence ratio – ER, then feedstock properties, gasifying agent and of course pressure.

Now among these parameters the equivalence ratio is regarded as the most important factor that affects the gasification process. And the optimum value is usually 0.25 to 0.28 according to the physicochemical properties of the biomass. Generally, it has been seen that when you increase the ER, that leads to an increase in the gasification temperature, which affects the quality of the biochar that is produced.

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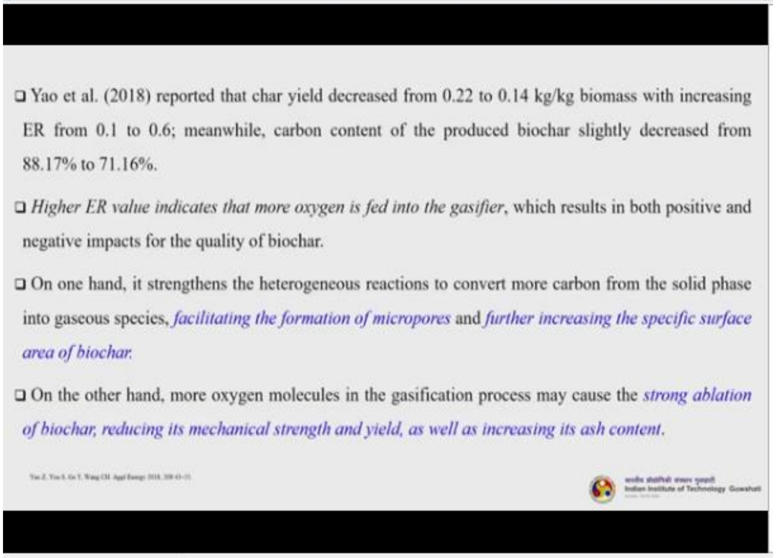

- Yao et al. (2018) reported that char yield decreased from 0.22 to 0.14 kg/kg biomass with increasing ER from 0.1 to 0.6; meanwhile, carbon content of the produced biochar slightly decreased from 88.17% to 71.16%.
- *Higher ER value indicates that more oxygen is fed into the gasifier*, which results in both positive and negative impacts for the quality of biochar.
- On one hand, it strengthens the heterogeneous reactions to convert more carbon from the solid phase into gaseous species, *facilitating the formation of micropores* and *further increasing the specific surface area of biochar.*
- On the other hand, more oxygen molecules in the gasification process may cause the *strong ablation of biochar, reducing its mechanical strength and yield, as well as increasing its ash content*.

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So, in a significant work Yao et al reported that char yield decreased from 0.22 to 0.14 kilogram per kilogram of biomass with increasing ER from 0.1 to 0.6. Meanwhile, carbon content of the produced biochar slightly decreased from 88.17% to 71.16%. So, it indicates that higher ER value needs more oxygen that is required to be fed into the gasifier, which results in both positive and negative impacts for the quality of the biochar.

On one hand, it strengthens the heterogeneous reactions to convert more carbon from the solid phase into the gaseous species, facilitating the formation of the micropores and further increasing the specific surface area of the biochar. On the other hand, more oxygen molecules in the gasification process may cause the strong ablation of biochar reducing its mechanical strength and yield as well as increasing its ash content.

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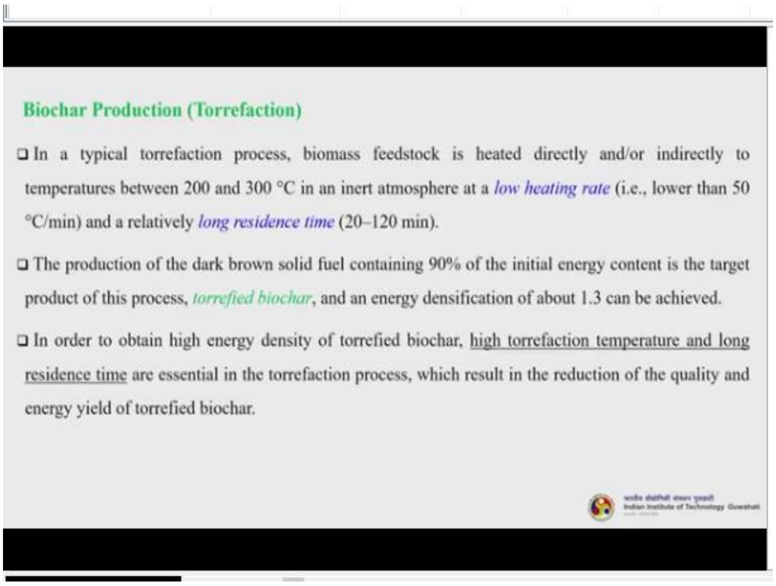

Biochar Production (Torrefaction)

- ❑ In a typical torrefaction process, biomass feedstock is heated directly and/or indirectly to temperatures between 200 and 300 °C in an inert atmosphere at a *low heating rate* (i.e., lower than 50 °C/min) and a relatively *long residence time* (20–120 min).
- ❑ The production of the dark brown solid fuel containing 90% of the initial energy content is the target product of this process, *torrefied biochar*, and an energy densification of about 1.3 can be achieved.
- ❑ In order to obtain high energy density of torrefied biochar, high torrefaction temperature and long residence time are essential in the torrefaction process, which result in the reduction of the quality and energy yield of torrefied biochar.

Let us now understand about torrefaction. So, in a typical torrefaction process, biomass feedstock is heated directly and/or indirectly to temperatures between 200 to 300 degrees centigrade in an inert atmosphere at a low heating rate - lower than 50 degrees centigrade per minute - and a relatively long residence time 20 to 120 minute. The production of the dark brown solid fuel containing 90% of the initial energy content is the target product of this process, which is known as the torrefied biochar, and an energy densification of about 1.3 can be achieved. Now, in order to obtain high energy density of the torrefied biochar, high torrefaction temperature and long residence time are essential in the torrefaction process, which result in the reduction of the quality and energy yield of the torrefied biochar. If you understand, then the main product of torrefaction is biochar. So, it does not produce any other byproducts. Of course, it will result in some gas, which is of no use or no commercial application.

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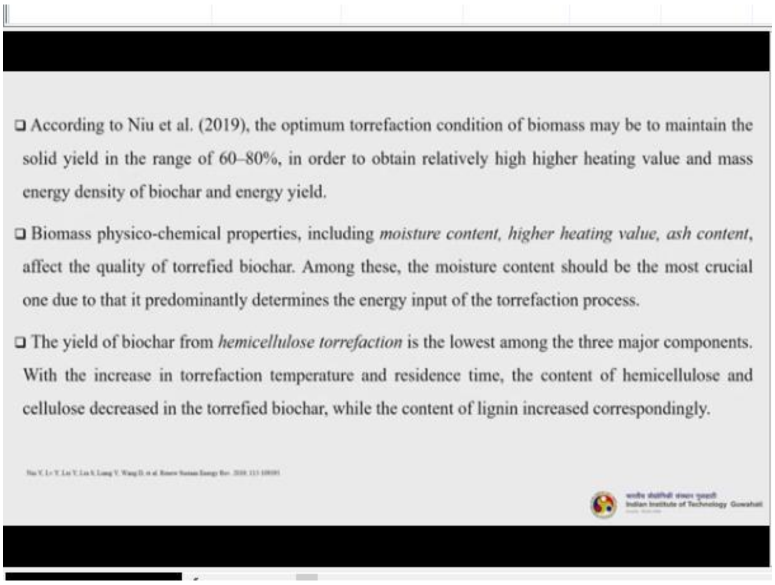

- ❑ According to Niu et al. (2019), the optimum torrefaction condition of biomass may be to maintain the solid yield in the range of 60–80%, in order to obtain relatively high higher heating value and mass energy density of biochar and energy yield.
- ❑ Biomass physico-chemical properties, including *moisture content, higher heating value, ash content*, affect the quality of torrefied biochar. Among these, the moisture content should be the most crucial one due to that it predominantly determines the energy input of the torrefaction process.
- ❑ The yield of biochar from *hemicellulose torrefaction* is the lowest among the three major components. With the increase in torrefaction temperature and residence time, the content of hemicellulose and cellulose decreased in the torrefied biochar, while the content of lignin increased correspondingly.

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So, according to Niu et al the optimum torrefaction condition of biomass may be to maintain the solid yield in the range of 60 to 80%, in order to obtain relatively high higher heating value and mass energy density of the biochar and the energy yield. So, another important thing is that biomass physicochemical properties such as moisture content, higher heating value, ash content. So, these properties significantly affect the quality of the torrefied biochar.

Among these, moisture content should be the most crucial, because due to that, it actually determines the energy that is required to carry out or even initiate the torrefaction process. So, more the moisture content, the more amount of energy will be required to carry out the torrefaction process. The yield of the biochar from hemicellulose torrefaction is the lowest among the 3 major components.

The 3 major components mean hemicellulose, lignin and cellulose. So, with the increase in the torrefaction temperature and residence time, the content of hemicellulose and cellulose decreased in the torrefied biochar while the content of lignin increased correspondingly.

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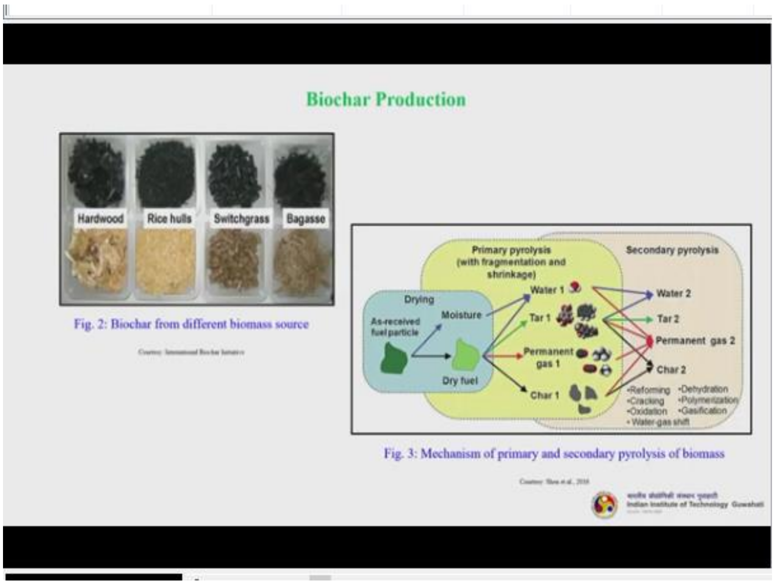

Biochar Production

Fig. 2: Biochar from different biomass source

Fig. 3: Mechanism of primary and secondary pyrolysis of biomass

So, you can see these are the biochars from different biomass sources, these are just representative to make you understand how they look like actually. So, these are 4 different types of biomasses. Hardwood, rice hulls, switchgrass and bagasse and they are corresponding biochar. And this is the mechanism of the primary and secondary pyrolysis of biomass, the pyrolysis reaction.

So, you can see that when there is a dry fuel. So, whatever you actually are taking as the feedstock, whether it is lignocellulosic biomass or say any such material, so, you need to dry it to remove its moisture content to certain level otherwise you cannot put it in the pyrolyser or pyrolysis reactor. Here whatever is happening after the drying basically the primary pyrolysis here fragmentation and sinkage is happening.

So, you can see that water, tar and permanent gas and char like this are getting generated during the primary pyrolysis reactions, then when it goes to again further higher temperature and you move towards secondary pyrolysis reactions. So, you get again water, tar, permanent gas and char consisting of different molecules and there are different stages.

And again, it is very important to note that pyrolysis is very complex. There are so many reactions primary and secondary, which are being simultaneously happening and it is very difficult to predict exact mechanism. But having said that, people have already studied pyrolysis reaction mechanism in detail and they have also told that there are various reactions which are simultaneously happening including the reforming, dehydration, cracking, oxidation, water gas shift, gasification and polymerization.

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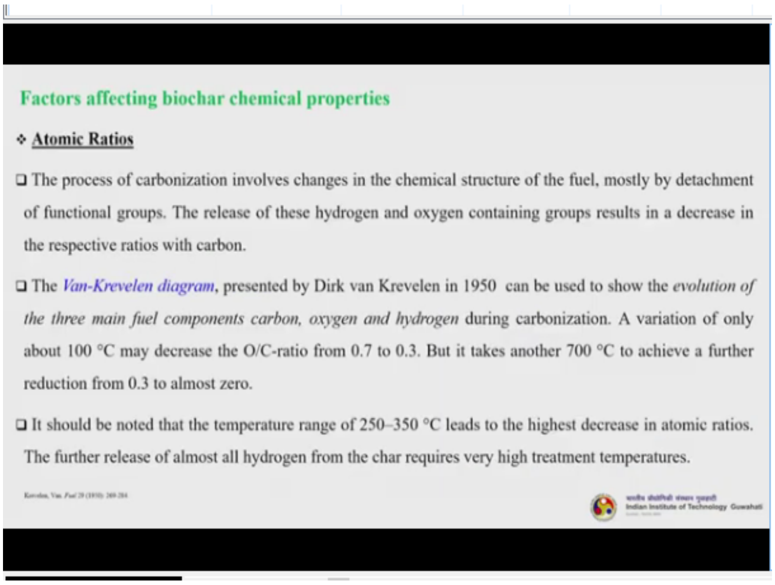

Factors affecting biochar chemical properties

- Atomic Ratios

- ❑ The process of carbonization involves changes in the chemical structure of the fuel, mostly by detachment of functional groups. The release of these hydrogen and oxygen containing groups results in a decrease in the respective ratios with carbon.
- ❑ The *Van-Krevelen diagram*, presented by Dirk van Krevelen in 1950 can be used to show the *evolution of the three main fuel components carbon, oxygen and hydrogen* during carbonization. A variation of only about 100 °C may decrease the O/C-ratio from 0.7 to 0.3. But it takes another 700 °C to achieve a further reduction from 0.3 to almost zero.
- ❑ It should be noted that the temperature range of 250–350 °C leads to the highest decrease in atomic ratios. The further release of almost all hydrogen from the char requires very high treatment temperatures.

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So, now let us understand the factors that affect the biochar chemical properties, we will be talking about biochar properties, 2 different types of properties, first is the chemical properties and second is the physical property. So, let us start with the chemical properties. Atomic ratio: So, the process of carbonization involves changes in the chemical structure of the fuel mostly by detachment of functional groups. The release of these hydrogen and oxygen containing groups results in a decrease in the respective ratios with carbon.

There is something called Van-Krevelen diagram. So, you can read more about this - the references given here below. So, Van-Krevelen diagram presented by Dirk van Krevelen in 1950 can be used to show the evolution of the 3 main fuel components that is carbon, oxygen and hydrogen during carbonization.

A variation of only about 100 degrees centigrade may decrease the oxygen carbon ratio from 0.7 to 0.3, but it takes another 700 degrees centigrade to achieve a further reduction from 0.3 to almost 0. Now, it should be noted that the temperature range of 250 to 350 degrees centigrade leads to the highest decrease in atomic ratios. The further release of almost all hydrogen from the char requires very high treatment temperatures.

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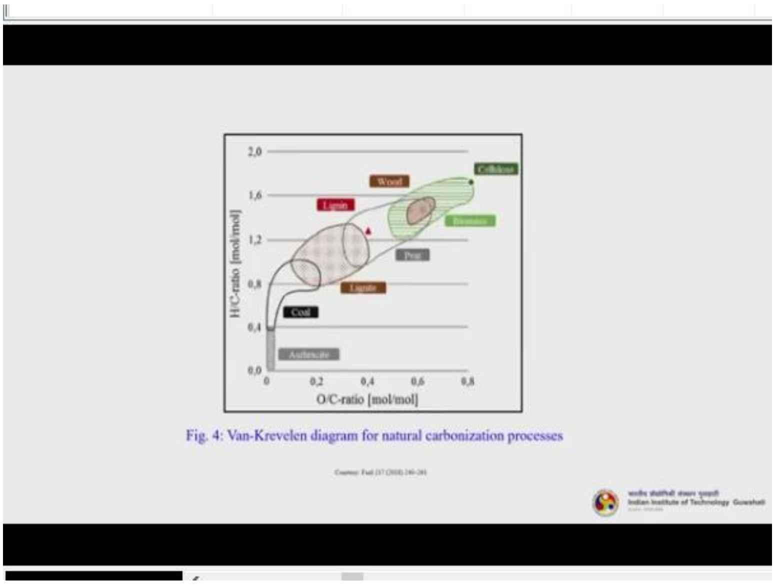

Fig. 4: Van-Krevelen diagram for natural carbonization processes

So, this is a classical Van-Krevelen diagram for the natural carbonization process. You can see that it is plotted between O by C ratio mol by mol and H by C ratio, again mol by mol. So, hydrogen to carbon ratio and oxygen to carbon ratio. Now, you can see that it lies from anthracite coal and then this is another type of coal, then we have lignite here, we have peat overlapping.

Then you can see that green one is the biomass. And from there the last one is the cellulose; here the lignin degradation will happen. So, from here we can get an understanding about what are the different temperatures also that is required and what is the O by C and H by C ratio that will give us an insight about the various reaction mechanisms also.

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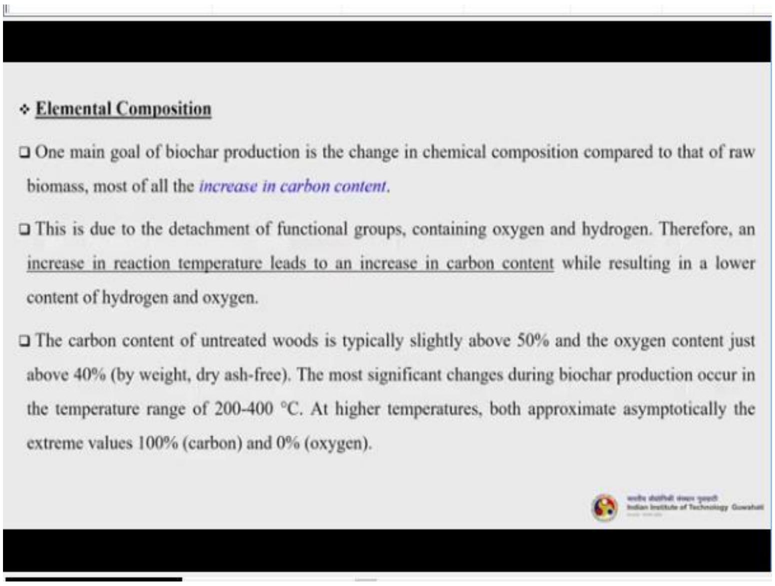

❖ **Elemental Composition**

- ❑ One main goal of biochar production is the change in chemical composition compared to that of raw biomass, most of all the *increase in carbon content*.
- ❑ This is due to the detachment of functional groups, containing oxygen and hydrogen. Therefore, an increase in reaction temperature leads to an increase in carbon content while resulting in a lower content of hydrogen and oxygen.
- ❑ The carbon content of untreated woods is typically slightly above 50% and the oxygen content just above 40% (by weight, dry ash-free). The most significant changes during biochar production occur in the temperature range of 200-400 °C. At higher temperatures, both approximate asymptotically the extreme values 100% (carbon) and 0% (oxygen).

So, next is elemental composition. So, one main goal of biochar production is the change in chemical composition compared to that of raw biomass, most of all the increase in the carbon content. Now, this is due to the detachment of functional groups containing oxygen and hydrogen. Therefore, an increase in reaction temperature leads to an increase in the carbon content while resulting in a lower content of hydrogen and oxygen.

The carbon content of untreated woods is typically slightly above 50% and the oxygen content is just over 40% that is basically by weight, dry ash free basis. The most significant changes during biochar production occur in the temperature range of 200 to 400 degrees centigrade. At higher temperatures both approximate asymptomatically the extreme values that is 100% carbon and 0% of oxygen.

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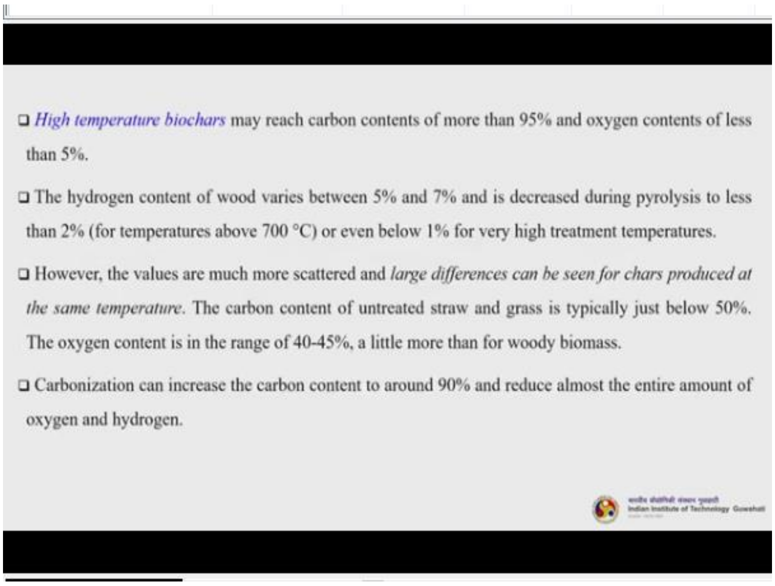

- ❑ *High temperature biochars* may reach carbon contents of more than 95% and oxygen contents of less than 5%.
- ❑ The hydrogen content of wood varies between 5% and 7% and is decreased during pyrolysis to less than 2% (for temperatures above 700 °C) or even below 1% for very high treatment temperatures.
- ❑ However, the values are much more scattered and *large differences can be seen for chars produced at the same temperature.* The carbon content of untreated straw and grass is typically just below 50%. The oxygen content is in the range of 40-45%, a little more than for woody biomass.
- ❑ Carbonization can increase the carbon content to around 90% and reduce almost the entire amount of oxygen and hydrogen.

High temperature biochars may each carbon contents of more than 95% and oxygen content of less than 5%. The hydrogen content of wood varies between 5% to 7% and is decreased during pyrolysis to less than 2%. So, when you go beyond or almost touching about 700 degrees centigrade or even below 1% for very high treatment temperatures more than 700 to 800 degrees centigrade.

However, the values are much more scattered and large differences can be seen for chars produced at the same temperature. Again please note that whatever we are talking about, these are generalized statements and process parameters and result will vary depending upon what is the feedstock and feedstock composition - it is better to say that feedstock composition. So, the carbon content of the untreated straw and grass is typically just below

50%. The oxygen content is in the range of 40 to 45%, a little more than the woody biomass. Carbonization can increase the carbon content to around 90% and reduce almost the entire amount of oxygen and hydrogen.

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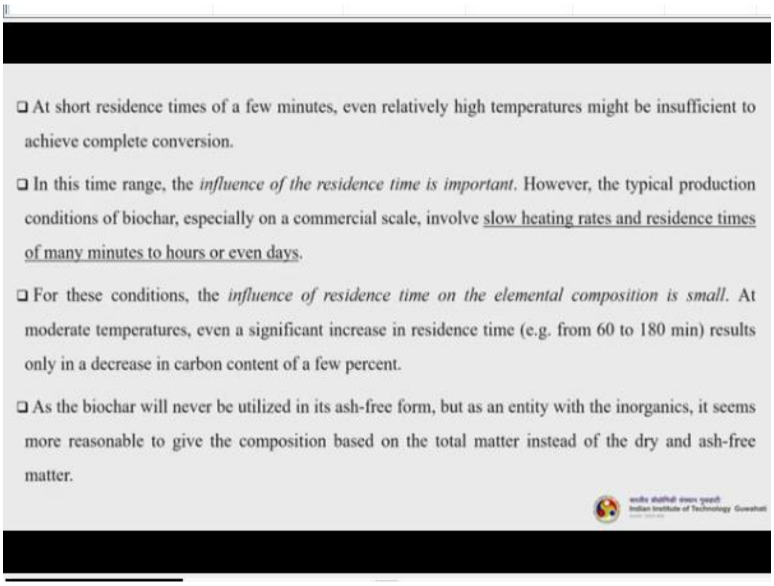

- At short residence times of a few minutes, even relatively high temperatures might be insufficient to achieve complete conversion.
- In this time range, the *influence of the residence time is important*. However, the typical production conditions of biochar, especially on a commercial scale, involve slow heating rates and residence times of many minutes to hours or even days.
- For these conditions, the *influence of residence time on the elemental composition is small*. At moderate temperatures, even a significant increase in residence time (e.g. from 60 to 180 min) results only in a decrease in carbon content of a few percent.
- As the biochar will never be utilized in its ash-free form, but as an entity with the inorganics, it seems more reasonable to give the composition based on the total matter instead of the dry and ash-free matter.

At short residence times of a few minutes, even relatively high temperatures might be insufficient to achieve complete conversion. In this time range, the influence of the residence time is important. However, the typical production conditions of biochar especially in a commercial scale involves slow heating rates and residence times of many minutes, sometimes hours and even days also.

Because the main aim is to produce as much as amount of biochar having excellent or let us say having the highest carbon content. Now, for these conditions, the influence of the residence time on the elemental composition is small. At moderate temperatures, even a significant increase in residence time, you can say from 60 to 180 minute results only in a decrease in carbon content of few percent. So, there is hardly any effect of the residence time. So, as the biochar will never be utilized in its, ash free from but as an entity with the inorganics, it seems more reasonable to give the composition based on the total matter instead of the dry or ash free matter.

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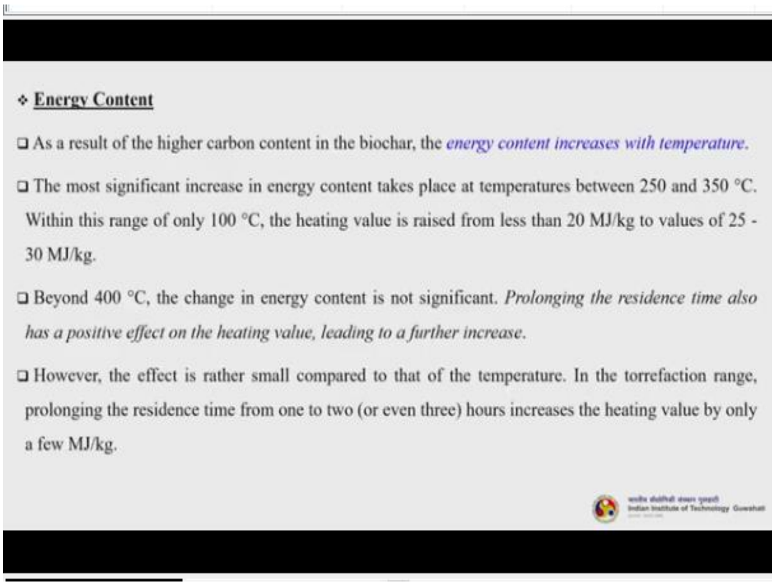

❖ **Energy Content**

❑ As a result of the higher carbon content in the biochar, the *energy content increases with temperature.*

❑ The most significant increase in energy content takes place at temperatures between 250 and 350 °C. Within this range of only 100 °C, the heating value is raised from less than 20 MJ/kg to values of 25 - 30 MJ/kg.

❑ Beyond 400 °C, the change in energy content is not significant. *Prolonging the residence time also has a positive effect on the heating value, leading to a further increase.*

❑ However, the effect is rather small compared to that of the temperature. In the torrefaction range, prolonging the residence time from one to two (or even three) hours increases the heating value by only a few MJ/kg.

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So, the next is energy content. So, as a result of the higher carbon content in the biochar the energy content increases with temperature. The most significant increase in energy content takes place at temperatures between 250 to 350 degrees centigrade, within this range of only 100 degrees centigrade, the heating value is raised from less than 20 mega joules per kg to a value of 25 to 30 mega joules per kg.

So, beyond 400 degrees centigrade, the change in energy content is not significant. Prolonging the residence time also has a positive impact on the heating value, leading to a further increase. However, the effect is rather small compared to that of the temperature. In the torrefaction range, prolonging the residence time from 1 to 2 or even 3 hours increases the heating value by only a few mega joules per kg.

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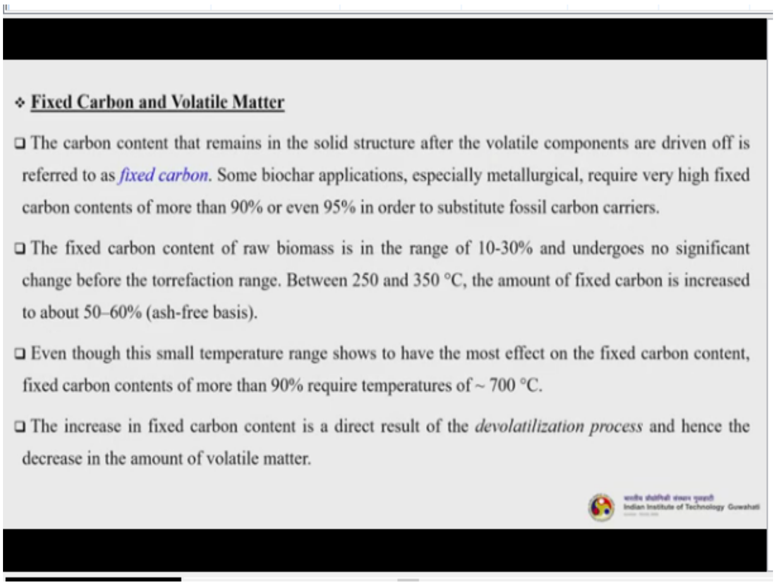

❖ **Fixed Carbon and Volatile Matter**

❑ The carbon content that remains in the solid structure after the volatile components are driven off is referred to as *fixed carbon*. Some biochar applications, especially metallurgical, require very high fixed carbon contents of more than 90% or even 95% in order to substitute fossil carbon carriers.

❑ The fixed carbon content of raw biomass is in the range of 10-30% and undergoes no significant change before the torrefaction range. Between 250 and 350 °C, the amount of fixed carbon is increased to about 50–60% (ash-free basis).

❑ Even though this small temperature range shows to have the most effect on the fixed carbon content, fixed carbon contents of more than 90% require temperatures of ~ 700 °C.

❑ The increase in fixed carbon content is a direct result of the *devolatilization process* and hence the decrease in the amount of volatile matter.

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So, next is fixed carbon and volatile matter. The carbon content that remains in the solid structure after the volatile components are driven off is referred to as the fixed carbon. Some biochar applications, especially metallurgical require very high fixed carbon contents of almost more than 90% or even 95% in order to substitute for the fossil carbon carriers. The fixed carbon content of raw biomass is in the range of 10 to 30% and undergoes no significant change before the torrefaction range. So, which is actually 200 to 300 degrees centigrade in that range. So, between 250 to 350 degrees centigrade, the amount of fixed carbon is increased to about 50 to 60%. It is again on ash free basis. Now, even though the small temperature range shows to have the most effect on the fixed carbon content, fixed carbon content of more than 90% required temperatures of approximately 700 degrees centigrade.

The increase in the fixed carbon content is a direct result of the devolatilization process and hence, decrease in the amount of volatile matter. So, when you are heating it with a higher temperature basically more than 400, 500 close to 700 degrees centigrade, almost all the volatile matters will escape. That is why the process is called devolatilization, resulting in higher amount of fixed carbon.

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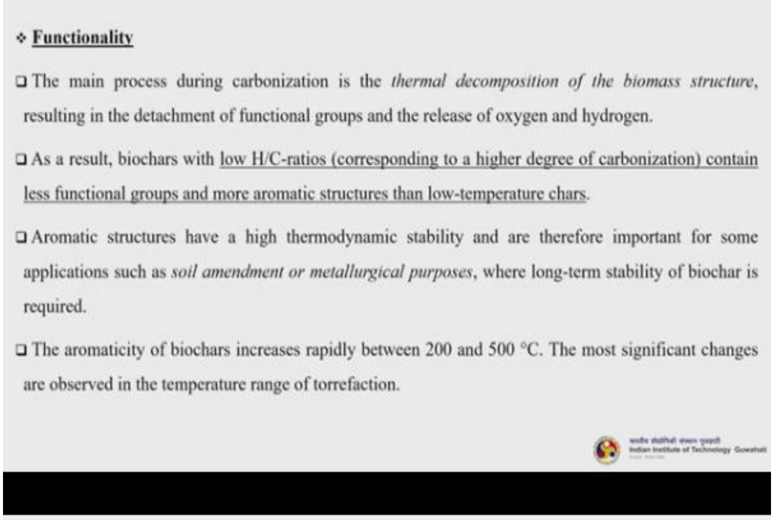

- **Functionality**

❑ The main process during carbonization is the *thermal decomposition of the biomass structure*, resulting in the detachment of functional groups and the release of oxygen and hydrogen.

❑ As a result, biochars with low H/C-ratios (corresponding to a higher degree of carbonization) contain less functional groups and more aromatic structures than low-temperature chars.

❑ Aromatic structures have a high thermodynamic stability and are therefore important for some applications such as *soil amendment or metallurgical purposes*, where long-term stability of biochar is required.

❑ The aromaticity of biochars increases rapidly between 200 and 500 °C. The most significant changes are observed in the temperature range of torrefaction.

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Then we will talk about functionality. So, the main process during carbonization is the thermal decomposition of the biomass structure, resulting in the detachment of functional groups and the release of oxygen and hydrogen. As a result, biochars with low hydrogen to carbon ratios, so that corresponds to a higher degree of carbonation contain less functional groups and more aromatic structures then low temperature chars.

Aromatic structures have a high thermodynamic stability and are therefore important for some applications such as soil amendment or metallurgical purposes, where long term stability of the biochar is required. So, the aromaticity of biochar increases rapidly between 200 to 500 degrees centigrade, the most significant changes are observed in the temperature range of torrefaction. That is again, if you recall 200 to 300 or 350 degrees centigrade maximum.

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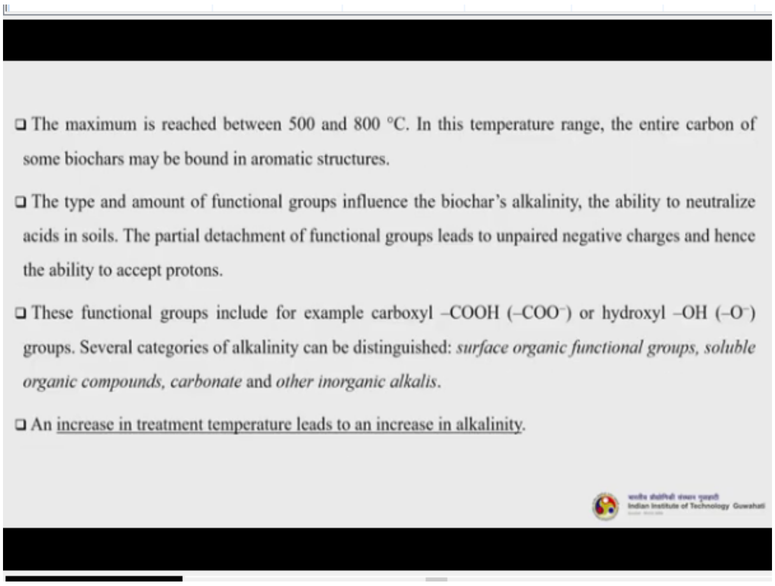

- ❑ The maximum is reached between 500 and 800 °C. In this temperature range, the entire carbon of some biochars may be bound in aromatic structures.
- ❑ The type and amount of functional groups influence the biochar's alkalinity, the ability to neutralize acids in soils. The partial detachment of functional groups leads to unpaired negative charges and hence the ability to accept protons.
- ❑ These functional groups include for example carboxyl $-COOH$ ($-COO^-$) or hydroxyl $-OH$ ($-O^-$) groups. Several categories of alkalinity can be distinguished: *surface organic functional groups, soluble organic compounds, carbonate* and *other inorganic alkalis*.
- ❑ An increase in treatment temperature leads to an increase in alkalinity.

The maximum is reached between 500 to 800 degrees centigrade. So, in this temperature range, the entire carbon of some biochars may be bound in the aromatic structures. The type and the amount of functional groups influence the biochar's alkalinity, the ability to neutralize acids in the soils. The partial detachment of functional groups leads to unpaired negative charges and hence the ability to accept protons.

These functional groups include for example, carboxyl and hydroxyl groups. Several categories of alkalinity can be distinguished like surface organic functional groups, soluble organic compounds, carbonate and other inorganic alkalis. An increase in the treatment temperature also leads to an increase in the alkalinity.

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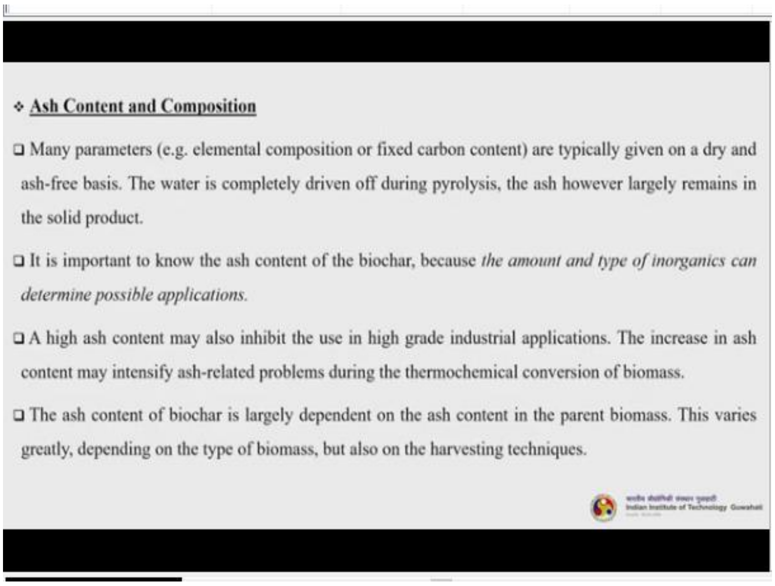

❖ **Ash Content and Composition**

- Many parameters (e.g. elemental composition or fixed carbon content) are typically given on a dry and ash-free basis. The water is completely driven off during pyrolysis, the ash however largely remains in the solid product.
- It is important to know the ash content of the biochar, because *the amount and type of inorganics can determine possible applications.*
- A high ash content may also inhibit the use in high grade industrial applications. The increase in ash content may intensify ash-related problems during the thermochemical conversion of biomass.
- The ash content of biochar is largely dependent on the ash content in the parent biomass. This varies greatly, depending on the type of biomass, but also on the harvesting techniques.

So, next we will talk about ash content and the composition. Many parameters for example, elemental composition or fixed carbon content are typically given on a dry and ash free basis. The water is completely driven off during pyrolysis. The ash however, largely remains in the solid product. It is important to know the ash content of the biochar, because the amount and type of inorganics can determine possible applications.

A high ash content may also inhibit the use in high grade industrial applications. The increase in ash content may intensify ash related problems during the thermochemical conversion of biomass. The ash content of biochar is largely dependent on the ash content in the parent biomass. This varies greatly depending on the type of biomass and also on the harvesting techniques also.

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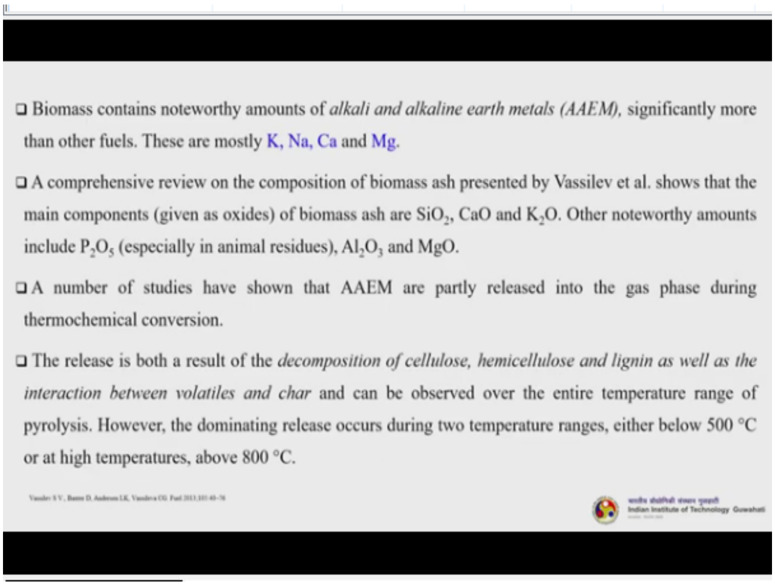

- Biomass contains noteworthy amounts of *alkali and alkaline earth metals (AAEM)*, significantly more than other fuels. These are mostly K, Na, Ca and Mg.
- A comprehensive review on the composition of biomass ash presented by Vassilev et al. shows that the main components (given as oxides) of biomass ash are SiO_2, CaO and K_2O. Other noteworthy amounts include P_2O_5 (especially in animal residues), Al_2O_3 and MgO.
- A number of studies have shown that AAEM are partly released into the gas phase during thermochemical conversion.
- The release is both a result of the *decomposition of cellulose, hemicellulose and lignin as well as the interaction between volatiles and char* and can be observed over the entire temperature range of pyrolysis. However, the dominating release occurs during two temperature ranges, either below 500 °C or at high temperatures, above 800 °C.

Biomass contents noteworthy amounts of alkali and alkaline earth metals. It is called AAEM, significantly more than other fuels. So, these are mostly sodium, potassium, calcium and magnesium. A comprehensive review of the composition of biomass presented by Vassilev et al, - the reference is given below - shows that the main components (given as oxides) of biomass ash are silicon dioxide, calcium oxide and potassium oxide.

And other noteworthy amounts include this one P_2O_5 - especially in the animal residues it is present - and then Al_2O_3 - which is alumina and magnesium oxide. A number of studies have also shown that AAEM are partly released into the gas phase during the thermochemical conversion. The release is both as a result of the decomposition of cellulose, hemicellulose and lignin as well as the interaction between the volatiles and the char and can be observed over the entire temperature range of pyrolysis.

However, the dominating release occurs during the 2 temperature ranges either below 500 degrees centigrade or at higher temperatures above 800 degrees centigrade. Here I want to tell something, you can see the interaction between volatiles and the char. Now, when the process begins initially at lower temperature, so, the dehydration is happening. So, the moisture whatever is left is getting out then devolatilization started.

Now, at the same time the char formation is happening. Now, when the volatile components are getting escaped and still inside the reactor and the char which is getting produced, they are interacting with each other. Now, this leads to some secondary and tertiary types of different reactions and thereby resulting in different products, it can be tar, it can be smaller molecular weight compounds and it may also result in fractions of different types of biooil.

Now, this cannot be stopped, because it is inherently happening inside the reactor which you cannot control. Because you are heating something inside a closed environment in a controlled atmosphere. And whatever is getting produced that gas is again reacting with the feed what is getting converted or getting either gasified or getting either torrefied or getting either pyrolyzed.

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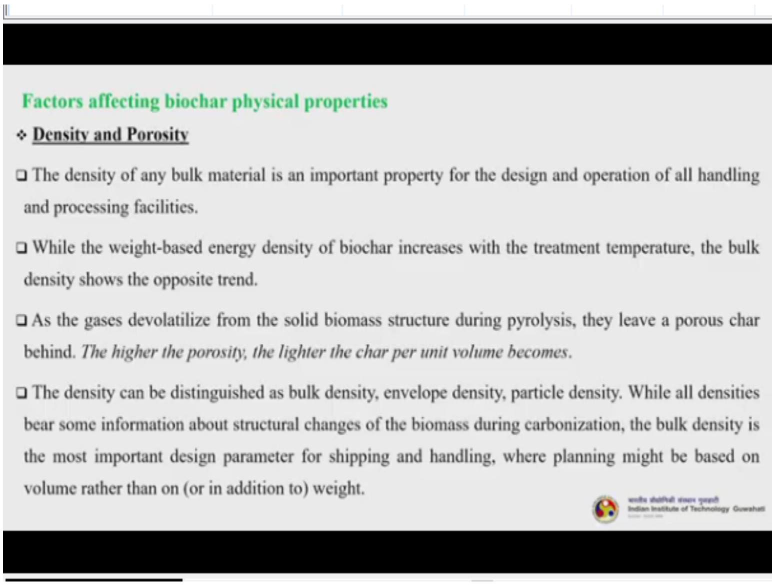

Factors affecting biochar physical properties

❖ **Density and Porosity**

- ❑ The density of any bulk material is an important property for the design and operation of all handling and processing facilities.
- ❑ While the weight-based energy density of biochar increases with the treatment temperature, the bulk density shows the opposite trend.
- ❑ As the gases devolatilize from the solid biomass structure during pyrolysis, they leave a porous char behind. *The higher the porosity, the lighter the char per unit volume becomes.*
- ❑ The density can be distinguished as bulk density, envelope density, particle density. While all densities bear some information about structural changes of the biomass during carbonization, the bulk density is the most important design parameter for shipping and handling, where planning might be based on volume rather than on (or in addition to) weight.

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So, now we will talk about the physical properties, factors affecting the biochar physical properties. The first and foremost important are density and porosity. So, if you recall, we have talked about density of biomass, how it is going to happen, how it is going to affect the transportation, storage and other things. Now we will talk about the biochar properties. So, the density of any bulk material is an important property for the design and operation of all handling and processing facilities, the storage, transportation, all these things.

While the weight-based energy density of biochar increases with the treatment temperature, the bulk density shows the opposite trend. As the gases devolatilize from the solid biomass structure, during pyrolysis, they leave a porous char behind, the higher the porosity the lighter the char per unit volume becomes. The density can be distinguished either as bulk density, envelope density or particle density.

While all densities bear some information about structural changes of the biomass during carbonization. The bulk density is the most important design parameter for shipping and handling, where planning might be based on volume rather than on (or in addition to) weight basically.

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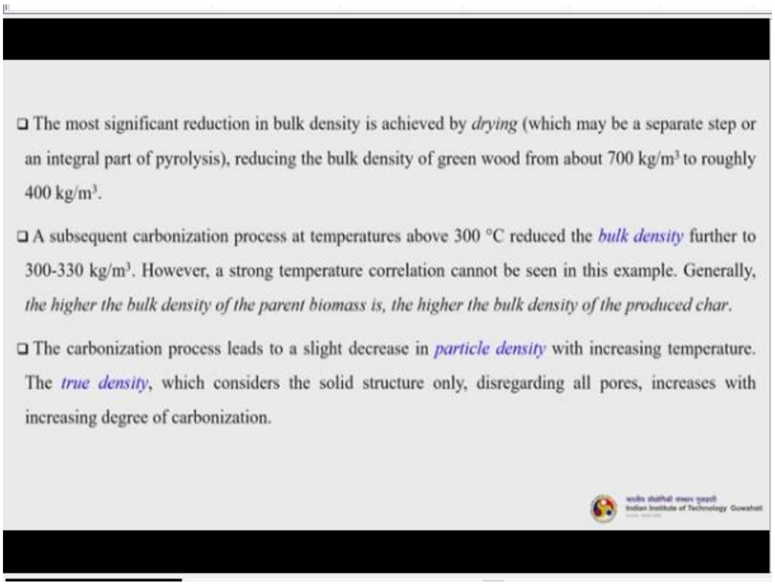

❑ The most significant reduction in bulk density is achieved by *drying* (which may be a separate step or an integral part of pyrolysis), reducing the bulk density of green wood from about 700 kg/m^3 to roughly 400 kg/m^3.

❑ A subsequent carbonization process at temperatures above 300 °C reduced the *bulk density* further to 300-330 kg/m^3. However, a strong temperature correlation cannot be seen in this example. Generally, *the higher the bulk density of the parent biomass is, the higher the bulk density of the produced char.*

❑ The carbonization process leads to a slight decrease in *particle density* with increasing temperature. The *true density*, which considers the solid structure only, disregarding all pores, increases with increasing degree of carbonization.

The most significant reduction in bulk density is achieved by drying, which may be a separate step or an integral part of pyrolysis, reducing the bulk density of green wood from about 700 kilogram per meter cube to roughly 400 kilogram per meter cube. A subsequent carbonization process at temperatures above 300 degrees centigrade reduced the bulk density further to 300 to 330 kilograms per meter cube.

However, a strong temperature correlation cannot be seen in this example. Generally, the higher the bulk density of the parent biomass is, the higher the bulk density of the produced char. The carbonization process leads to a slight decrease in the particle density with increasing temperature. The true density which considers the solid structure only, disregarding of all the pores increases with increasing the degree of carbonation.

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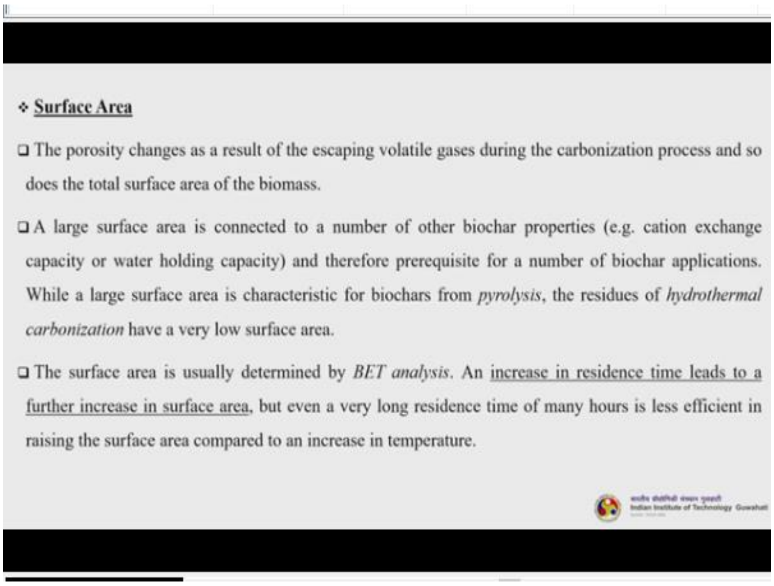

❖ **Surface Area**

❑ The porosity changes as a result of the escaping volatile gases during the carbonization process and so does the total surface area of the biomass.

❑ A large surface area is connected to a number of other biochar properties (e.g. cation exchange capacity or water holding capacity) and therefore prerequisite for a number of biochar applications. While a large surface area is characteristic for biochars from *pyrolysis*, the residues of *hydrothermal carbonization* have a very low surface area.

❑ The surface area is usually determined by *BET analysis*. An increase in residence time leads to a further increase in surface area, but even a very long residence time of many hours is less efficient in raising the surface area compared to an increase in temperature.

So, the next one of the most important parameter of the biochar is the surface area. The porosity changes as a result of the escaping volatile gases during the carbonization process and so does that total surface area of the biomass. A large surface area is connected to a number of other biochar properties, as for example, cation exchange capacity or water holding capacity and therefore prerequisite for a number of biochar applications.

While a large surface area is characteristic of biochars from pyrolysis, the residues of hydrothermal carbonization have a very low surface area. The surface area is usually determined by BET analysis. An increase in residence time leads to a further increase in surface area, but even a very long residence time of many hours is less efficient in raising the surface area compared to an increase in temperature.

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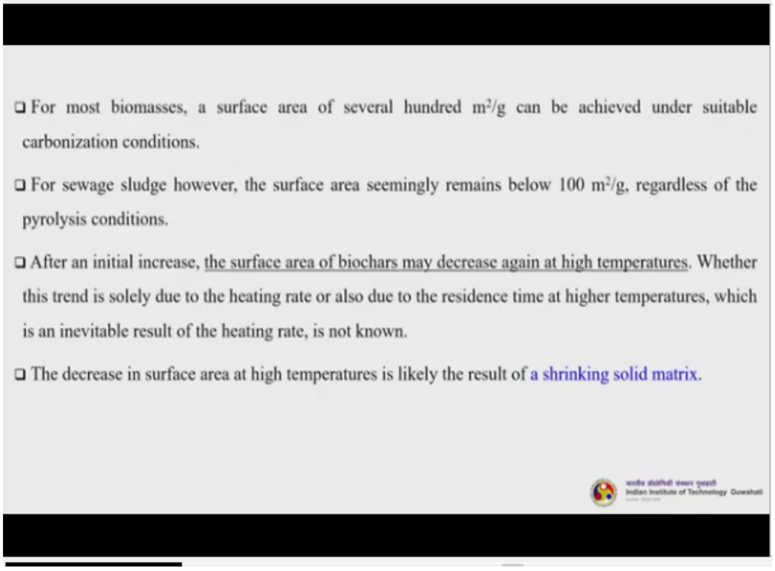

- For most biomasses, a surface area of several hundred m^2/g can be achieved under suitable carbonization conditions.
- For sewage sludge however, the surface area seemingly remains below 100 m^2/g, regardless of the pyrolysis conditions.
- After an initial increase, the surface area of biochars may decrease again at high temperatures. Whether this trend is solely due to the heating rate or also due to the residence time at higher temperatures, which is an inevitable result of the heating rate, is not known.
- The decrease in surface area at high temperatures is likely the result of a shrinking solid matrix.

For most biomasses, a surface area of several 100 meters square per gram can be achieved under suitable carbonization conditions. For sewage sludge however, the surface area seemingly remains below 100 meters square per gram regardless of the paralysis conditions. After an initial increase, the surface area of biochars may decrease again at high temperatures. Whether this trend is solely due to the heating rate, or also due to the residence time at higher temperatures, which is an inevitable result of the heating rate, actually, it is not so clear. The decrease in surface area at high temperatures is likely the result of a shrinking solid matrix.

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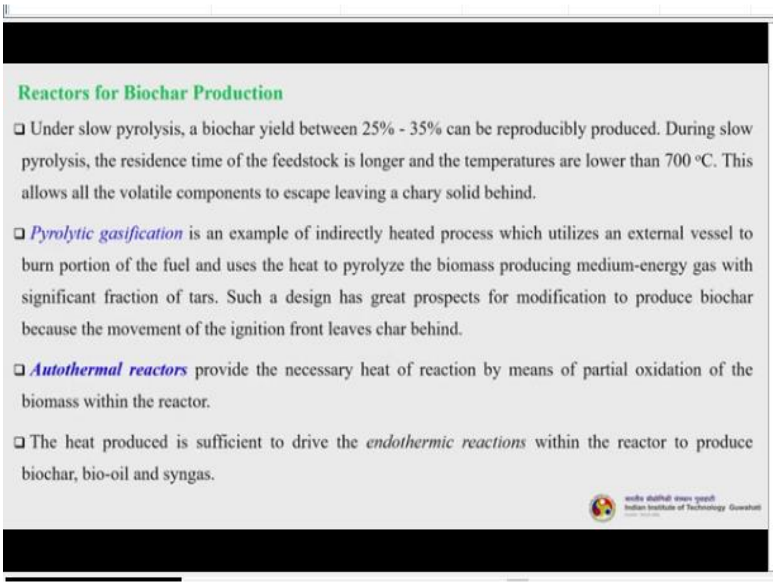

Reactors for Biochar Production

- Under slow pyrolysis, a biochar yield between 25% - 35% can be reproducibly produced. During slow pyrolysis, the residence time of the feedstock is longer and the temperatures are lower than 700 °C. This allows all the volatile components to escape leaving a chary solid behind.
- *Pyrolytic gasification* is an example of indirectly heated process which utilizes an external vessel to burn portion of the fuel and uses the heat to pyrolyze the biomass producing medium-energy gas with significant fraction of tars. Such a design has great prospects for modification to produce biochar because the movement of the ignition front leaves char behind.
- ***Autothermal reactors*** provide the necessary heat of reaction by means of partial oxidation of the biomass within the reactor.
- The heat produced is sufficient to drive the *endothermic reactions* within the reactor to produce biochar, bio-oil and syngas.

So, now we will discuss about the various reactors that is required for the biochar production. So, under slow pyrolysis, biochar yield between 25 to 35% can be reproducibly produced. During slow pyrolysis the residence time of the feedstock is longer and the temperature are lower than 700 degrees centigrade. This allows all the volatile components to escape leaving a chary solid behind.

A pyrolytic gasification is an example of indirectly heated process which utilizes an external vessel to burn portion of the fuel and uses the heat to pyrolyze the biomass producing medium energy gas with significant fraction of tars. If you recall, we have discussed this during our gasification discussion. So, such a design has a great prospect for modification to produce biochar, because the movement of the ignition front leaves the char behind.

Autothermal reactors provide the necessary heat of reaction by means of partial oxidation of the biomass within the reactor. The heat produced is sufficient to drive the endothermic reactions within the reactor to produce biochar, biooil and syngas.

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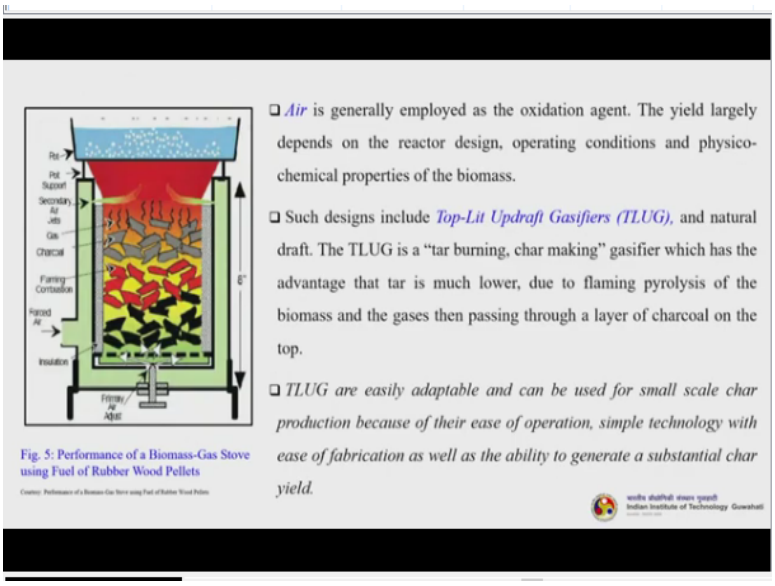

Fig. 5: Performance of a Biomass-Gas Stove using Fuel of Rubber Wood Pellets

Courtesy: Performance of a Biomass-Gas Stove using Fuel of Rubber Wood Pellets

- ❑ *Air* is generally employed as the oxidation agent. The yield largely depends on the reactor design, operating conditions and physico-chemical properties of the biomass.
- ❑ Such designs include *Top-Lit Updraft Gasifiers (TLUG)*, and natural draft. The TLUG is a "tar burning, char making" gasifier which has the advantage that tar is much lower, due to flaming pyrolysis of the biomass and the gases then passing through a layer of charcoal on the top.
- ❑ *TLUG are easily adaptable and can be used for small scale char production because of their ease of operation, simple technology with ease of fabrication as well as the ability to generate a substantial char yield.*

So, this is a typical schematic representation of the biomass gas stove. So, air is generally employed as the oxidation agent. The yield largely depends on the reactor design, operating conditions and physicochemical properties of the biomass. So, such designs include one of the most significant design which was being used by many - is called top-lit updraft gasifier (TLUG) and natural draft.

So, TLUG is a "tar burning, char making" gasifier which has the advantage that tar is much lower due to the flaming pyrolysis of the biomass and the gases then passing through a layer of the charcoal on the top. So, you can see that you are passing basically the air here, the forced air, here primary air is getting inside your reactor. So, here the combustion is happening. So, the bed of charcoal is present here.

And then secondary air is there and it is a very simple design. So, TLUG are easily adaptable and can be used for small scale char production, because of their ease of operation simple technology with ease of fabrication, as well as the ability to generate a substantial char yield.

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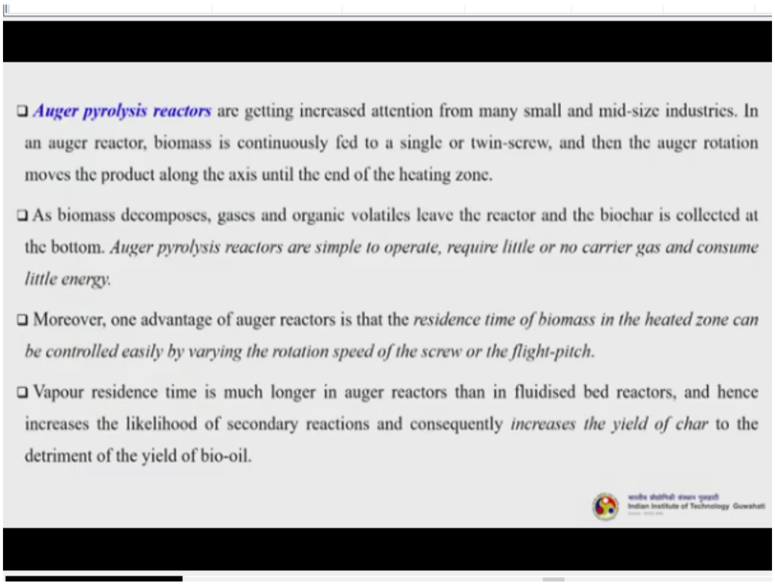

- ❑ ***Auger pyrolysis reactors*** are getting increased attention from many small and mid-size industries. In an auger reactor, biomass is continuously fed to a single or twin-screw, and then the auger rotation moves the product along the axis until the end of the heating zone.
- ❑ As biomass decomposes, gases and organic volatiles leave the reactor and the biochar is collected at the bottom. *Auger pyrolysis reactors are simple to operate, require little or no carrier gas and consume little energy.*
- ❑ Moreover, one advantage of auger reactors is that the *residence time of biomass in the heated zone can be controlled easily by varying the rotation speed of the screw or the flight-pitch.*
- ❑ Vapour residence time is much longer in auger reactors than in fluidised bed reactors, and hence increases the likelihood of secondary reactions and consequently *increases the yield of char* to the detriment of the yield of bio-oil.

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So, Auger pyrolysis reactors are getting increased attention from many small and midsize industries. In an auger reactor, biomass is continuously fed to a single or twin-screw and then the auger rotation moves the product along the axis until the end of the heating zone.

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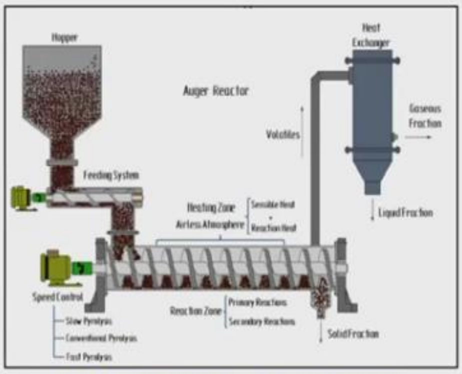

Fig. 6: Pyrolysis process scheme in a single-auger reactor

Courtesy: Campuzano et al., Renewable and Sustainable Energy Reviews, 102, 2019, 372-409

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So I will show you this image, this is the hopper; it is a feed storage we can say. From here, through a screw conveyor type of belt rotating system which is rotating. So, it is the feeding system. It is coming to the reactor. So, this is a single auger reactor. Here also you can see some sort of screw and belt rotation system that is rotating. And the rotation speed also plays a very vital role in determining - the residence time - how much time the feed is spending inside the reactor is all determined by this rotation speed.

Then, you get the solid fraction here, all the volatiles can be condensed and gaseous fraction can be collected if it is useful, otherwise other condensable parts can be condensed if required. So, as the biomass decomposes, gases and organic volatiles leave the reactor and the biochar is collected at the bottom. Auger pyrolysis reactors are simple to operate, require little or no carrier gas and consume little energy.

Moreover, one advantage of auger reactor is that, the residence time of biomass in the heated zone can be controlled easily by varying the rotation speed; this is what I just told you - speed of the screw or the flight pitch. Vapour residence time is much longer in auger reactors than in the fluidized bed reactors and hence increases the likelihood of the secondary reactions and consequently increases the yield of the char to the detriment of the yield of biooil. So, yes, this we have already discussed.

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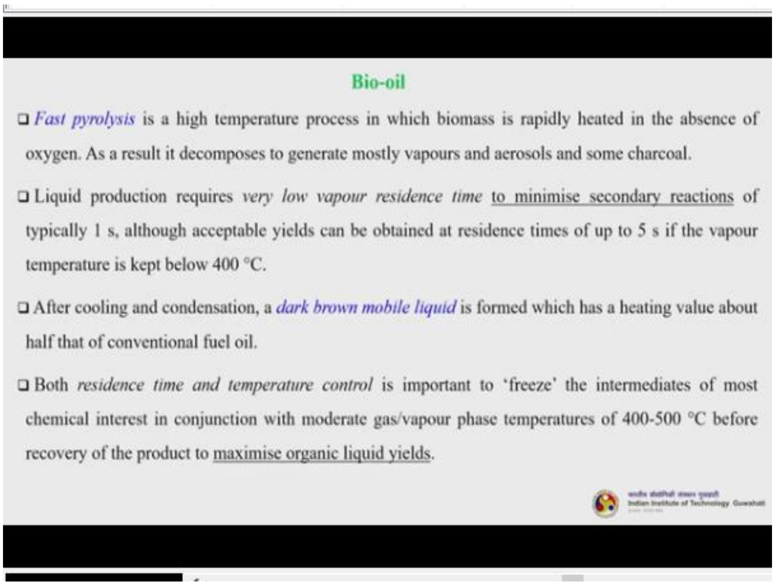

Bio-oil

- ❑ *Fast pyrolysis* is a high temperature process in which biomass is rapidly heated in the absence of oxygen. As a result it decomposes to generate mostly vapours and aerosols and some charcoal.
- ❑ Liquid production requires *very low vapour residence time* to minimise secondary reactions of typically 1 s, although acceptable yields can be obtained at residence times of up to 5 s if the vapour temperature is kept below 400 °C.
- ❑ After cooling and condensation, a *dark brown mobile liquid* is formed which has a heating value about half that of conventional fuel oil.
- ❑ Both *residence time and temperature control* is important to 'freeze' the intermediates of most chemical interest in conjunction with moderate gas/vapour phase temperatures of 400-500 °C before recovery of the product to maximise organic liquid yields.

And now we will discuss about biooil. So, till now we have just discussed about the biochar. We will now focus our discussion on biooil which is another significant product of interest especially from the pyrolysis. So, fast pyrolysis is a high temperature process in which biomass is rapidly heated in absence of oxygen. As a result, it decomposes to generate mostly vapours and aerosols and some charcoal.

Liquid production requires very low vapour residence time to minimize secondary reactions of typically one second, although acceptable yields can be obtained at residence times up to 5 second, if the vapour temperature is kept below 400 degrees centigrade. After cooling and condensation, a dark brown mobile liquid is formed which has a heating below about half of that of the conventional fuel oil.

Both residence time and temperature control is important to freeze the intermediates of most chemical interest in conjunction with moderate gas/vapour phase temperatures of 400 to 500 degrees centigrade before recovery of the product to maximize organic liquid yields.

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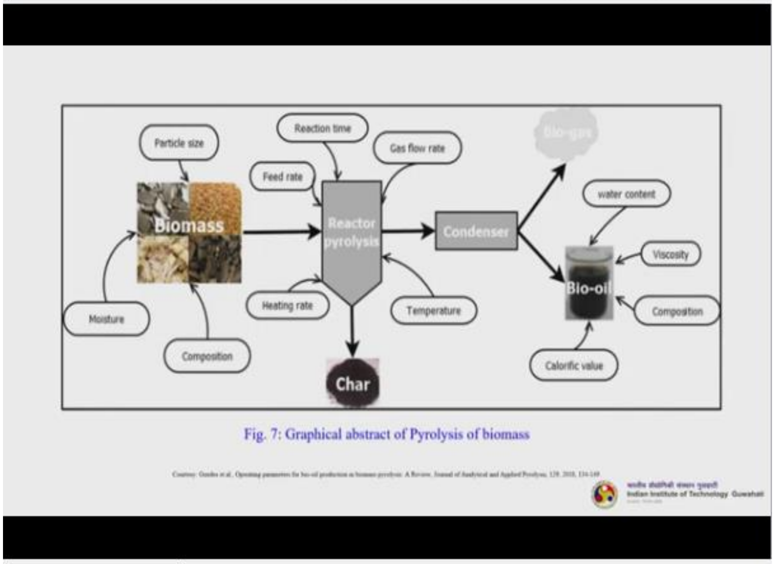

Fig. 7: Graphical abstract of Pyrolysis of biomass

So, this is the typical graphical abstract of the pyrolysis of the biomass. So, the biomass**.** so you talk about the particular size, moisture, composition, these things we have discussed already and then it goes to the pyrolysis reactor, you can have different types of pyrolysis reactors, we have already discussed about that. So, the feed rate, reaction time, gases flow rate, temperature, heating rate, all this will affect the quality of the biochar or biooil that you are going to produce.

So, you get a char here. Then all the volatile components go to a condenser, whatever condensable will be condensed as a liquid phase, which you get as biooil and whatever non-condensable - It will be left off. Now, it also contains some of the important gaseous components. If required, it can be also captured and converted to value added fuel.

So, whatever biooil you get here, there are many things that you need to do - we will discuss about the fuel properties, calorific value, viscosity, water content, all these things are very important features of the biooil. Now, whatever biooil you get here are usually containing a huge amount of the aqueous phase. So, if you leave it under the density separation, it will be separated into 2 distinct phases.

One phase is your organic rich phase - the heavier part, which is actually the oil part and the another part is the more aqueous part the lighter part, but please remember in one class I have already told you again I am repeating that even that lighter part also contains so many valuable chemicals. Now, again what type of chemicals that depend upon the what type of biomass we are using.

And some of the chemicals, some are rare - we have also done some work in this thing. And there are various interesting works already reported in literature you can see. Depending upon that biomass we get very different types of platform chemicals and some chemicals are of very high value like D-glucose and all. So, those can be purified even if it is in small quantity, you are producing in a large quantity biooil then you can do some downstream processing, purify it. And it can be used as different value added products.

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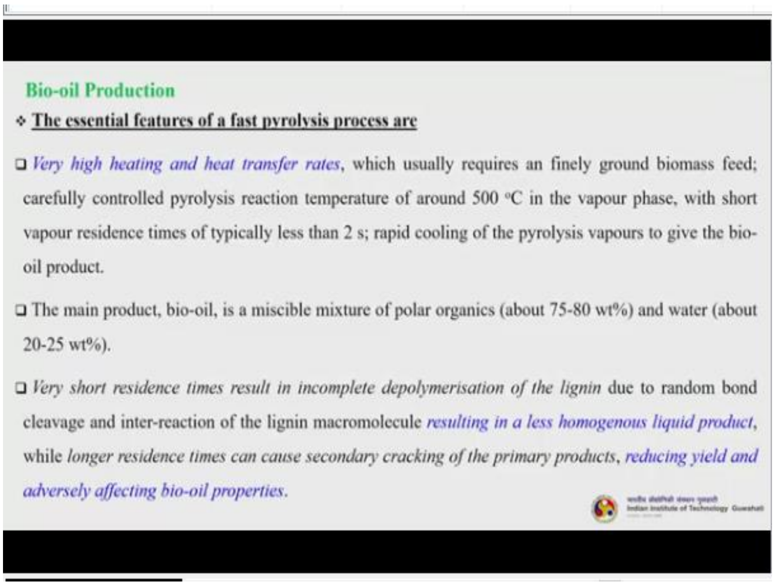

Bio-oil Production

- **The essential features of a fast pyrolysis process are**

❑ *Very high heating and heat transfer rates*, which usually requires an finely ground biomass feed; carefully controlled pyrolysis reaction temperature of around 500 °C in the vapour phase, with short vapour residence times of typically less than 2 s; rapid cooling of the pyrolysis vapours to give the bio-oil product.

❑ The main product, bio-oil, is a miscible mixture of polar organics (about 75-80 wt%) and water (about 20-25 wt%).

❑ *Very short residence times result in incomplete depolymerisation of the lignin* due to random bond cleavage and inter-reaction of the lignin macromolecule *resulting in a less homogenous liquid product*, while *longer residence times can cause secondary cracking of the primary products*, *reducing yield and adversely affecting bio-oil properties.*

So, we will talk about the essential features of a fast pyrolysis process, towards biooil production as you understand that for biooil production, the most important pyrolysis is the fast pyrolysis process. So, very high heating and heat transfer rates, which usually requires finely ground biomass feed; carefully control pyrolysis reaction temperature about 500 degrees centigrade in the vapour phase, with short vapour residence times of typically less than 2 second; rapid cooling of the pyrolysis vapours to give the biooil products.

So, all these are very important. The main product biooil is a miscible mixture of polar organics, this is what exactly I was mentioning just one slide before, it is about 75 to 80% by weight and rest is water requires about 20 to 25%. So, very short residence times results in complete depolymerization of the lignin due to random bond cleavage and the interaction of the lignin macromolecules resulting in a less homogeneous liquid product. While longer residence times can cause secondary cracking of the primary products, reducing yield and adversely affecting biooil properties.

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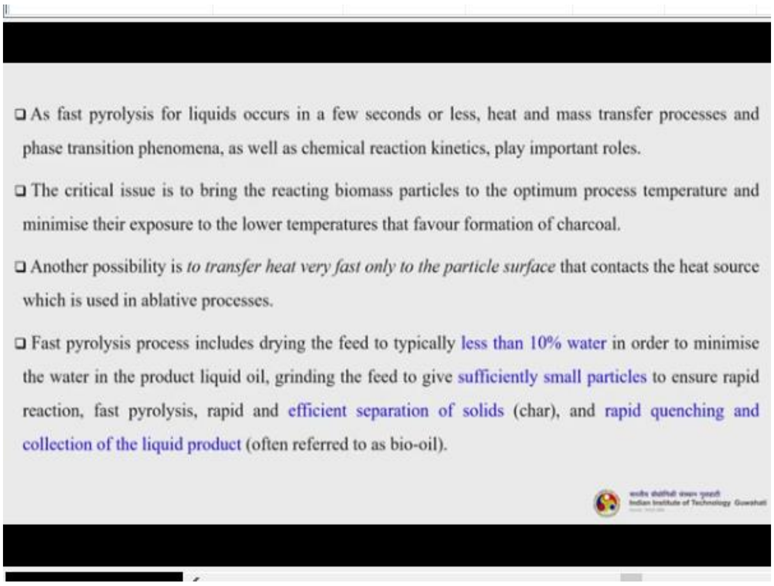

- ❑ As fast pyrolysis for liquids occurs in a few seconds or less, heat and mass transfer processes and phase transition phenomena, as well as chemical reaction kinetics, play important roles.
- ❑ The critical issue is to bring the reacting biomass particles to the optimum process temperature and minimise their exposure to the lower temperatures that favour formation of charcoal.
- ❑ Another possibility is *to transfer heat very fast only to the particle surface* that contacts the heat source which is used in ablative processes.
- ❑ Fast pyrolysis process includes drying the feed to typically less than 10% water in order to minimise the water in the product liquid oil, grinding the feed to give sufficiently small particles to ensure rapid reaction, fast pyrolysis, rapid and efficient separation of solids (char), and rapid quenching and collection of the liquid product (often referred to as bio-oil).

As fast pyrolysis for liquids occurs in a few seconds are less, heat and mass transfer processes and phase transition phenomena as well as chemical reaction kinetics play important roles. The critical issue is to bring the reacting biomass particles to the optimum process parameter and minimize their exposure to the lower temperatures that favor formation of charcoal.

Another possibility is to transfer heat very fast only to the particule surface that contacts the heat source, which is used in ablative processes. Fast pyrolysis process includes drying the feed to typically less than 10% water in order to minimize the water in the product liquid oil, grinding the feed to give sufficiently small particles to ensure rapid reaction, then fast pyrolysis, rapid and efficient separation of solids - that is also very important part (basically solid means char here) and rapid quenching and collection of the liquid product (often referred to as the biooil).

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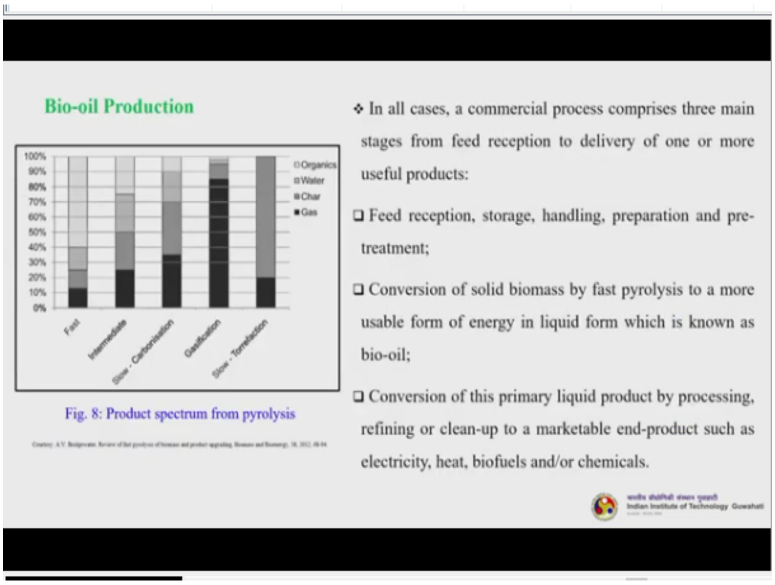

Bio-oil Production

Fig. 8: Product spectrum from pyrolysis

- In all cases, a commercial process comprises three main stages from feed reception to delivery of one or more useful products:
- ❑ Feed reception, storage, handling, preparation and pre-treatment;
- ❑ Conversion of solid biomass by fast pyrolysis to a more usable form of energy in liquid form which is known as bio-oil;
- ❑ Conversion of this primary liquid product by processing, refining or clean-up to a marketable end-product such as electricity, heat, biofuels and/or chemicals.

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So, this particular plot or graph will make you understand about the broad spectrum of different types of pyrolysis products. So, you can see here we have compared this fast, intermediate, slow carbonization, gasification and slow torrefaction. So, let us see the fast paralysis here. In the fast pyrolysis the amount of the gas is very low - you can see this is the black one – gas, followed by the char.

The second portion here is the char, then this is your water and whatever the rest all left out till the 100% is all your organic compounds. So, you can understand that we are getting more amount of biooil in the fast pyrolysis - it is quite clear. So, if you compare to intermediate, slow and all these things, you can see that the gaseous components are increasing in the gasification of course, the product is syngas. So, that is why the gaseous component is highest. And in the slow torrefaction, you can see that the char, there is no organics and water phase, it is either little gas phase here and the rest everything is char. So, in all cases, a commercial process comprises 3 main stages from the feed reception to the delivery of one or more of the useful products. So, these are the different steps or we can say stages.

The first one is the feed reception, storage handling, preparation and pre-treatment. The second is the conversion of solid biomass by fast pyrolysis to a more usable form of energy in liquid form, which is known as biooil and the third is the conversion of this primary liquid product by processing, refining or cleanup (or we many times call as upgradation) to a marketable end product such as electricity, heat, biofuels and/or different platform chemicals.

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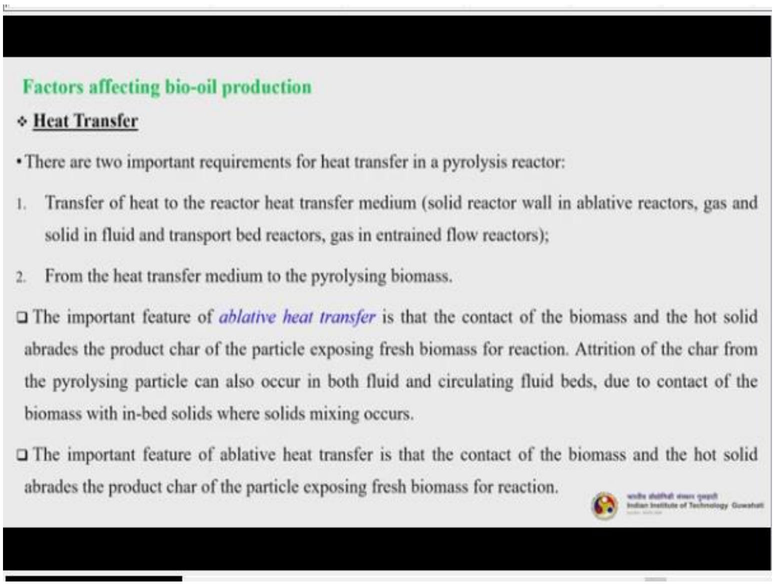

Factors affecting bio-oil production

❖ **Heat Transfer**

- There are two important requirements for heat transfer in a pyrolysis reactor:

1. Transfer of heat to the reactor heat transfer medium (solid reactor wall in ablative reactors, gas and solid in fluid and transport bed reactors, gas in entrained flow reactors);
2. From the heat transfer medium to the pyrolysing biomass.

❑ The important feature of *ablative heat transfer* is that the contact of the biomass and the hot solid abrades the product char of the particle exposing fresh biomass for reaction. Attrition of the char from the pyrolysing particle can also occur in both fluid and circulating fluid beds, due to contact of the biomass with in-bed solids where solids mixing occurs.

❑ The important feature of ablative heat transfer is that the contact of the biomass and the hot solid abrades the product char of the particle exposing fresh biomass for reaction.

Now, we will talk about the heat transport. So, there are 2 important requirements for heat transfer in a pyrolysis reactor. The first is that transfer of heat to the reactor heat transfer medium. So, it is solid reactor wall in ablative reactors, gas and solid in the fluid and transport bed reactors and gas in the entrained flow reactors. And the second is, from the heat transfer medium to the pyrolysing biomass.

Now, the important feature of the ablative heat transfer is that, the contact of the biomass and the hot solid abrades the product char of the particle exposing fresh biomass for reaction. Now, this is actually not good. So, attrition of the char from the pyrolysing particle can also occur in both fluid and circulating fluid beds due to the contact of the biomass with in-bed solids where the solid mixing occurs.

The important feature of the ablative heat transfer is that the contact of the biomass and the hot solid abrades the product char of the particle exposing fresh biomass for reaction.

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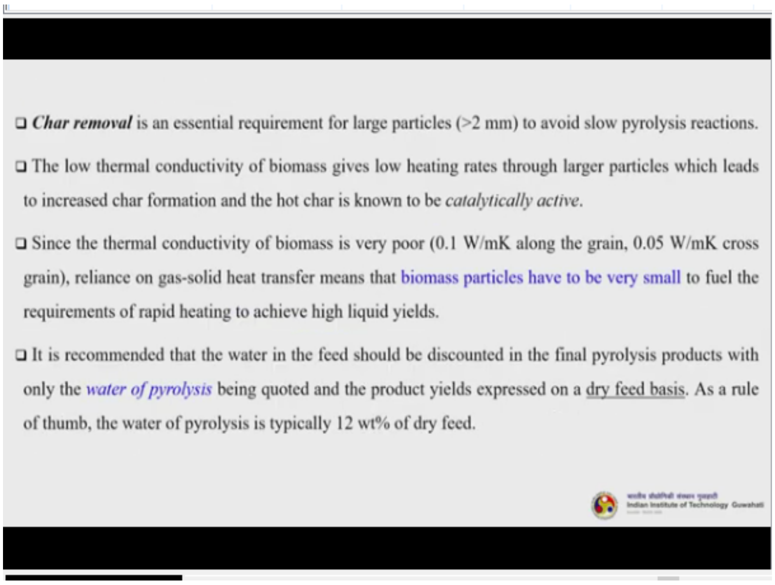

❑ ***Char removal*** is an essential requirement for large particles (>2 mm) to avoid slow pyrolysis reactions.

❑ The low thermal conductivity of biomass gives low heating rates through larger particles which leads to increased char formation and the hot char is known to be *catalytically active*.

❑ Since the thermal conductivity of biomass is very poor (0.1 W/mK along the grain, 0.05 W/mK cross grain), reliance on gas-solid heat transfer means that biomass particles have to be very small to fuel the requirements of rapid heating to achieve high liquid yields.

❑ It is recommended that the water in the feed should be discounted in the final pyrolysis products with only the *water of pyrolysis* being quoted and the product yields expressed on a dry feed basis. As a rule of thumb, the water of pyrolysis is typically 12 wt% of dry feed.

Char removal is an essential requirement for the larger particles especially if it is greater than 2 mm to avoid the slow pyrolysis reactions. Now, the low thermal conductivity of biomass gives low heating rates through larger particles which lead to increased char formation and the hot char is known as the catalytically active char. Since the thermal conductivity of biomass is very poor, reliance on gas-solid heat transfer means that biomass particles have to be very small to fuel the requirements of rapid heating to achieve high liquid yields.

It is recommended that the water in the feed should be discounted in the final pyrolysis products with only the water of pyrolysis being quoted, because that is what is getting produced during pyrolysis, the biomass is not having that water content. So, that is known as water of pyrolysis. And the product yields expressed on a dry feed basis. As a rule of thumb, the water of pyrolysis is typically 12 weight percent of the dry feed.

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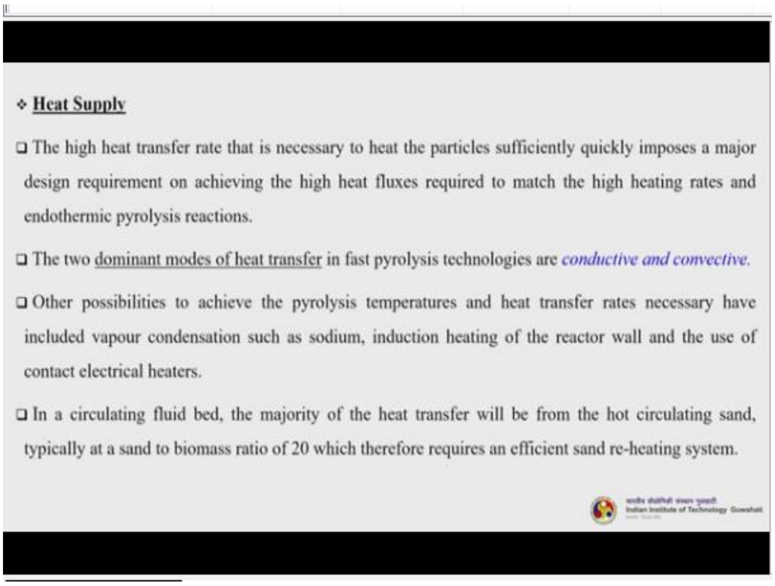

❖ **Heat Supply**

- The high heat transfer rate that is necessary to heat the particles sufficiently quickly imposes a major design requirement on achieving the high heat fluxes required to match the high heating rates and endothermic pyrolysis reactions.
- The two dominant modes of heat transfer in fast pyrolysis technologies are *conductive and convective.*
- Other possibilities to achieve the pyrolysis temperatures and heat transfer rates necessary have included vapour condensation such as sodium, induction heating of the reactor wall and the use of contact electrical heaters.
- In a circulating fluid bed, the majority of the heat transfer will be from the hot circulating sand, typically at a sand to biomass ratio of 20 which therefore requires an efficient sand re-heating system.

So, the next is heat supply. The high heat transfer rate that is necessary to heat the particles sufficiently quickly imposes a major design requirement on achieving the high heat fluxes required to match the high heating rates and endothermic pyrolysis reactions. The 2 dominant modes of heat transport in the fast pyrolysis technologies are conductive and convective. Other possibilities to achieve the pyrolysis temperature and heat transfer rates necessary have included vapour condensation such as sodium, induction heating of the reactor wall and the use of the contact electrical heaters.

In a circulating fluid bed the majority of the heat transfer will be from the hot circulating sand, typically at a sand to biomass ratio of 20 which therefore requires an efficient sand reheating system.

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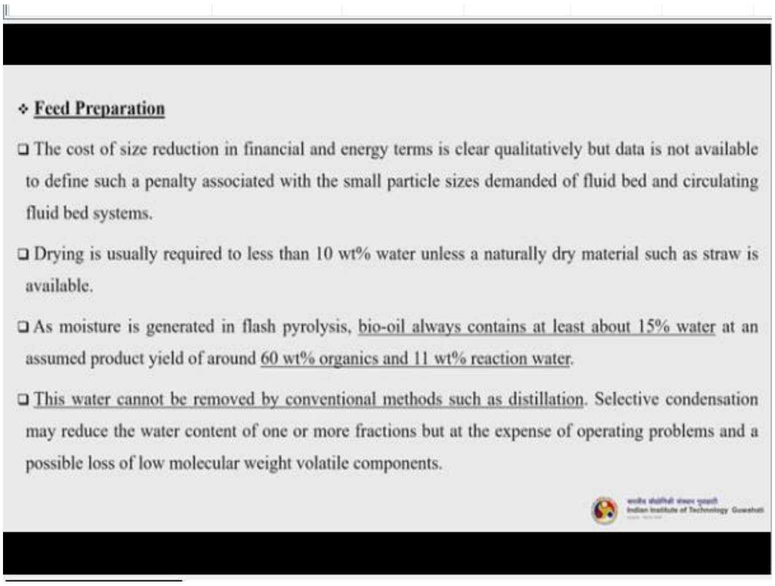

❖ **Feed Preparation**

- The cost of size reduction in financial and energy terms is clear qualitatively but data is not available to define such a penalty associated with the small particle sizes demanded of fluid bed and circulating fluid bed systems.
- Drying is usually required to less than 10 wt% water unless a naturally dry material such as straw is available.
- As moisture is generated in flash pyrolysis, bio-oil always contains at least about 15% water at an assumed product yield of around 60 wt% organics and 11 wt% reaction water.
- This water cannot be removed by conventional methods such as distillation. Selective condensation may reduce the water content of one or more fractions but at the expense of operating problems and a possible loss of low molecular weight volatile components.

Next is feed preparation. The cost of size reduction in financial and energy terms is clear qualitatively but data is not available to define such a penalty associated with the small particle sizes demanded of fluid bed and circulating fluid bed system. Drying is usually required to less than 10 weight percent water unless a naturally dry material such as straw is available.

As moisture is generated in fast pyrolysis, biooil always contains at least about 15% water at an assumed product yield of around 60 weight % organics and 11 weight % reaction water. This water cannot be removed by conventional methods such as distillation. Now, selective condensation may reduce the water content of one or more fractions, but at the expense of operating problems and a possible loss of low molecular weight volatile components.

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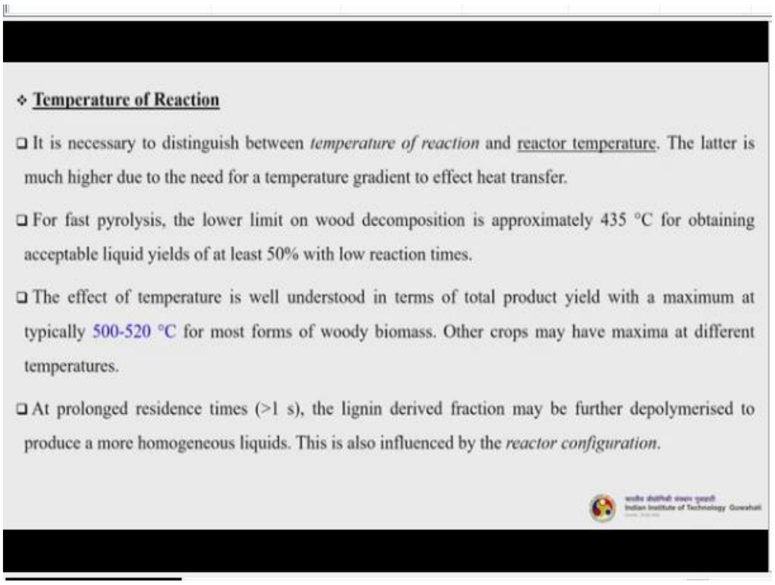

❖ **Temperature of Reaction**

- ❑ It is necessary to distinguish between *temperature of reaction* and reactor temperature. The latter is much higher due to the need for a temperature gradient to effect heat transfer.
- ❑ For fast pyrolysis, the lower limit on wood decomposition is approximately 435 °C for obtaining acceptable liquid yields of at least 50% with low reaction times.
- ❑ The effect of temperature is well understood in terms of total product yield with a maximum at typically 500-520 °C for most forms of woody biomass. Other crops may have maxima at different temperatures.
- ❑ At prolonged residence times (>1 s), the lignin derived fraction may be further depolymerised to produce a more homogeneous liquids. This is also influenced by the *reactor configuration*.

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Then temperature of reaction. Now it is necessary to understand that there is a distinction between the temperature of reaction and the reactor temperature. The latter that is the reactor temperature is much, much higher due to the need for the temperature gradient to do the heat transfer. For fast paralysis the lower limit on wood decomposition is approximately 435 degree centigrade for obtaining acceptable liquid yields of at least 50% with low reaction time.

Again that particular temperature which is mentioned here may vary slightly this side or that side depending upon the type of biomass. The effect of temperature is well understood in terms of total product yield with the maximum typically about 500 to 520 degree centigrade for most forms of woody biomass. The other crops may have a maximum at different temperatures.

But as I have mentioned you again I am telling you that it is not so significant difference maybe 25, 30 degrees or something like that sometimes may be 50 not more than that. At prolonged residence times (>1 second) the lignin derived fraction may be further depolymerised to produce more homogenous liquid. This is also influenced by the reactor configuration.

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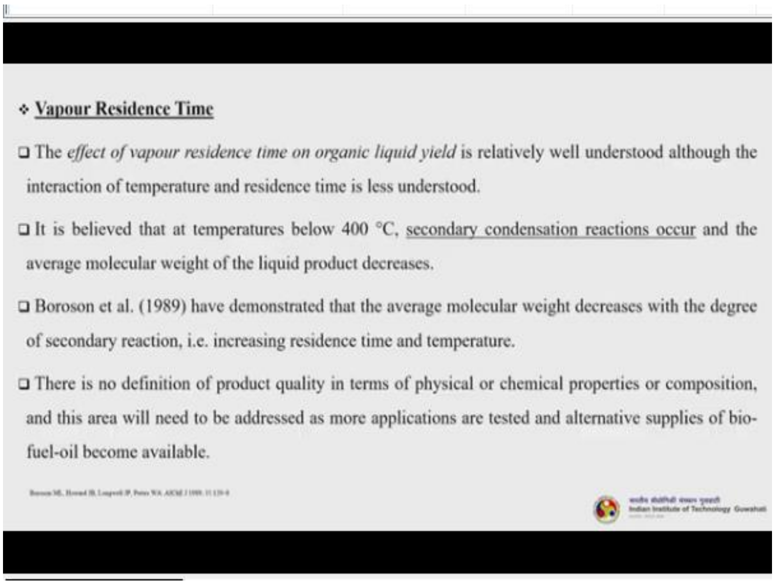

- **Vapour Residence Time**
- ❑ The *effect of vapour residence time on organic liquid yield* is relatively well understood although the interaction of temperature and residence time is less understood.
- ❑ It is believed that at temperatures below 400 °C, secondary condensation reactions occur and the average molecular weight of the liquid product decreases.
- ❑ Boroson et al. (1989) have demonstrated that the average molecular weight decreases with the degree of secondary reaction, i.e. increasing residence time and temperature.
- ❑ There is no definition of product quality in terms of physical or chemical properties or composition, and this area will need to be addressed as more applications are tested and alternative supplies of bio-fuel-oil become available.

The next is vapour residence time, one of the most important parameter. The effect of vapour residence time on organic liquid yield is relatively well understood, although the interaction of temperature and residence time is less understood. It is believed that at temperatures below 400 degree centigrade secondary condensation reactions occur and the average molecular weight of the liquid product decreases.

Boroson et al have demonstrated that average molecular weight decreases with degree of secondary reaction that is basically increasing the residence time and temperature. The reference is given below. There is no definition of product quality in terms of physical or chemical properties or composition and this area needs further or need to be addressed as more applications are tested and alternative supplies of bio fuel oil become available.

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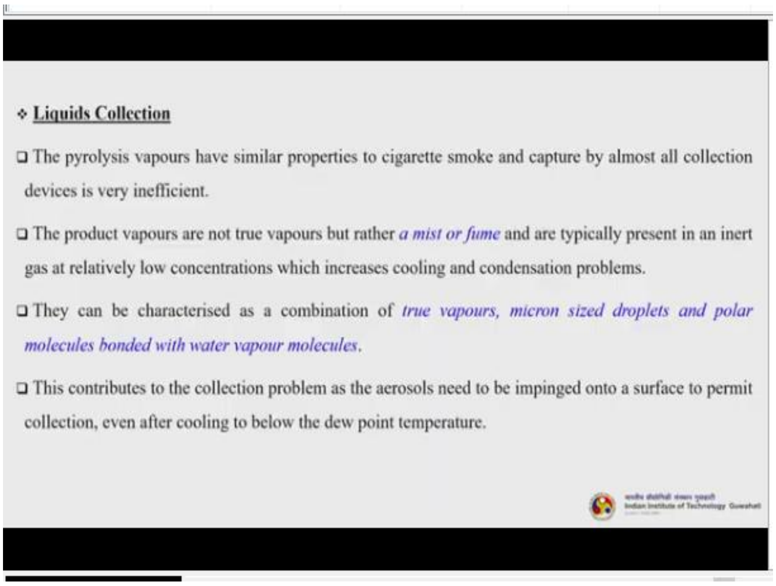

❖ **Liquids Collection**

- ❑ The pyrolysis vapours have similar properties to cigarette smoke and capture by almost all collection devices is very inefficient.
- ❑ The product vapours are not true vapours but rather *a mist or fume* and are typically present in an inert gas at relatively low concentrations which increases cooling and condensation problems.
- ❑ They can be characterised as a combination of *true vapours, micron sized droplets and polar molecules bonded with water vapour molecules*.
- ❑ This contributes to the collection problem as the aerosols need to be impinged onto a surface to permit collection, even after cooling to below the dew point temperature.

Then the next one is how do you collect the liquid basically? The pyrolysis vapours have similar properties to cigarette smoke and capture by almost all collection devices is very inefficient. The product vapours are not true vapours but rather the mist or fume and typically present in an inert gas at relatively low concentrations which increases the cooling and condensation problem. They can be characterized as a combination of true vapours, micron size droplets and polar molecules bonded with water vapour molecules.

It is a complex mixture basically. Now this contributes to the collection problem as the aerosols need to be impinged onto a surface to permit collection, even after cooling to below the dew point temperature.

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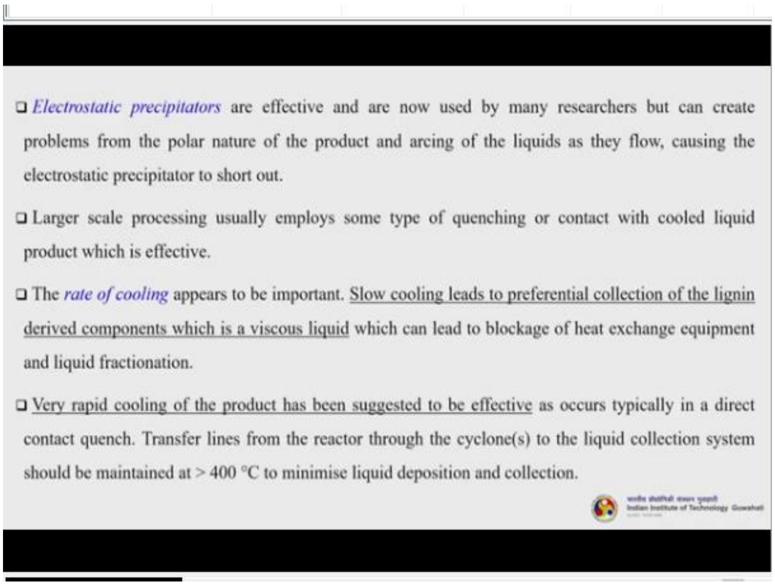

- ❑ *Electrostatic precipitators* are effective and are now used by many researchers but can create problems from the polar nature of the product and arcing of the liquids as they flow, causing the electrostatic precipitator to short out.
- ❑ Larger scale processing usually employs some type of quenching or contact with cooled liquid product which is effective.
- ❑ The *rate of cooling* appears to be important. Slow cooling leads to preferential collection of the lignin derived components which is a viscous liquid which can lead to blockage of heat exchange equipment and liquid fractionation.
- ❑ Very rapid cooling of the product has been suggested to be effective as occurs typically in a direct contact quench. Transfer lines from the reactor through the cyclone(s) to the liquid collection system should be maintained at > 400 °C to minimise liquid deposition and collection.

Electrostatic precipitators are effective and are now used by many researchers, but can create problems from the polar nature of the product and arcing of the liquid as they flow, causing the electrostatic precipitator to short out. Larger scale processing usually employs some type of quenching or contact with cooled liquid product which is effective. The rate of cooling appears to be very important.

Now slow cooling leads to preferential collection of the lignin derived components which results in a viscous liquid and it can also lead to the blockage of the heat exchange equipment and liquid fractionation. Very rapid cooling of the product has been suggested to be effective as occurs typically in a direct contact quench. Transfer lines from the reactor to the cyclones to the liquid collection system should be maintained at more than or greater than 400 degree centigrade to minimise the liquid deposition and collection.

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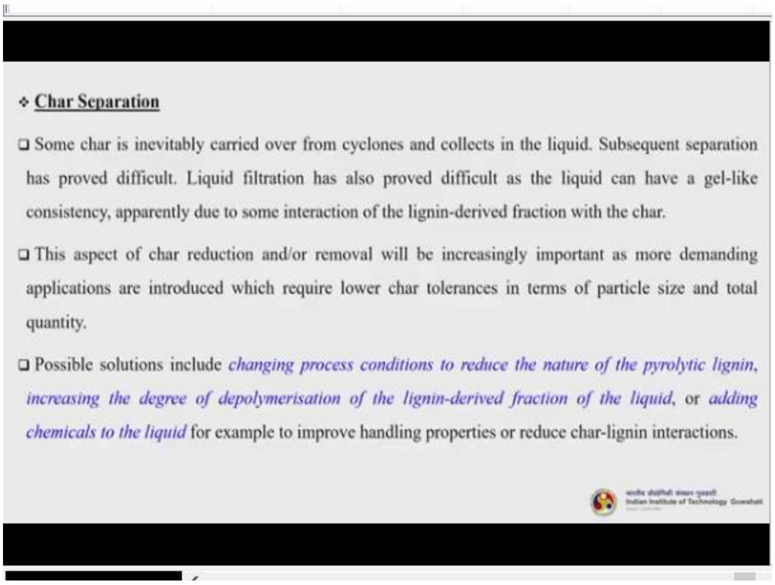

❖ **Char Separation**

- ❑ Some char is inevitably carried over from cyclones and collects in the liquid. Subsequent separation has proved difficult. Liquid filtration has also proved difficult as the liquid can have a gel-like consistency, apparently due to some interaction of the lignin-derived fraction with the char.
- ❑ This aspect of char reduction and/or removal will be increasingly important as more demanding applications are introduced which require lower char tolerances in terms of particle size and total quantity.
- ❑ Possible solutions include *changing process conditions to reduce the nature of the pyrolytic lignin*, *increasing the degree of depolymerisation of the lignin-derived fraction of the liquid*, or *adding chemicals to the liquid* for example to improve handling properties or reduce char-lignin interactions.

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Then the next one is the char separation. Now some char is inevitably carried over from the cyclones and collects in the liquid. Subsequent separation has proved difficult, because they are very fine and it is very difficult to separate them from a very high viscous liquid. So, liquid filtration has also proved difficult as the liquid can have a gel like consistency apparently due to some interaction of lignin derived fraction with the char.

Now this aspect of char reduction and/or removal will be increasingly important as more demanding applications are introduced which require lowered char tolerances in terms of particle size and total quantity. Possible solutions include changing process conditions to reduce the nature of the pyrolytic lignin, increasing the degree of the depolymerization of the lignin derived fraction of the liquid or adding chemicals to the liquid.

For example, to improve the handling properties or reduce the char lignin interaction, some sort of additives - chemical additives.

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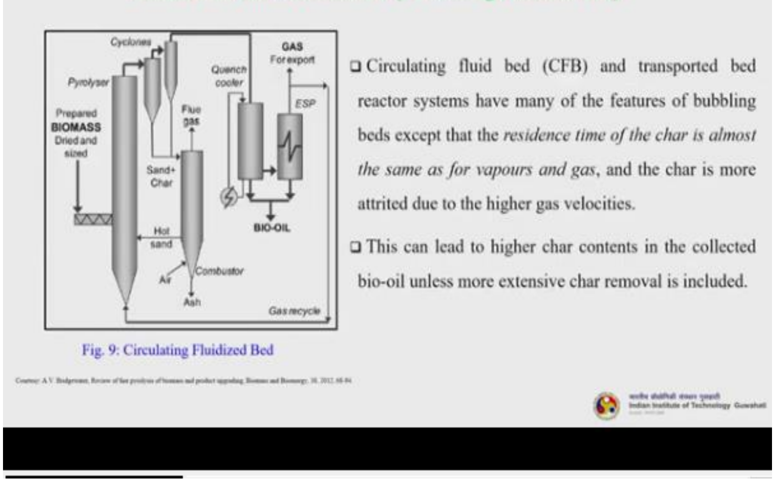

Reactors for Bio-oil Production (Circulating Fluidized Bed)

Fig. 9: Circulating Fluidized Bed

- ❑ Circulating fluid bed (CFB) and transported bed reactor systems have many of the features of bubbling beds except that the *residence time of the char is almost the same as for vapours and gas*, and the char is more attrited due to the higher gas velocities.
- ❑ This can lead to higher char contents in the collected bio-oil unless more extensive char removal is included.

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So, now we will talk about the reactors for biooil production. So, this is one classical circulating fluidized bed. You can see that it is a simplified schematic representation. So, circulating fluid bed and transport bed reactor systems have many of the features of bubbling bed except that the residence time of the char is almost the same as for vapours and gas.

And the char is more attrited due to the higher gas velocities. So, you can see that biomass that is dried and made into the desired particle size is being fed through some Hopper mechanism to the pyrolyser. So, this is the pyrolyzer. Then whatever the gas that is coming - the volatiles, the vapours, that is passing through the cyclones either 1 cyclone, 2 cyclone, or multiple cyclones and it will remove the sand and char.

Then this sand, then it goes to another system or it is another cyclone where the hot sand will be recycled back to the pyrolyzer and the ash will be collected here. And the vapours that is coming will go to a quenching facility or we can say that a condensing facility where the oil will be basically separated and some of the gas whatever is left out it can be taken out or can be recycled back to the system depending upon what it contains basically.

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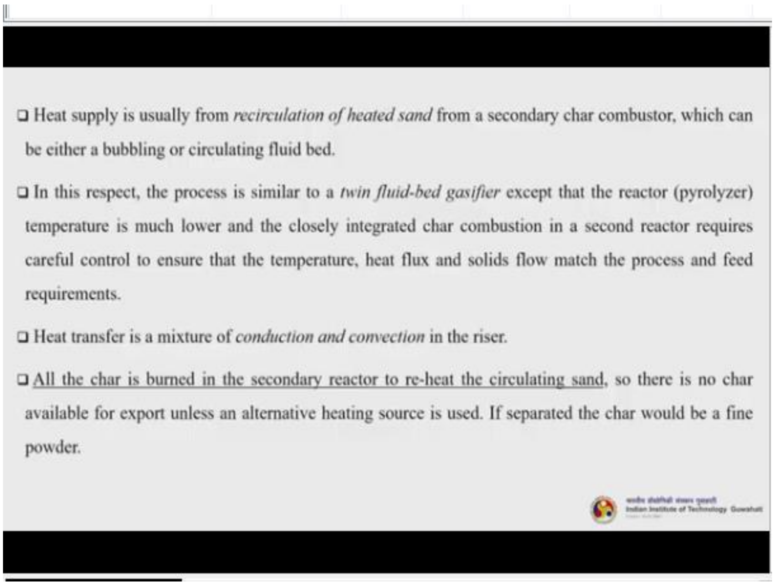

- Heat supply is usually from *recirculation of heated sand* from a secondary char combustor, which can be either a bubbling or circulating fluid bed.
- In this respect, the process is similar to a *twin fluid-bed gasifier* except that the reactor (pyrolyzer) temperature is much lower and the closely integrated char combustion in a second reactor requires careful control to ensure that the temperature, heat flux and solids flow match the process and feed requirements.
- Heat transfer is a mixture of *conduction and convection* in the riser.
- All the char is burned in the secondary reactor to re-heat the circulating sand, so there is no char available for export unless an alternative heating source is used. If separated the char would be a fine powder.

So, heat supply is usually from recirculation of the heated sand from a secondary char combustor which can be either a bubbling a circulating fluid bed. Now in this respect, the process is similar to a twin fluid bed gasifier except that the reactor temperature is much lower and the closely integrated char combustion in a secondary reactor requires careful control to ensure that the temperature, heat flux and solid flow match the process and feed requirements.

Heat transfer is a mixture of conduction and convection in the riser. All the char is burned in the secondary reactor to reheat the circulating sand. This is you can say that the secondary reactor - the combustor - to reheat the char and all the char is burned in the secondary reactor to reheat the circulating sand, so there is no char available for export unless an alternative heating source is used. If separated, the char would be a fine powder, but this fine powder biochar is of no much commercial value. However, it can be used for some processes like soil amendments and all.

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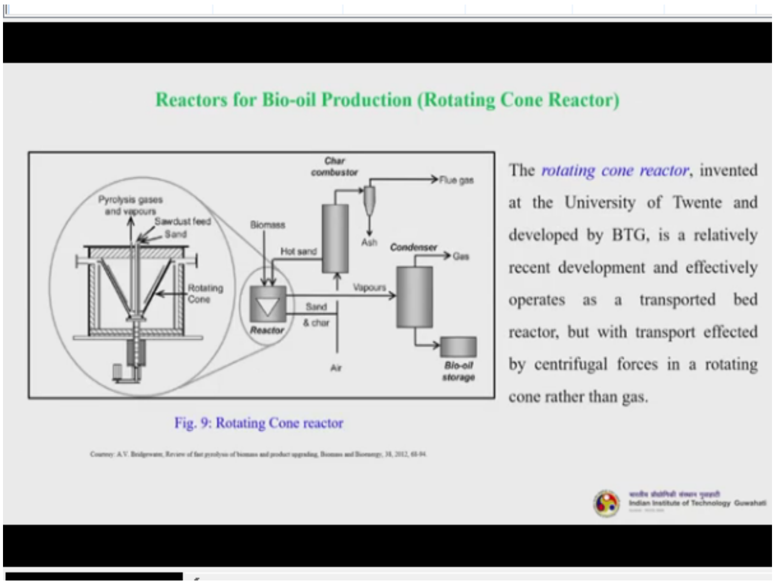

Reactors for Bio-oil Production (Rotating Cone Reactor)

Fig. 9: Rotating Cone reactor

Courtesy: A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy, 38, 2012, 68-94.

The *rotating cone reactor*, invented at the University of Twente and developed by BTG, is a relatively recent development and effectively operates as a transported bed reactor, but with transport effected by centrifugal forces in a rotating cone rather than gas.

So, this is another reactor which is also been widely adapted. It is called a rotating cone reactor. So, the rotating cone reactor - it was invented by the University of Twente and developed by the BTG group, is a relatively recent development and effectively operates as a transported bed reactor but with transport effected by the centrifugal forces in a rotating cone rather than gas. So, this is the cone - will explain.

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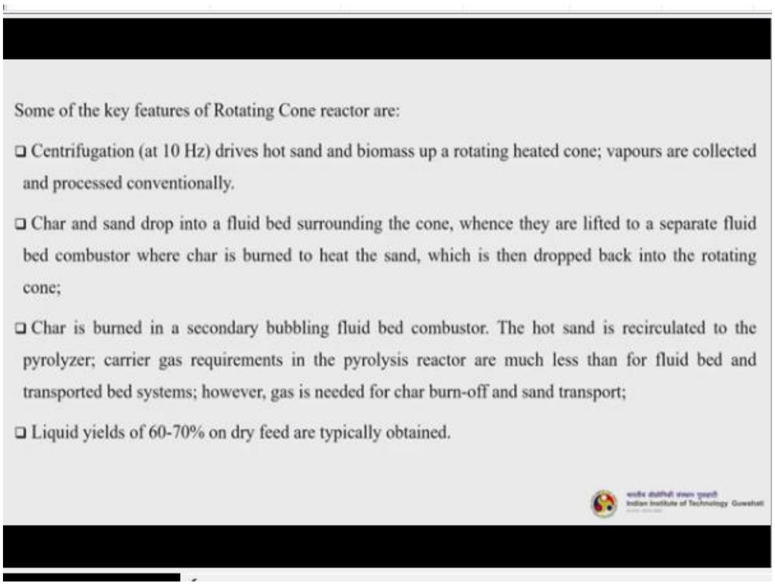

Some of the key features of Rotating Cone reactor are:

- ❑ Centrifugation (at 10 Hz) drives hot sand and biomass up a rotating heated cone; vapours are collected and processed conventionally.
- ❑ Char and sand drop into a fluid bed surrounding the cone, whence they are lifted to a separate fluid bed combustor where char is burned to heat the sand, which is then dropped back into the rotating cone;
- ❑ Char is burned in a secondary bubbling fluid bed combustor. The hot sand is recirculated to the pyrolyzer; carrier gas requirements in the pyrolysis reactor are much less than for fluid bed and transported bed systems; however, gas is needed for char burn-off and sand transport;
- ❑ Liquid yields of 60-70% on dry feed are typically obtained.

So, how it happens? So, some of the key features. So, the centrifugation drives hot sand and biomass up a rotating heated cone; vapours are collected and processed conveniently. So, this is a cone you can see that this is a cone is rotating basically. So, here saw dust (this is written sawdust, but it can be any biomass) and sand is being fed to the cone, now it is rotating and here the temperature is maintained.

So, the pyrolysis gases and vapours are escaping from here. This is the large view. This is the reactor. Then the sand and char can be collected and recycled back. The vapours goes to a condenser where the uncondensable gas will be left out and whatever you get is the biooil storage. Anyway you get aqueous fraction mixed with that and you need to do further processing of that.

The char and sand drop into the fluid bed surrounding the cone, whence they are lifted to a separate fluid bed combustor where char is burned to heat the sand which is then dropped back into the rotating cone. So, basically we are talking about this one. So, where the char and sand are getting separated and the sand is again re-circulated back. Char is burned in a secondary bubbling fluid bed combustor. The hot sand is re-circulated to the pyrolyzer; carrier gas requirements in the pyrolysis reactor are much less than for the fluid bed and transported bed systems.

However, gas is needed for the char to burn off and the sand transport. Liquid yields of about 60 to 70% on dry feed are typically obtained in this type of a rotating corn bed pyrolysis.

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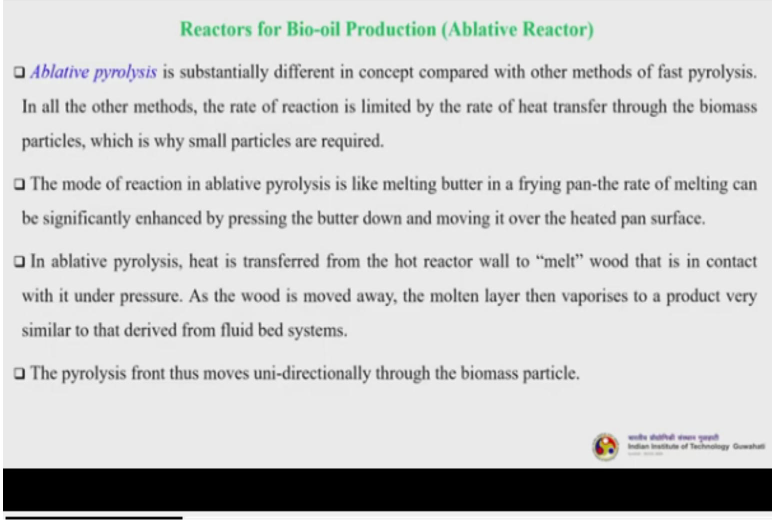

Reactors for Bio-oil Production (Ablative Reactor)

- *Ablative pyrolysis* is substantially different in concept compared with other methods of fast pyrolysis. In all the other methods, the rate of reaction is limited by the rate of heat transfer through the biomass particles, which is why small particles are required.
- The mode of reaction in ablative pyrolysis is like melting butter in a frying pan-the rate of melting can be significantly enhanced by pressing the butter down and moving it over the heated pan surface.
- In ablative pyrolysis, heat is transferred from the hot reactor wall to "melt" wood that is in contact with it under pressure. As the wood is moved away, the molten layer then vaporises to a product very similar to that derived from fluid bed systems.
- The pyrolysis front thus moves uni-directionally through the biomass particle.

So, then we will talk about ablative reactor. Ablative pyrolysis is substantially different in concept compared to other methods of fast pyrolysis. In all the other methods the rate of reaction is limited by the rate of heat transfer through the biomass particles which is why small particles are required**.** In fast pyrolysis, slow pyrolysis whatever you talk about. So, the mode of reaction ablative pyrolysis is like melting butter in the frying pan.

So, the rate of melting can be significantly enhanced by pressing the butter down and moving it over or spreading it over the heated pan surface. So, similar things happen actually. So, in ablative pyrolysis heat is transferred from the hot reactor wall to melt wood that is in contact with it under pressure. As the wood is moved away the molten layer then vaporizers to a product very similar to that derived from the fluid bed system. The pyrolysis front thus moves uni-directionally through the biomass particle.

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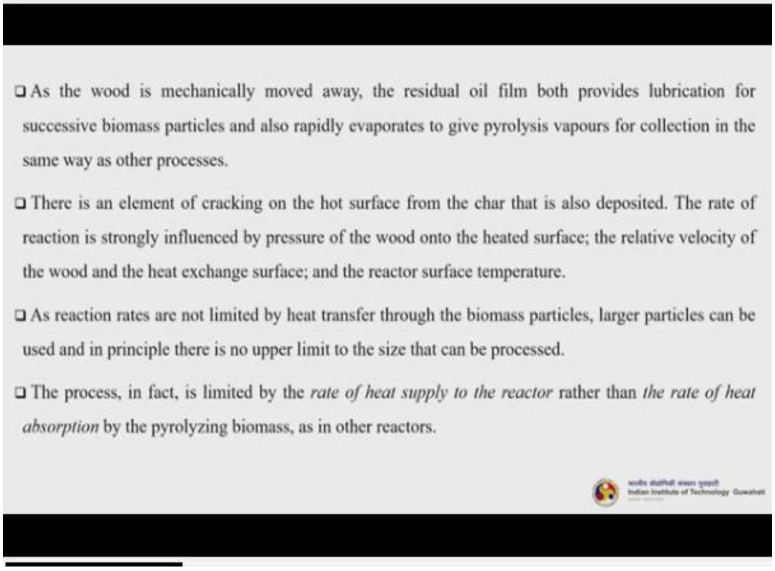

- ❑ As the wood is mechanically moved away, the residual oil film both provides lubrication for successive biomass particles and also rapidly evaporates to give pyrolysis vapours for collection in the same way as other processes.
- ❑ There is an element of cracking on the hot surface from the char that is also deposited. The rate of reaction is strongly influenced by pressure of the wood onto the heated surface; the relative velocity of the wood and the heat exchange surface; and the reactor surface temperature.
- ❑ As reaction rates are not limited by heat transfer through the biomass particles, larger particles can be used and in principle there is no upper limit to the size that can be processed.
- ❑ The process, in fact, is limited by the *rate of heat supply to the reactor* rather than *the rate of heat absorption* by the pyrolyzing biomass, as in other reactors.

As the wood is mechanically moved away the residual oil film both provides lubrication for successive biomass particles and also rapidly evaporates to give pyrolysis vapour for collection in the same way as other processes.

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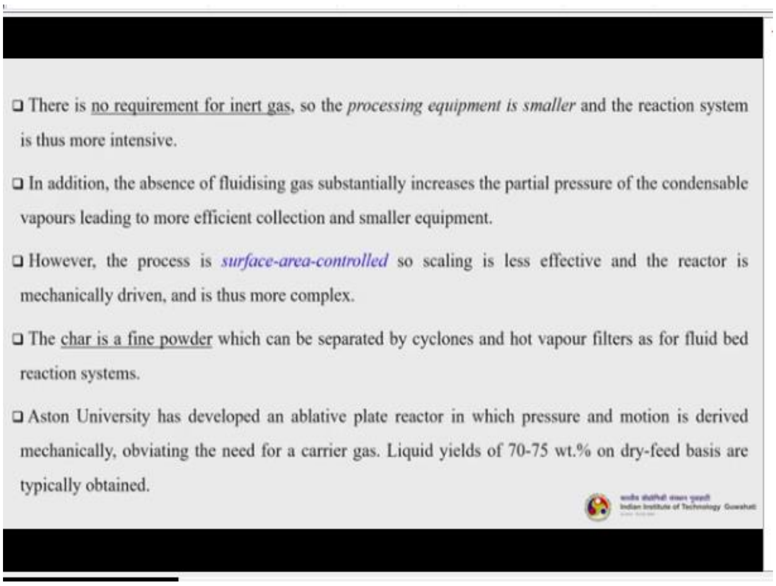

- ❑ There is no requirement for inert gas, so the *processing equipment is smaller* and the reaction system is thus more intensive.
- ❑ In addition, the absence of fluidising gas substantially increases the partial pressure of the condensable vapours leading to more efficient collection and smaller equipment.
- ❑ However, the process is *surface-area-controlled* so scaling is less effective and the reactor is mechanically driven, and is thus more complex.
- ❑ The char is a fine powder which can be separated by cyclones and hot vapour filters as for fluid bed reaction systems.
- ❑ Aston University has developed an ablative plate reactor in which pressure and motion is derived mechanically, obviating the need for a carrier gas. Liquid yields of 70-75 wt.% on dry-feed basis are typically obtained.

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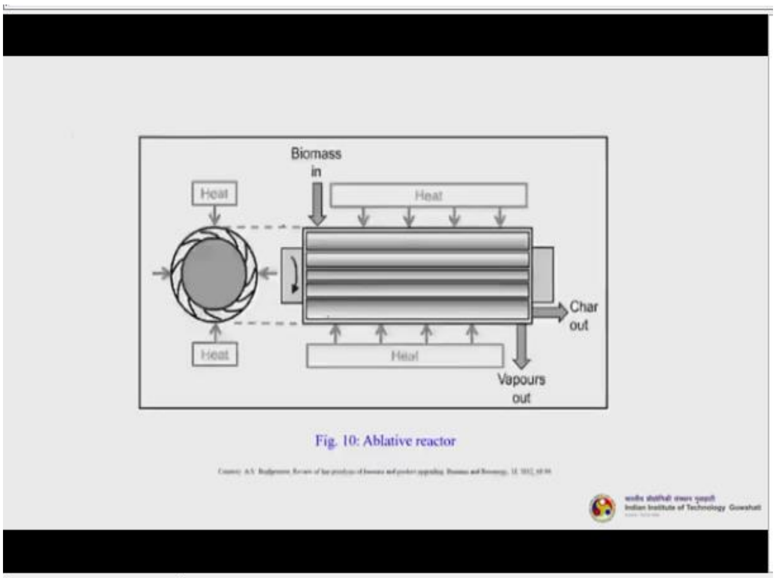

Fig. 10: Ablative reactor

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So, you can have a look here, this is how the ablative reactor looks like. So, you can see this is the reactor heating zone, this actually moves like this. So, from here starting to the end. So the entire reaction or the heat transfer zone is moving along with the wood particles. So, the vapors will be collected here and it will be further condensed to get the biooil and the char will be taken out from that side.

There is an element of cracking on the hot surface from the char that is also deposited. The rate of reaction is strongly influenced by the pressure of the wood onto the heated surface; the relative velocity of the wood and the heat exchange surface; and the reactor surface temperature. As reaction rates are not limited by heat transfer through the biomass particles, larger particles can be used and in principle there is no upper limit to the size that can be processed. The process, in fact, is limited by the rate of heat supplied to the reactor rather than the rate of heat absorption by the pyrolysing biomass as in other reactors.

There is no requirement for inert gas so the processing equipment is smaller and the reaction system is thus more intensive. In addition, the absence of fluidising gas substantially increases the partial pressure of the condensable vapour leading to more efficient collection and smaller equipment. However, the process is surface area controlled so scaling is less effective and the reactor is mechanically driven and is thus more complex.

The char is a fine powder which can be separated by cyclones and hot vapour filters as for the fluid bed reaction system. Aston University has developed an ablative plate reactor - which I just showed you - in which pressure and motion is derived mechanically obviating the need for a carrier gas. Liquid yields of 70 to 75 weight percent on dry-feed basis are typically obtained. So, this we have already discussed.

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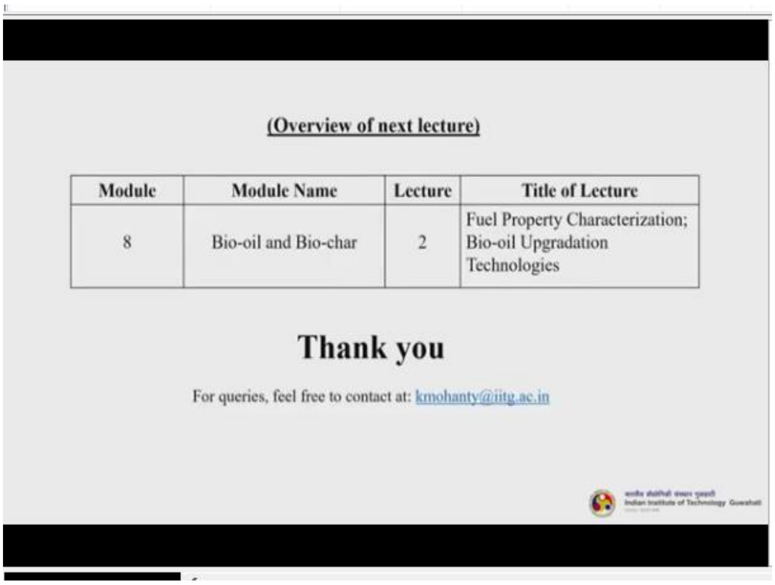

(Overview of next lecture)

Module	Module Name	Lecture	Title of Lecture
8	Bio-oil and Bio-char	2	Fuel Property Characterization; Bio-oil Upgradation Technologies

Thank you

For queries, feel free to contact at: kmohanty@iitg.ac.in

So, with this I conclude today's lecture and in our next class we will discuss about the fuel property characterization. And the most important aspect of the biooil production is a biooil upgradation technology. How do you upgrade the biooil so that you can use the major transportation fuel or at least as a blending agent. Thank you very much. If you have any query please register your queries in the swayam portal or drop a mail to me at kmohanty@iitg.ac.in.