Energy Conversion Technologies (Biomass And Coal)

Prof. Vaibhav V. Goud

Department of Chemical Engineering

Indian Institute of Technology, Guwahati

Lecture 15

Thermal / Thermochemical processes

Good morning everyone.

Welcome to this second lecture of the module 3. In this lecture, we will discuss about the thermochemical processes, mainly the carbonization and the torrefaction process.

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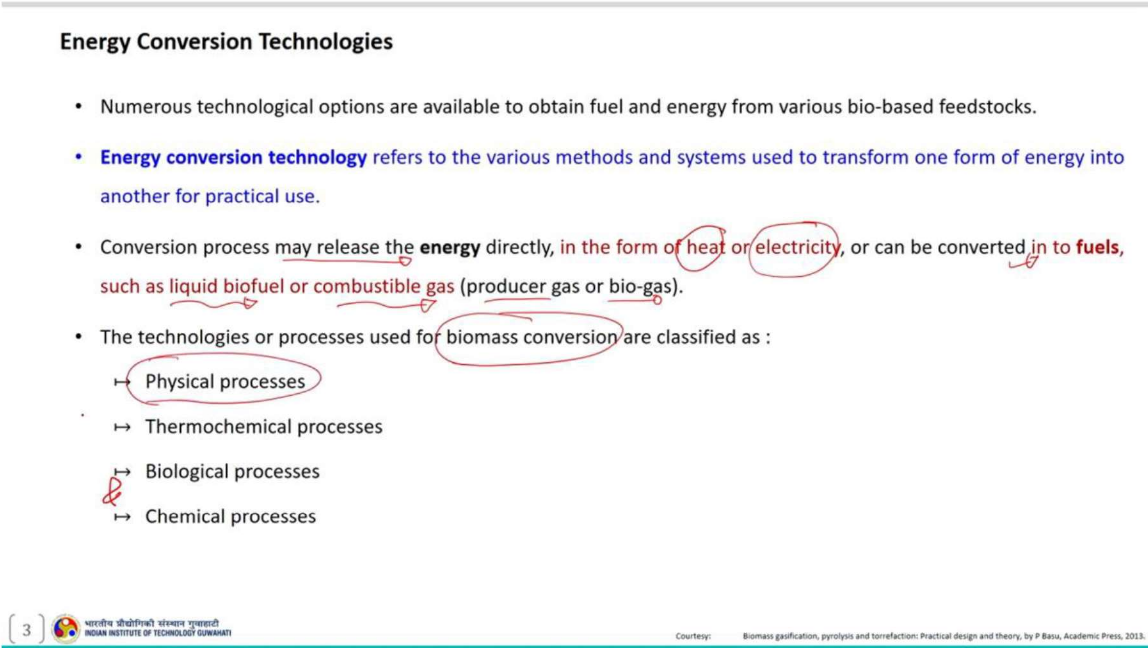

So, let us first discuss about the energy conversion technologies. Numerous technological options are available to obtain fuel and energy from various bio-based feedstock. And the energy conversion technology here refers to the methods or the systems that converts one form of energy to another one for practical use. And the practical use here, refers to the fuel or the product produced should have certain commercial use. The conversion processes may release the energy directly in the form of heat or the electricity or can be converted into the fuels. So, it can be a liquid biofuel or combustible gas as well. So, the combustible gas includes the producer gas or the bio gas. And the technologies or the processes that can be used for biomass conversion to convert this source of biomass to suitable form of energy, are classified as the physical processes, thermochemical processes, biological processes, (so biological processes here is also termed as a biochemical processes) and then the chemical processes. So, if you recollect in one of the lectures in the previous module, we discussed about the physical processes. So, in this particular module and in this lecture, we will discuss about the thermochemical conversion processes.

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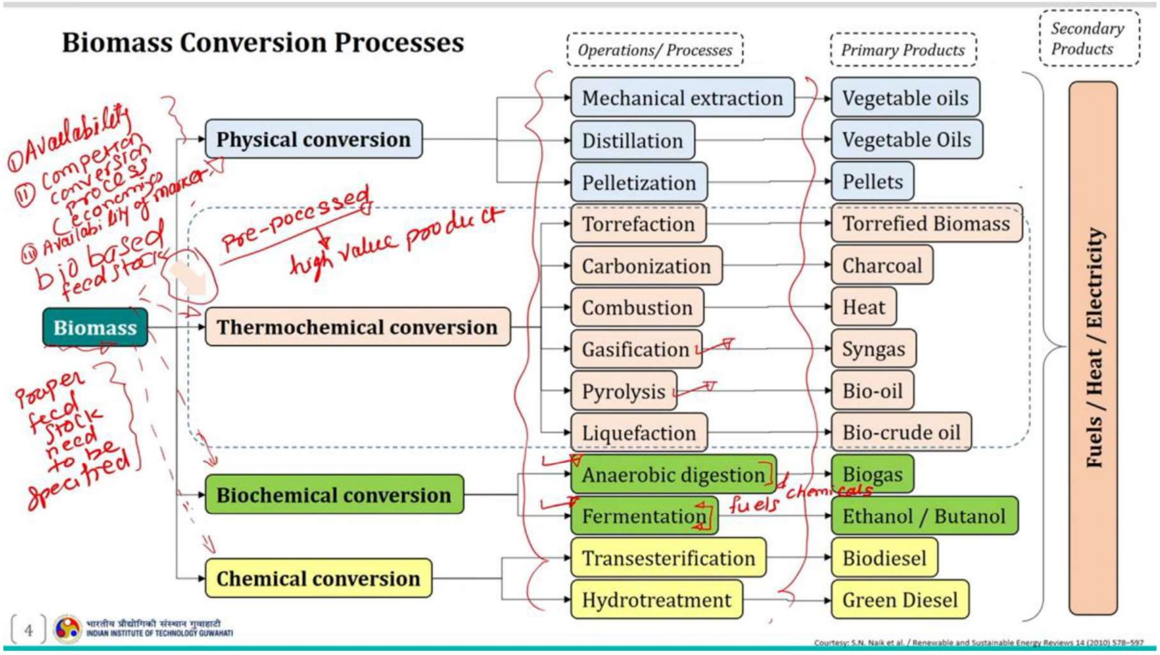

So, from this chart it appears that, several technological options are available to convert one form of energy into the another one, and to obtain also the premium fuels from the bio-based feedstock. And some of these technologies, such as anaerobic digestion and the fermentation are well understood technologies and are simple as well. While the technologies such as gasification and the pyrolysis are tested at pilot scale and are now being commercialized. While the technologies or the processes such as anaerobic digestion and the fermentation are widely being used for commercial production of fuels and chemicals. And hence, it indicates that each biomass here can be treated in many different ways to provide wide spectrum of useful products. So just take an example of the domestic refuse. So, the domestic refuse, it can be treated in a different way to produce wide spectrum of product.

For example, the domestic refuse can be dried and then burned to produce heat energy as a product. Apart from that, the domestic refuse after drying can be converted through a pyrolysis process into a low calorific value gas as well. Apart from that if the pre-processing of the biomass is not essential, in that case the domestic refuse as it is can be grinded and then digested using anaerobic digester to produce biogas as a product. So, it indicates here, the same source can be converted into a wide range of the products. So likewise, different products can be obtained from same bio-based feedstock. But, the conversion of this raw biomass to specific fuel, it depends on various factor. The first factor is the availability of the resources. Second one is it also depends on the economics of the competing process. That is economics of the competing conversion processes. It means here, if the two different processes are producing the same product and even from the same bio-based feedstock, then the economics of these two different processes need to be considered.

The process which is slightly economical or which is more economical need to be considered to produce value added product. Or you can say the fuel or energy from the specific bio-based feedstock source. Apart from that the availability of the market. So, third point is availability of so these three factors need to be considered. And based on these three factors the conversion technologies which need to be selected. And even the proper feedstock needs to be specified to the specific conversion system. And if required, the feedstock need to be pre-processed before being used in the conversion system to produce high value product. So, this gives the brief idea about the processing of various bio-based feedstock and the specific conditions of the feedstock before being used in the conversion system. That is well understood through this particular chart and this also shows the wide range of product which can be obtained using these different conversion technologies. And this middle part of the chart indicates the different conversion technologies which are available for the conversion of wide spectrum of bio-based feedstock to an even wide spectrum of products.

So, as I mentioned earlier in the previous module in one of the lectures, we discuss about the physical conversion processes. So, in this lecture as well as in this module we will focus on the thermochemical conversion processes.

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Thermochemical conversion processes

- ***Thermochemical process*** *is defined as the conversion of biomass into a range of products, by thermal decay and chemical reformation, and essentially involves heating biomass in the presence of different concentrations of oxygen.*
- Thermochemical processes include: (1) torrefaction, (2) carbonization, (3) combustion, (4) pyrolysis, (5) gasification, and (6) liquefaction.
- Thermochemical processes convert biomass into higher-value or more convenient products.
- Thermochemical process can target various product depending on the technology and process conditions:
  - ↦ Gas (~6 MJ/kg),
  - ↦ Liquid (oil) (~17-22 MJ/kg),
  - ↦ Char (~18 MJ/kg).

Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

So, the thermochemical conversion process, it is basically defined as the conversion of biomass into the range of product by thermal decay and chemical reformation of feedstock material. And essentially involves heating of biomass in the presence of different concentration of oxygen or in some cases the conversion is carried out in absence of oxygen as well. And these thermochemical processes include torrefaction, carbonization, combustion, pyrolysis, gasification and the liquefaction process. The advantage of using this thermochemical conversion process is it converts raw material that is biomass into high value product or more convenient product. The thermochemical processes here it can target various product depending on the technology and the process conditions which are used. And mainly it produces gaseous products, liquid and solid char as a product.

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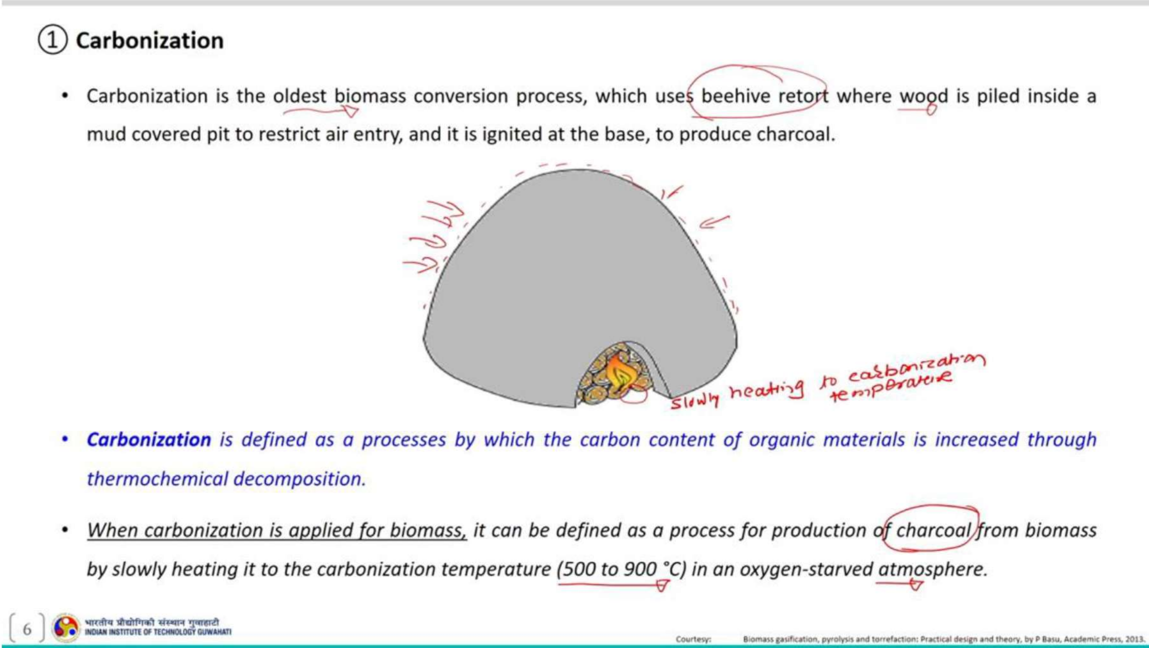

So first we will discuss about the carbonization process. Carbonization is the art of reinventing the waste biomass into carbon or energy rich charcoal. And it is the oldest biomass conversion process which uses beehive retort where wood is piled inside a mud-covered pit, to restrict the entry of air. And it is ignited at the base to produce the charcoal. And carbonization is defined as a process by which the carbon contained in the organic material is increased through thermal decomposition of the biomass. And when carbonization is applied to biomass it can be defined as a process for production of charcoal from biomass by slowly heating it to the carbonization temperature, say range of 500 to 900 °C in an oxygen starved atmosphere. So, that is also known as oxygen deficient environment.

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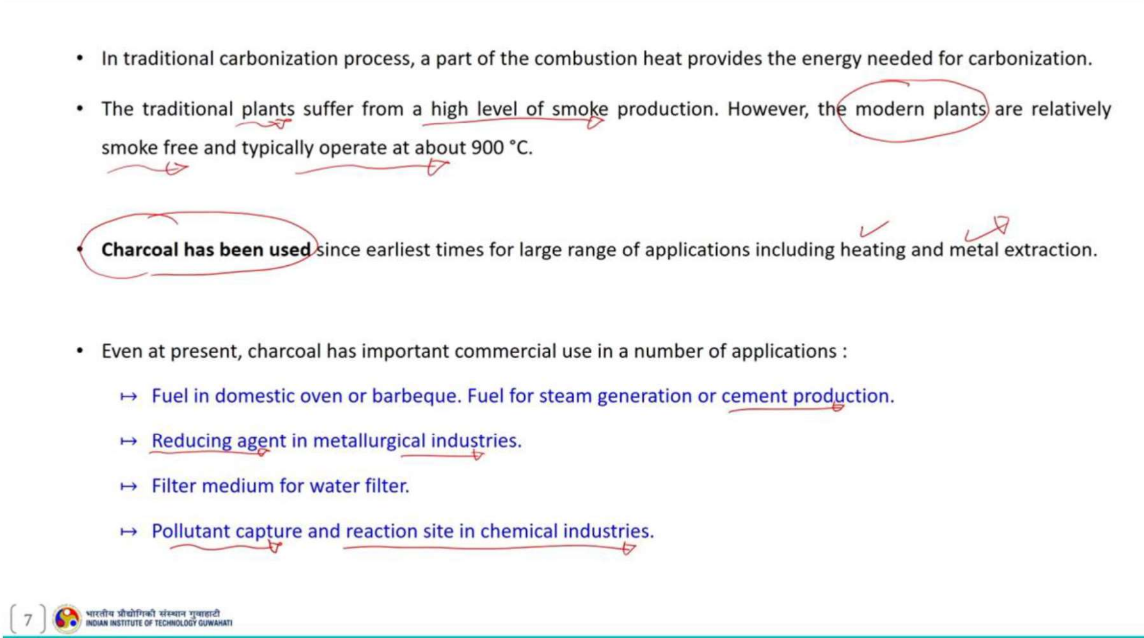

And in the traditional carbonization processes the part of the combustion heat provides the energy which is required for the carbonization process. That is what is the advantage of carbonization of the biomass using this traditional pit process. The traditional plant, it suffers from high level of smoke production. However, the modern plants, which has come with some modern designs are relatively smoke free and typically operate at about 900 °C. And also, it utilizes the energy very effectively during the carbonization process. And the charcoal which is a major product of the carbonization process, it has been used since earliest time for a large range of application including the heating and the metal extractions. And at present the charcoal has important commercial use in number of applications. Say for example, charcoal is used as a fuel in the domestic oven or the barbeque, fuel for the steam generation or cement production. It is also used as a reducing agent in metallurgical industries. And one of the most widely known use of the charcoal is, it is used as a filter medium for the water filter, and as a pollutant capture, and reaction site in chemical industries. So, these are the wide use or the importance of these produced charcoal and it is widely being used in the industries as well.

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Process conditions *(Carbonization)*

- Carbonization of biomass requires relatively high temperature and is a slow and long process.
- The amount of charcoal produced depends on the peak temperature of carbonization.

Type	Temperature	Heating rate	Process	Products
Low Temperature Carbonization	300 – 400 °C	Low	Biomass structure continues to break down. Tar release starts to predominate.	Low fixed carbon charcoal
Moderate Temperature Carbonization	400 – 500 °C	Low	Residual tar from charcoal is released	High fixed carbon charcoal
High Temperature Carbonization	500 – 900 °C	Low	Carbonization is complete.	Tar-free charcoal

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Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

So, let us talk about the process condition of the carbonization process. Carbonization process occurs at relatively higher temperature and for several hours. And the amount of charcoal produced during this carbonization process, it depends on the peak temperature of the carbonization and based on that the carbonization process is categorized into three types. That is low temperature carbonization, moderate temperature carbonization, and the high temperature carbonization. In case of low temperature carbonization, it is carried out in the temperature range of 300 to 400 °C, where the heating rate is low. And in this process the biomass structure continues to break down. As we know the biomass structure it is consist of cellulose, hemicellulose and lignin. So, in this particular stage of low temperature carbonization, so the biomass structure continues to break down and the release of tar starts to predominant in this particular step. And the product, which can be obtained from the low temperature carbonization is a low fixed carbon charcoal.

While if you talk about the moderate temperature carbonization, it occurs between the temperature of 400 to 500 °C and the heating rate is relatively low, in case of moderate temperature carbonization as well as in the low temperature carbonization. And in this particular process, so the residual tar as formed during this particular step, here from the charcoal is released during this particular step. And eventually it produces high fixed carbon containing charcoal. However, if you try to go for the high temperature carbonization process, so temperature is also relatively high in this particular process. However, the heating rate is still low and this particular process gives the complete carbonization of the feedstock. And it produces tar free charcoal as a product. So, this gives the detail information about the carbonization process and its conditions.

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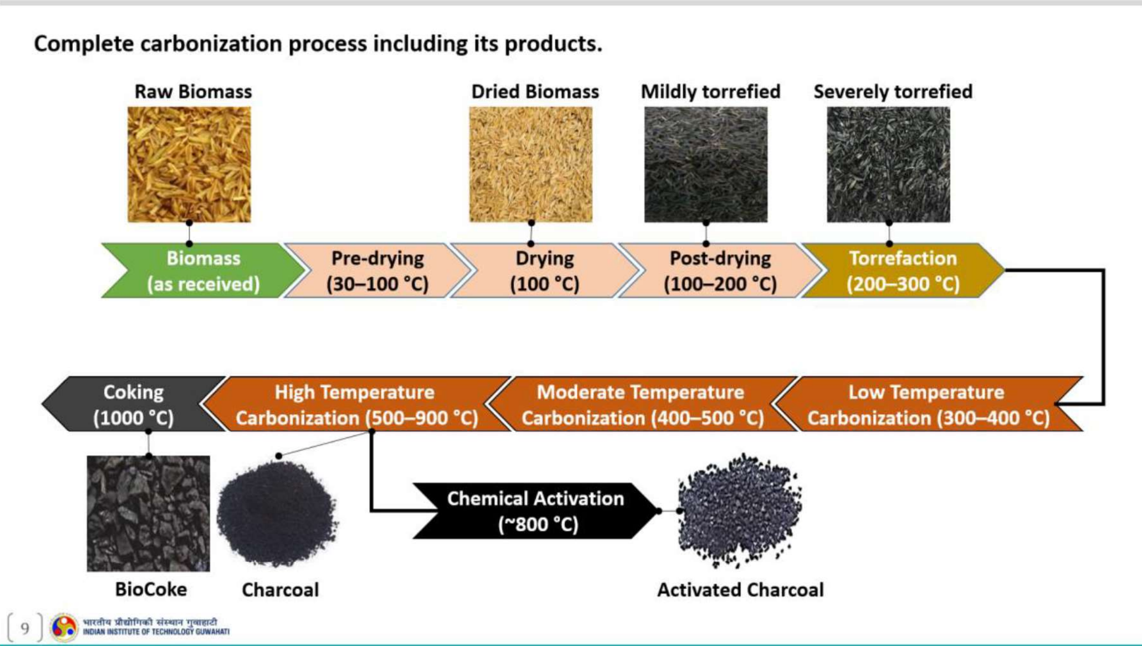

And this schematic here, it represents the complete carbonization process including its products. So, if you just start with this first step in the carbonization process, which is a raw biomass, it is first pre-dried using this pre-drying operation. And in this step, the carbonization process, where the biomass is heated from room temperature, that is say 20 to 25 °C to around approximately 100 °C. And this stage usually has a steep temperature rise during this particular pre-drying stage, which is called as a steep temperature rise. And the heat supplied to the biomass in this particular step accounts mainly for increasing the moisture temperature to the evaporation temperature. Followed by that is the drying step. So, in the drying step this is the highest step in energy consumption because the high latent heat of water specifically for the biomass which has a relatively high moisture content. So, if the biomass which has relatively high moisture content, this particular step, it consumes significant amount of the energy. And all heat which is supplied during this step is just to convert the moisture in the biomass from liquid to the vapor. And in order to avoid the heat loss during this particular stage, so sun drying should be employed for the raw biomass before introducing it to the conversion process. Followed by drying is the first drying operation, so, after drying is complete the heat which is added to the biomass start to increase its temperature and this stage it ranges between the 100 to 200 °C. And during this stage, no significant decomposition starts within the biomass. Only the water molecules which are in the form of bound moisture inside the fibers and very light volatile compounds, are expelled during this particular stage.

And this stage does not require even high heat as this particular stage is a very quick step in the carbonization process. Followed by that is the torrefaction process. So, the torrefaction, which occurs between the temperature range of 200 to 300 °C. And during this stage the decomposition of the compound starts. And the first constituent of the biomass, which undergoes the decomposition here is the hemicellulose. And by the end of this stage almost all the hemicellulose is decomposed and only small fraction of cellulose starts decomposing. And the next after torrefaction is the low temperature carbonization. And this particular stage we already discussed in previous slide. It occurs between the temperature range of 300 to 400 °C. And during this stage both the hemicellulose and cellulose completely decomposed. And the lignin starts to degrade at this particular step. Followed by that is the high temperature carbonization. We also discussed about the high temperature carbonization in the previous slide. It occurs between the temperature range of 400 to say 800 °C here. And in this particular stage, very high carbon rich charcoal is obtained.

So, if you see here, this particular picture, which is after the high temperature carbonization, which indicates the very high carbon rich charcoal. And if the purpose of carbonization is to use the product in the metal over extraction, then the heating is increased till 1000 °C. And this produce biocoke, which is extremely rich in carbon, which is also known as a bio-coke. And if the purpose is to produce activated carbon for adsorption, then the heating continues till 800 °C here in the superheated steam to remove the tar. And the product at this stage has a very large pore volume, making it most suited for adsorption and purification applications. So, this way, this particular process shows the complete carbonization process including its product. And as we discussed earlier, the same raw material can be used to produce different types of product like charcoal, the biocoke, and activated charcoal, just by tuning some of the temperature conditions. So, with the help of tuning the temperature condition, the same raw material can be converted into multiple products.

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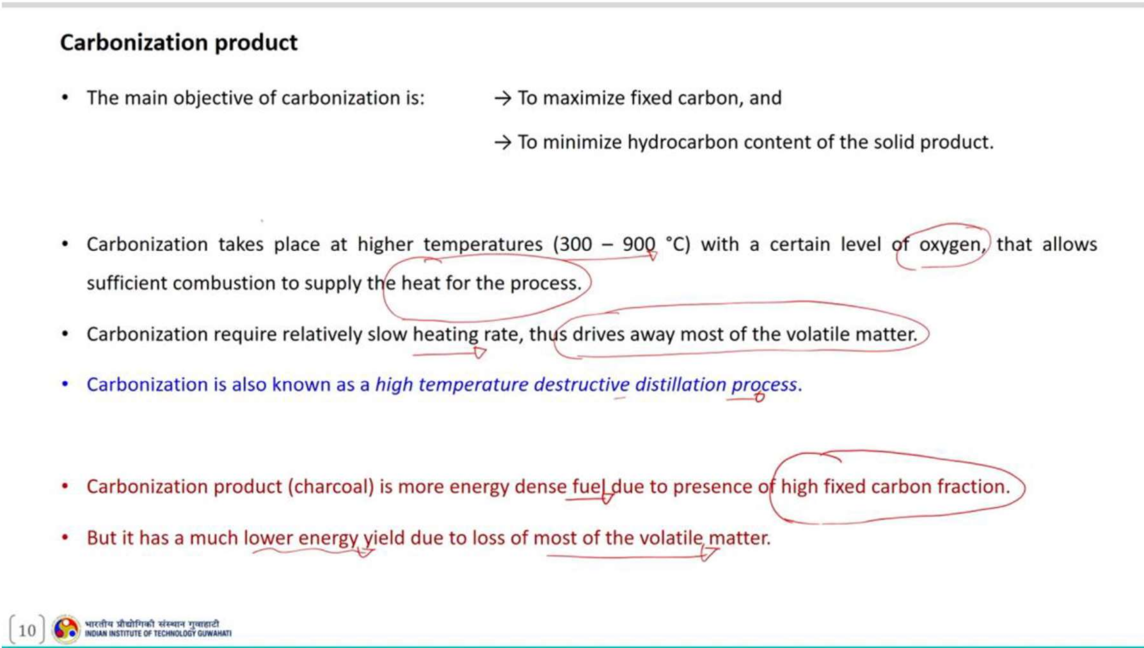

So, after learning about the carbonization process, the main objective of the carbonization process is to maximize the fixed carbon content and to minimize the hydrocarbon content in the solid fuel or the solid product. The carbonization process, it takes place at relatively higher temperature as we discussed earlier, which is 300 to 900 °C with a certain level of oxygen. And that allows sufficient combustion to supply the necessary heat, which is required during the carbonization process. And it also required relatively slow heating rate to drive away most of the volatile matter content present in the biomass feedstock. And the carbonization process, it is also known as a high temperature destructive distillation process. And the product of carbonization process that is charcoal is more energy dense fuel due to presence of high fixed carbon fraction in its composition at the end of the process. But it has much low energy yield and that is due to loss of most of the volatile matter, which are present in the biomass or bio-base feedstock.

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- Low Fixed Charcoal:
  - ↦ Low fixed charcoal refers to charcoal with a lower percentage of fixed carbon content.
  - ↦ It has a relatively higher proportion of volatile matter.
  - ↦ It burns more easily due to its higher volatile content and may produce a larger flame with visible smoke.
- High Fixed Charcoal:
  - ↦ High fixed charcoal has a higher fixed carbon content, and lower volatile matter content.
  - ↦ It is commonly used for household cooking/grilling due to its ease of ignition and higher heat output.
- Tar-Free Charcoal:
  - ↦ Tar-free charcoal contains no tar and other impurities.
  - ↦ Tar is removed as a byproduct of carbonization.
  - ↦ Reduced levels of tar/VM results in cleaner burning and reduced emissions during combustion.

So, if you recollect, few slides back, we discussed about the low temperature carbonization, the moderate temperature carbonization, and then the high temperature carbonization. And the product obtained during the low temperature carbonization, which is also known as a low fixed charcoal. It refers to the charcoal with lower percentage of the fixed carbon content. And it has relatively higher proportion of volatile matter in its composition. And it burns more easily due to its higher volatile matter content and may produce a larger flame with a visible smoke as well. Whereas in case of the high fixed charcoal, it has a higher fixed carbon content, but relatively lower volatile material content in its composition. And that is why it is commonly used for the household cooking and the grilling purpose due to ease of ignition and higher heat output which can be obtained from the high fixed charcoal. And the last is the tar free charcoal. So, the tar free charcoal here contains no tar and other impurities. That is why it is called as a tar free charcoal. And the tar is removed here as a byproduct of the carbonization process. And reduced the levels of tar and volatile matter results in cleaner burning and reduced emission during the combustion operation.

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Comparison of Carbonized Charcoal with Wood and Coal

Parameter	Typical Wood	Charcoal (Carbonization)	Bituminous Coal
Temperature (°C)	-	>300	-
Moisture (%)(wb)	30-60	1–5	3–20
Volatile (%db)	70-80	10–12	28–45
Fixed Carbon (%db)	15-25	85-87	45–60
Mass yield	-	~30%	-
Energy density (db)(MJ/kg)	~18	30–32	24–33
Volumetric energy density (GJ/m³)	~5.8	18.5–19.8	30–40
Apparent density (kg/m³)	350-680	600–640	1100–1350
Hydrophobicity	Hygroscopic	Hydrophobic	Hydrophobic

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Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

As I mentioned earlier, the carbon content, that is the fixed carbon content need to be preserved during the carbonization process. And because of that here if you see the mass yield is around 30 percent and the energy density of the charcoal is significantly high compared to that of the original feedstock. And it is even comparable with the coal sample. And the volumetric energy density here is significantly high compared to that of the original feed stock material. But, it is relatively low than the coal sample. Whereas the apparent density is quite high in case of the charcoal, but compared to the coal it is relatively low. And the hydrophobicity of the charcoal is it is hydrophobic in nature similar to that of the coal because the biomass is hygroscopic in nature.

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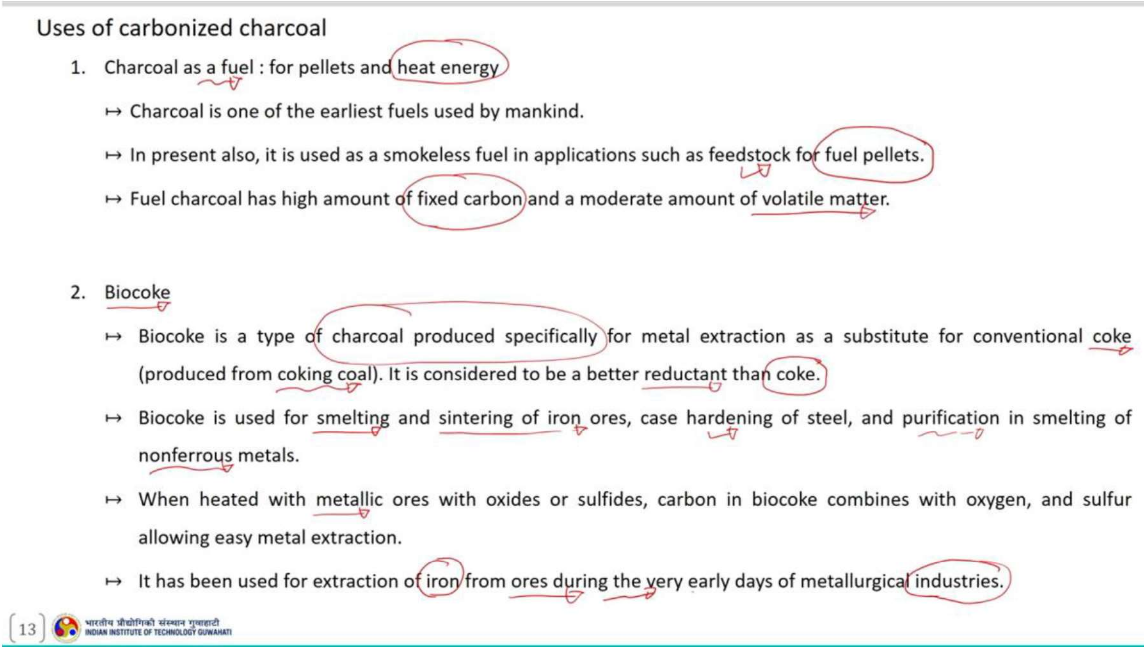

So now after understanding about the carbonization process, its process condition and the quality of the charcoal which can be obtained from the carbonization process, let us discuss about the uses of the carbonized charcoal. So, charcoal can be used as a fuel for pellets and for heat energy application. And it is one of the earliest fuels used by the mankind. In present scenario also, it is used as a smokeless fuel in the application such as feed stock for fuel pellets. So, as I just mentioned before, the carbonized charcoal can be used as a feed stock material for the preparation of the fuel pellets. And the fuel charcoal has high amount of the fixed carbon and the moderate amount of the volatile matter in its composition. Similarly, the carbonized charcoal can further be converted into the biocoke, as we discussed few slides back. Because the biocoke is a type of charcoal which is produced specifically for the metal extraction, as a substitute for the conventional coke. And the conventional coke is produced from the coking coal material. And it is considered to be a better reductant than the coke. Even the biocoke, it is used for the smelting purpose and sintering of iron ores, hardening of steel, and purification in smelting of non-ferrous metals as well. And when this biocoke is treated with the metallic ores with oxides or sulfides then the carbon in the biocoke combines with the oxygen and sulfur allowing easy metal extraction. As well as this bio coke also used for the extraction of the iron from ores during the very early days of metallurgical industries. And the charcoal that is why it has a very long history. And it has been used widely for the extraction of the iron from the ores and during the very early days of the metallurgical industries.

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3. Biochar
   - ↦ Biochar is a charcoal product of pyrolysis process, where carbonization takes place at relatively higher temperatures (700-900 °C).
   - ↦ Biochar has the excellent carbon sequestration potential and soil remediation properties.
   - ↦ The higher the carbonization, the better is the property of biochar though carbon retention as solid is less.

4. Charcoal as chemical reagent
   - ↦ Charcoal used as carbon source in the manufacture of carbon disulfide CS_2, sodium cyanide NaCN, and carbides.
   - ↦ E.g. Carbon disulphide produced by the reaction of charcoal with sulfur vapours at 750°C.

Similarly, biochar is a charcoal produced by the pyrolysis process but here the process is carried out at relatively higher temperature. And the temperature range in the case of pyrolysis process is shown here between 700 to 900 °C. And this biochar it has an excellent carbon sequestration potential. And also, it has a soil remediation property. The higher the level of the carbonization, as we discuss about the carbonization processes, the better is the property of biochar, though carbon retention as solid is less in case of a biochar. And this produced charcoal is also used as a chemical reagent as a carbon source in the manufacture of carbon disulfide, sodium cyanide, and carbides. And this carbon disulfide, it can be produced by the reaction of charcoal with the sulfur vapor but at relatively higher temperature, close to around 750 °C. So, this charcoal also has used in the chemical industries to produce this carbon disulfide. And this is the process which is used to produce the carbon disulfide from the charcoal.

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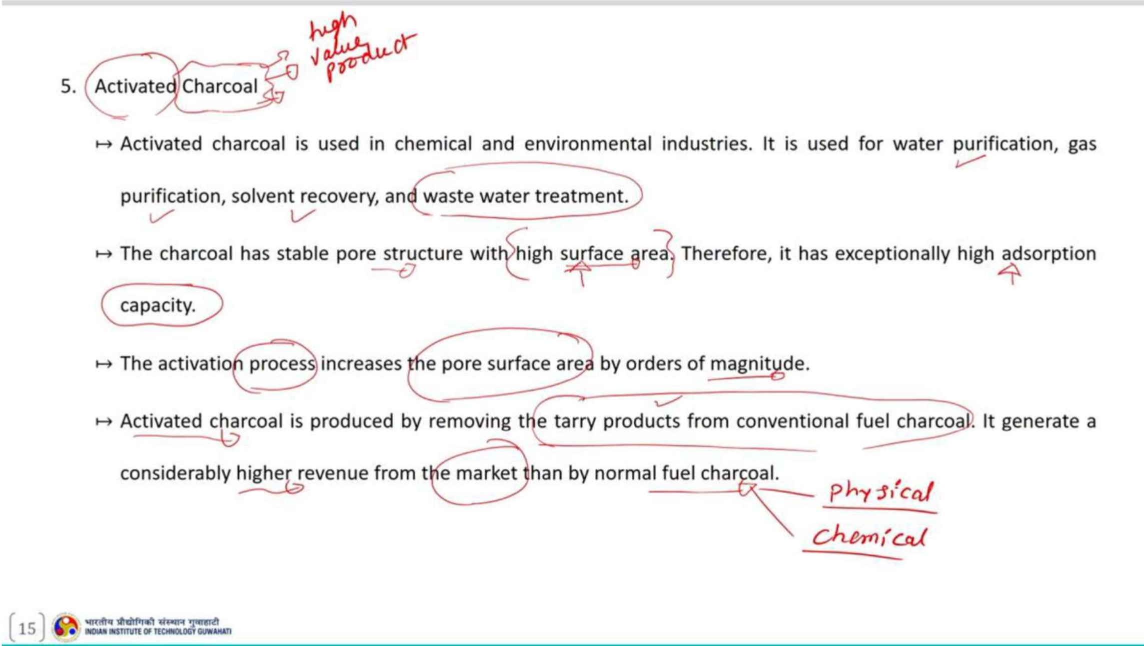

And the activated charcoal is one of the most widely used product for various application. Activated charcoal is used in the chemical and the environmental industries. It is used for water purification, gas purification, solvent recovery, and the waste water treatment as well. Because this charcoal has a stable pore structure with relatively high surface area. Because this is a activated charcoal, because of that it has a stable pore structure and relatively higher surface area than the charcoal material. And therefore, it has exceptionally high absorption capacity as it has relatively higher surface area. So, it increases its absorption capacity as well. And the activation process increases the pore surface area by order of the magnitude as well. And because of that the activation of the charcoal is preferred to produce high value product. The activated charcoal is produced by removing the tarry product from the conventional fuel charcoal. And we discussed this point before also. And because of this it generates a considerably higher revenue from the market than the normal fuel charcoal. And as I mentioned earlier, this activation process can be carried out by two different ways, that is called as a physical activation and the chemical activation. And the product produced by this process of requisite standard can be used for the wider application in the chemical and the environmental industries.

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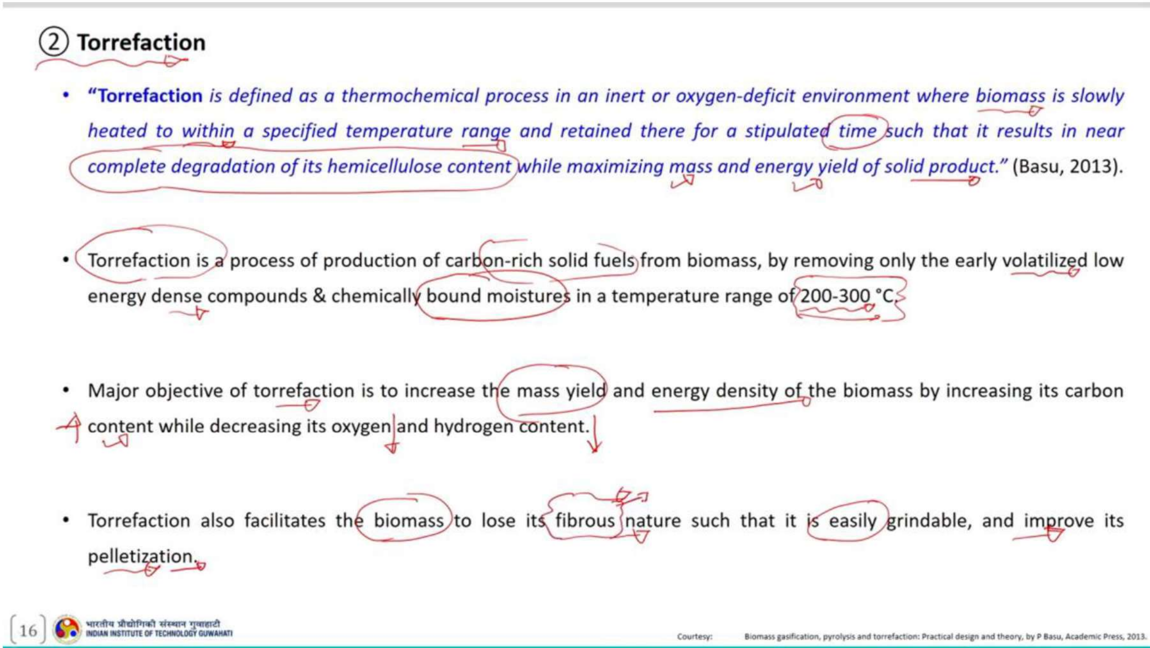

And the next in the thermochemical conversion process is the Torrefaction. Torrefaction is defined as the thermochemical conversion process carried out in inert or oxygen deficient environment where the biomass is slowly heated to within a specified temperature range and retain there for a stipulated time, such that it results in near complete degradation of its hemicellulose content while maximizing the mass and energy yield of the solid product. Because the Torrefaction process, it is a well-known process for the production of carbon rich solid fuel from biomass by removing only the early, volatilized, low energy dense compounds and chemically bound moisture in the temperature range of 200 to 300 °C.

And that is the limit of Torrefaction reaction. It carries out between this temperature range. And the major objective of Torrefaction process is to increase the mass yield and the energy density of the biomass by increasing its carbon content but decreasing its oxygen and the hydrogen content. And this particular process is also facilitating the biomass to lose its fibrous nature such that, it is easily grindable and then it improves its palletization properties as well. Because once these fibers are softening then this act as a natural binder during the palletization process.

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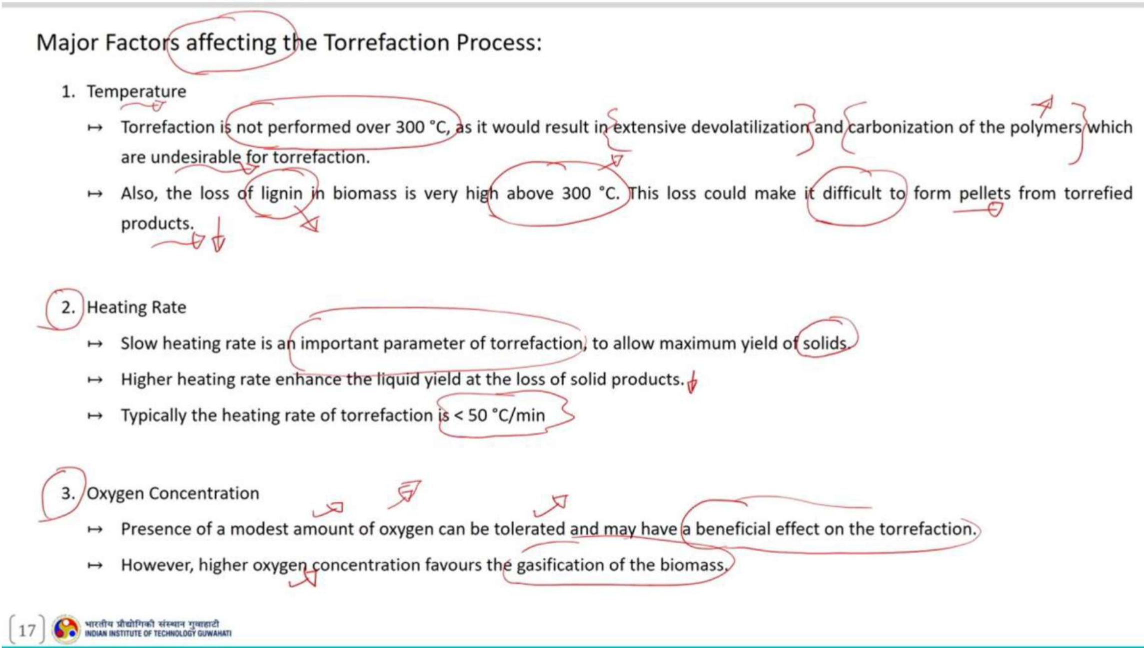

The major factor which affect the Torrefaction process are summarized here. So, the first factor which influences or affects the Torrefaction process is the temperature. And as we discussed earlier, the Torrefaction process is carried out in the specific temperature range. And that is the reason the temperature is more important and the crucial parameter or the factor in the Torrefaction process. And Torrefaction is not perform over the temperature of 300 °C because it may result in the extensive de-volatilization, carbonization of polymers. So, polymers here referred as a natural bio polymer that is cellulose, hemicellulose and lignin which are undesirable for the Torrefaction process. Also, the loss of lignin in biomass is very high above 300 °C. And this loss could made it difficult to form pallet from the Torrefied product. And that is the reason I discuss in the previous slide, that if the temperature goes beyond 300 °C then there will be a more loss of the lignin in the biomass and the lignin is nothing but the natural binder. And if this content of the lignin gets reduced in the Torrefied biomass, then it becomes very difficult to form a pallet from the Torrefied biomass. So, another important factor in the Torrefaction process is the heating rate. And normally the slow heating rate is preferred for the Torrefaction process to allow maximum yield of the solid product. And higher heating rate, it enhances the liquid yield but at the loss of solid product.

which is used during the Torrefaction process is less than 50 °C per minute. Oxygen concentration is also one of the important factors in the Torrefaction process. Because the presence of modest amount of oxygen can be tolerated in the Torrefaction process and may have beneficial effect on the Torrefaction process as well. But, if the amount of oxygen becomes relatively high then it favors the gasification of the biomass. Because as we know, if the oxygen content goes on increasing during the Torrefaction process then eventually it may lead to the gasification of the biomass. And most of the content in the biomass feedstock will be converted into a gaseous product rather than the solid product.

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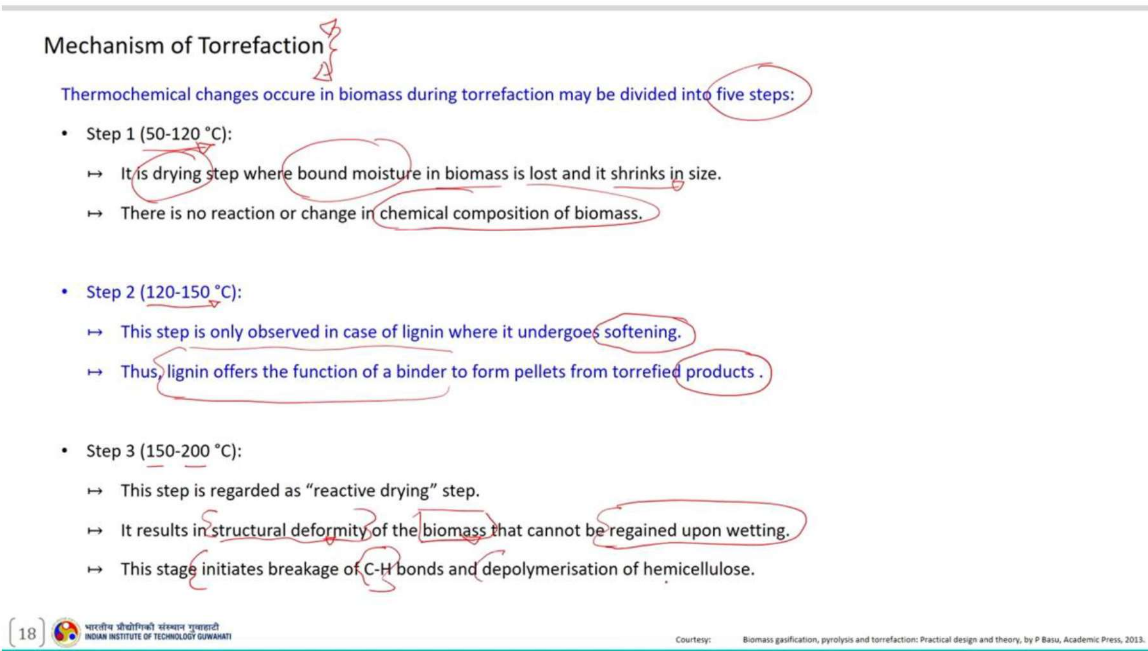

And the mechanism, which occurs during the Torrefaction process is basically divided into five steps. So, the first step is which is between 50 to 120 °C. So, this is also called as a drying step, where the bound moisture in the biomass is lost and it shrinks in size. And there is no reaction or the change in the chemical composition of biomass in this particular stage. As this is a drying step, here most of the moisture, which is present in the biomass is removed and then it shrinks in a size. Apart from that, there is no chemical change happens during this particular step in the Torrefaction process. And the next step in the Torrefaction is between 120 to 150 °C and this step is only observed in case of the lignin where it undergoes the softening. And thus, lignin offers the function of binder to form pellet from the torrefied product. And the next step is between 150 to 200 °C. And this step is regarded as a reactive drying step and it results in the structural deformation of the feedstock material that cannot be regain upon wetting. So, in this particular stage, some structural deformation of the native constituents of the biomass occurs and then it cannot be regaining to its original structure upon wetting. And this stage initiates the breakage of hydrocarbon bonds and depolymerization of the hemicellulose.

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- Step 4 (200-250 °C):
    - ↦ Torrefaction of hemicellulose starts in this step and continues in step 5.
    - ↦ It starts limited devolatilization and carbonization of solids structure formed in previous step.
    - ↦ It involve the breakdown of intra- and intermolecular hydrogen, C-C and C-O bonds, to produce condensable liquids and noncondensable gases.

- Step 5 (250-300 °C):
    - ↦ Extensive decomposition of hemicellulose occur to produce volatiles and solid products.
    - ↦ Also it starts the devolatilization and carbonization of a small amount of cellulose and lignin.
    - ↦ Biomass cell structure is completely destroyed to form brittle and nonfibrous matter.
    - ↦ Biomass composition is changed.

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And the next step in the Torrefaction is the step 4 which is between 200 to 250 °C. And in this step, the Torrefaction of the hemicellulose starts and even continues in the step 5 as well. It starts limited devolatilization and carbonization of the solid structure formed in the previous step, that is step number 3. And it involves the breakdown of intra and intermolecular hydrogen, carbon, and carbon-oxygen bonds to produce condensable liquids and non-condensable gases as well. And the last step in the Torrefaction process is a step number 5. Which is between 250 to 300 °C. And in this step extensive decomposition of the hemicellulose occur to produce volatiles and solid as a product. And even in this step, there is a start of the devolatilization and the carbonization of small amount of cellulose and lignin fraction. And in this step the biomass cell structure is completely destroyed to form brittle and non-fibrous matter. And at the end of this particular step the biomass composition is totally changed. Because the major constant of the biomass that is hemicellulose is extensively decomposed during this particular stage.

And even there is a start of devolatilization and the carbonization of small amount of the cellulose and the lignin. Because of that the biomass composition is totally gets changed in the fifth step of Torrefaction process.

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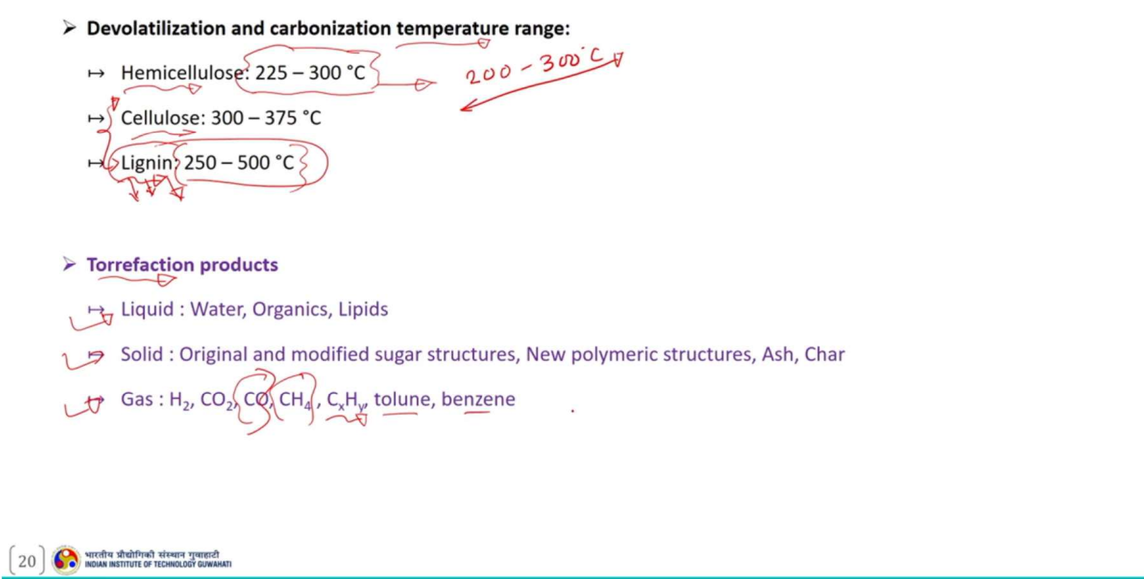

And this particular slide here, it represents the devolatilization and the carbonization temperature range of different constituents of the biomass. If you see here, the hemicellulose is devolatilization and the carbonization temperature range is mentioned as 225 to 300 °C, cellulose between 300 to 375 °C, and lignin between 250 to 500 °C. And if you recollect our discussion, the Torrefaction process is performed between 200 to 300 °C. So that most of the cellulose and the lignin can be retained in the solid product as lignin after softening act as a natural binder and which is useful during pelletization of the torrefied product.

And the main product which can be obtained during the Torrefaction process or after the Torrefaction process are liquid, solid and gaseous product. The liquid product includes water, organics and the lipids and the solid air includes the original and the modified sugar structures, new polymeric structure, ash and the char. And the gases include hydrogen, carbon dioxide, carbon monoxide, methane, and slightly higher hydrocarbon gases, toluene and benzene.

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Degree of Torrefaction

- The degree of torrefaction is the function of the reaction temperature (T) and the residence time of biomass subjected to torrefaction (t).

Degree of Torrefaction	Temperature range	Processes
Light torrefaction:	200-240 °C (or ~ 230 °C)	Only hemicellulose starts degrading. Lignin and cellulose are unaffected.
Medium torrefaction:	240-260 °C (or ~ 250 °C).	Cellulose is mildly affected.
Severe torrefaction:	260-300 °C (or ~ 275 °C)	Depolymerization of hemicellulose, cellulose, & lignin.

Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

Similar to that of the carbonization, the Torrefaction also divided into three main types. And that is termed as a degree of Torrefaction. And it is a function of reaction, temperature and the residence time of biomass which is subjected to the Torrefaction reaction. So, if you look at this particular table here, the degree of Torrefaction is categorized as light Torrefaction, medium Torrefaction and the severe Torrefaction process. In case of light Torrefaction process, the temperature ranges between 200 to 240 °C or you can say roughly about 300 °C. And in this process only hemicellulose starts degrading, lignin and cellulose remains unaffected during this particular light Torrefaction process. Whereas, in case of the medium Torrefaction, which is between 240 to 260 °C, the cellulose is mildly get affected in this particular temperature range.

Followed by the severe Torrefaction reaction. Now the temperature range in this severe Torrefaction has reached to up to 300 °C and you can say roughly about 275 °C. And in this step the complete depolymerization of the hemicellulose occurs, followed by the start of depolymerization of the cellulose and the lignin.

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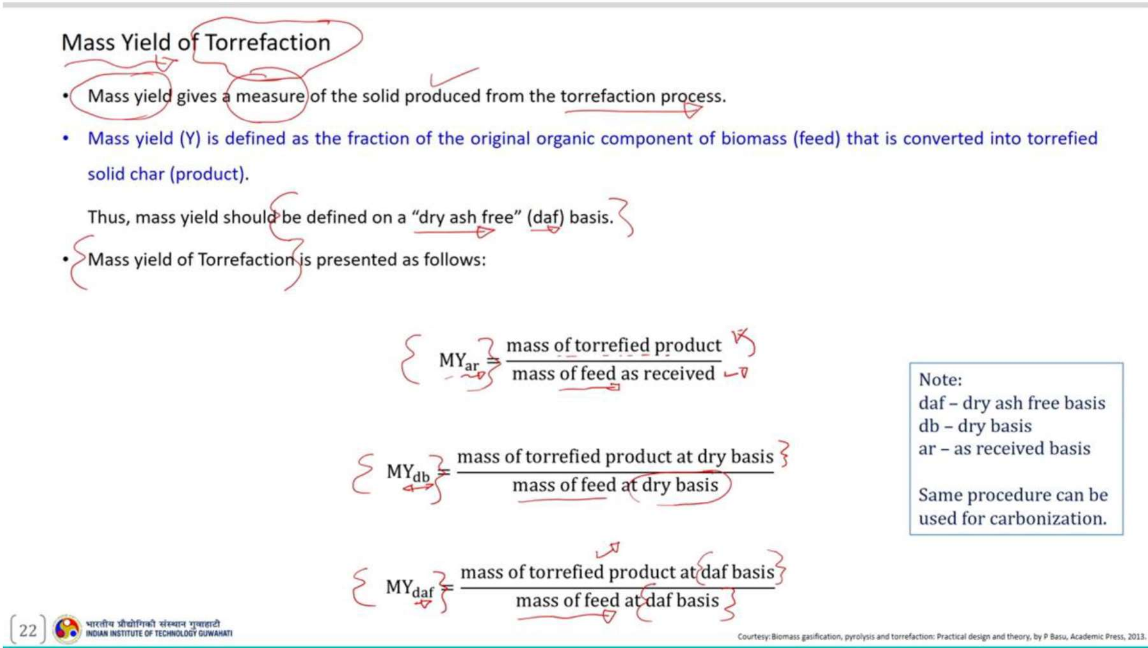

So, after understanding about the Torrefaction reaction, let us discuss about how to obtain the mass yield of the Torrefied product. So, the mass yield it gives an amount of solid product which is produced from the Torrefaction process here. That is the representation of the mass yield, because it gives the amount of solid product which is produced at the end of the Torrefaction process. And it is defined as the fraction of original organic component of biomass that is mass of the feed that is converted into a Torrefied solid char, that is a product. And this mass yield should be defined on the basis of dry ash free basis that is "daf". And this mass yield of Torrefaction process is presented in the following way. So, here it is represented in the form of mass yield as received basis right.

$$MY_{ar} = \frac{\text{mass of torrefied product}}{\text{mass of feed as received}}$$

$$MY_{db} = \frac{\text{mass of torrefied product at dry basis}}{\text{mass of feed at dry basis}}$$

$$MY_{daf} = \frac{\text{mass of torrefied product at daf basis}}{\text{mass of feed at daf basis}}$$

So, you are already familiarized with this particular term that is as received basis, dry basis, dry ash free basis. So, if we need to calculate the mass yield on as received basis, so it is simply a ratio of mass of the Torrefied product by mass of the feed as received. That means the mass of the biomass as received before undergoing any pre-processing stage. Whereas this particular mass yield it represents on the dry basis and it is the ratio of mass of the Torrefied product at dry basis divided by the mass of feed at dry basis. Similarly, this particular term, it represents the mass yield on dry and ash free basis. So, it is the ratio of mass of the Torrefied product at dry and ash free basis divided by the mass of the feed at dry and the ash free basis. So how to get this particular term, that is mass of feed at dry ash free basis, dry basis and the as received basis, we already discussed about this in one of the lectures in the previous module.

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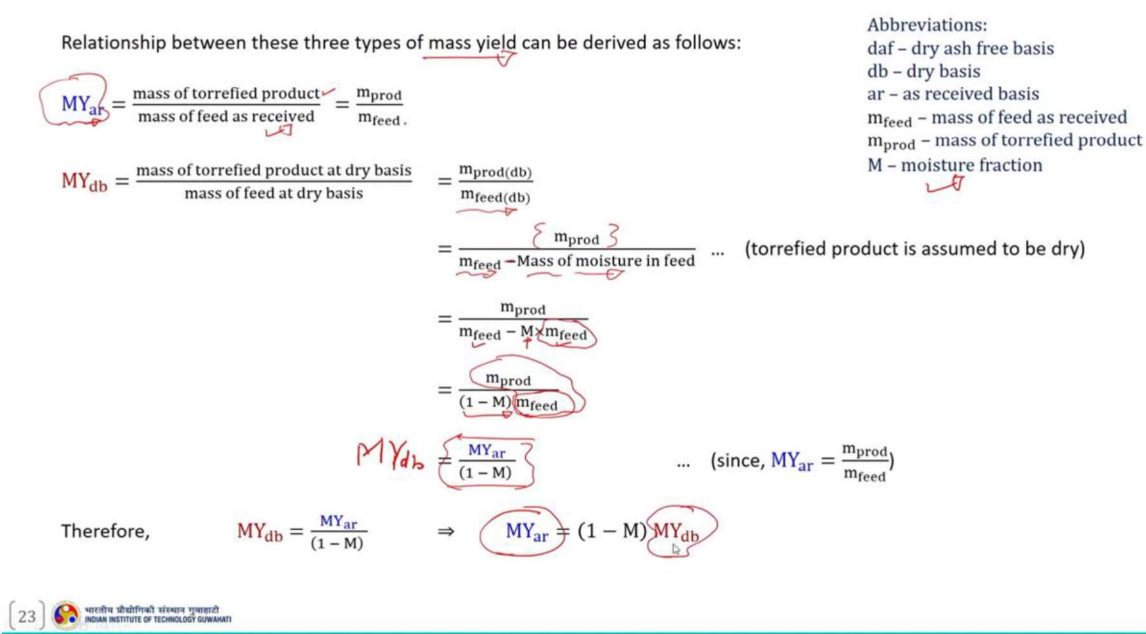

And if you just try to see, the relationship between these three types of mass yield then, it can be derived as follows.

$$MY_{ar} = \frac{\text{mass of torrefied product}}{\text{mass of feed as received}} = \frac{m_{prod}}{m_{feed}}$$

$$MY_{db} = \frac{\text{mass of torrefied product at dry basis}}{\text{mass of feed at dry basis}} = \frac{m_{prod(db)}}{m_{feed(db)}}$$

$$MY_{db} = \frac{m_{prod}}{m_{feed} - \text{Mass of moisture in feed}}$$

$$MY_{db} = \frac{m_{prod}}{m_{feed} - M \times m_{feed}}$$

Because the mass yield as received basis is represented as mass of the Torrefied product divided by the mass of feed as received basis. And we are representing it in the form of m_product and m_feed. Similarly, the mass yield on dry basis, it is represented in the form of mass of product on dry basis and mass of feed at dry basis. So, if you just expand this equation here, so mass of the product we know at the end of the Torrefaction process, the mass of the feed on the dry basis means mass of the feed minus mass of moisture in the feed. And we can represent it in the form of this capital M which indicates the moisture fraction in the feed material into the mass of the feed. So, it will give us the mass of moisture in the feed. And as these two terms are common, if you take these two common terms out, so we will get the equation in the form of 1 minus M. And this m_product by m_feed is represented as mass yield on as received basis. So, once you substitute this term here we will get the final equation in this form.

$$MY_{db} = \frac{m_{prod}}{(1 - M)\, m_{feed}}$$

$$MY_{db} = \frac{MY_{ar}}{(1 - M)}$$

And then this is mass yield on dry basis and this can be also correlated using this equation, that is mass yield on as received basis equal to 1 minus M into mass yield on dry basis.

$$MY_{ar} = (1 - M)\, MY_{db}$$

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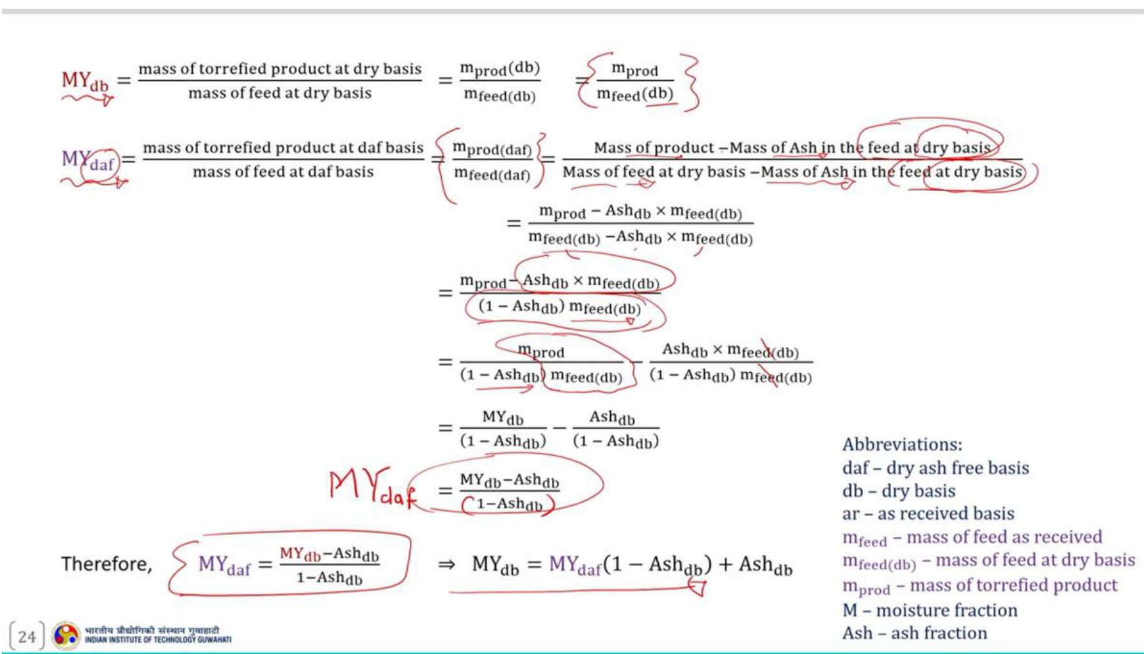

Similarly, these particular terms can be correlated with the mass yield on dry ash free basis. As we represented this equation in the form of mass of product by the mass of feed on dry basis here. Similarly, the mass yield on dry ash free basis can be represented in this form and this equation can be expanded in this particular way here. Because mass of the product on dry ash free basis, it can be represented in this form, that is mass of the product minus mass of ash in the feed at dry basis.

$$MY_{db} = \frac{\text{mass of torrefied product at dry basis}}{\text{mass of feed at dry basis}} = \frac{m_{prod}(db)}{m_{feed(db)}} = \frac{m_{prod}}{m_{feed}(db)}$$

Similarly, mass of the feed at dry basis minus mass of ash in the feed at dry basis. And this can be represented as ash dry basis into mass of the feed dry basis. Similarly, ash dry basis into mass of the feed dry basis. Because this is with respect to the feed. That is why we are represented in the form of the feed material here.

$$MY_{daf} = \frac{\text{mass of torrefied product at daf basis}}{\text{mass of feed at daf basis}} = \frac{m_{prod(daf)}}{m_{feed(daf)}}$$

$$MY_{daf} = \frac{\text{Mass of product} - \text{Mass of Ash in the feed at dry basis}}{\text{Mass of feed at dry basis} - \text{Mass of Ash in the feed at dry basis}}$$

$$MY_{daf} = \frac{m_{prod} - Ash_{db} \times m_{feed(db)}}{m_{feed(db)} - Ash_{db} \times m_{feed(db)}}$$

Now once you see this equation here, in this case these two terms are common. So, once you take out its common term equation will be in the form of 1 minus ash on dry basis. And just split this term here, that is m product divided by 1 minus ash on dry basis into this particular term and minus this term divided by this whole term here. So simply here these two terms will get cancelled out, will get the equation and if you remember, again this particular term here it represents the mass yield on the dry basis. After simplification of this term here, will get in the form of ash on dry basis divided by 1 minus ash dry basis. So, after combining this will get the equation in the form of mass yield on dry basis minus ash dry basis divided by 1 minus ash dry basis. And this term is equal to mass yield on dry ash free basis. Similarly, these two terms can be also correlated using this equation.

$$MY_{daf} = \frac{MY_{db} - Ash_{db}}{1 - Ash_{db}}$$

$$MY_{db} = MY_{daf}(1 - Ash_{db}) + Ash_{db}$$

So, once we know the mass yield on as received basis, we can calculate the mass yield on dry basis. And once you know the mass yield on dry basis we can easily calculate the mass yield on dry ash free basis of the torrefied product.

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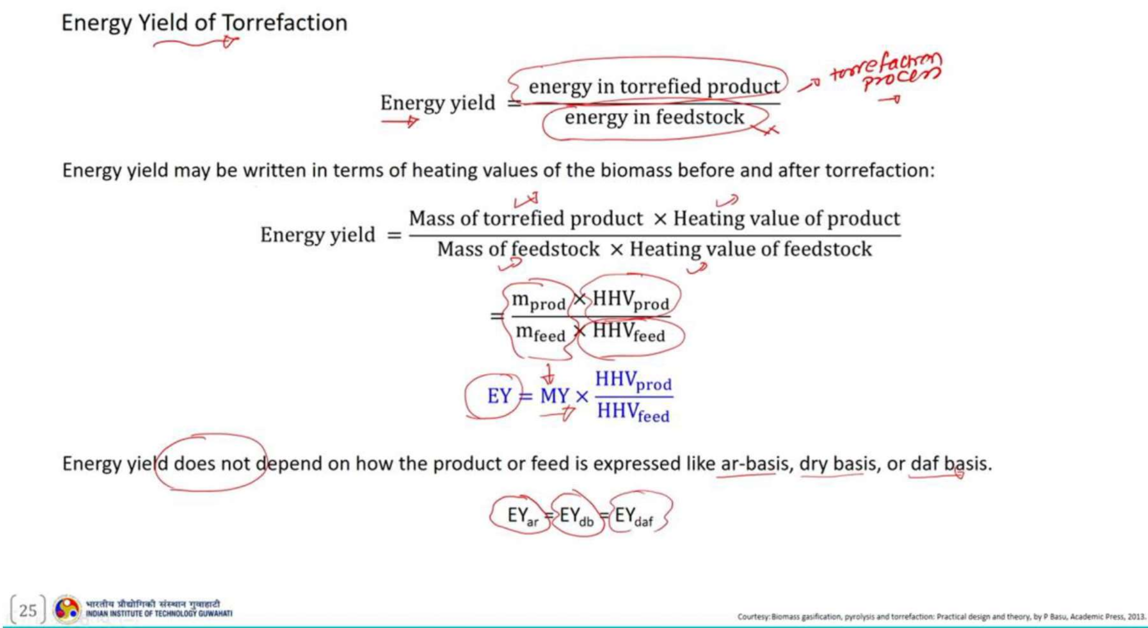

So, next important point in the torrefaction process is the energy yield of the torrefied product here. Because the energy yield here, it gives the fraction of original energy in the biomass retained after the torrefaction process. Because after torrefaction process energy rich components remain in the biomass but some energy lean components are lost. And this led to some loss in the overall energy content of the biomass. And this energy yield it defines this retention as such it is of great and practical importance, especially where the biomass is used for the energy conversion purpose. And this energy yield is defined as the ratio of energy in the torrefied product divided by the energy in the feedstock material.

$$\text{Energy yield} = \frac{\text{energy in torrefied product}}{\text{energy in feedstock}}$$

$$\text{Energy yield} = \frac{\text{Mass of torrefied product} \times \text{Heating value of product}}{\text{Mass of feedstock} \times \text{Heating value of feedstock}}$$

$$\text{EY} = \frac{\text{m}_{\text{prod}} \times \text{HHV}_{\text{prod}}}{\text{m}_{\text{feed}} \times \text{HHV}_{\text{feed}}}$$

$$\text{EY} = \text{MY} \times \frac{\text{HHV}_{\text{prod}}}{\text{HHV}_{\text{feed}}}$$

And this energy yield may be written in terms of the heating values of biomass before and after torrefaction reaction as well. That means the mass of torrefied product into its heating value gives the energy in the torrefied product. Similarly, the mass of the feedstock into its heating value gives the energy in the feedstock. And if you remember, this mass of the torrefied product can be represented as m product and this can be represented as a m feed. And this ratio is mass yield of the torrefied product. And this is the high rating value of the torrefied product. And this is the high rating value of the feed material. So that way, the energy yield ratio can also be correlated with the mass yield. However, this energy yield, it does not depend on how the product or the food is expressed, like as received basis, dry basis, or dry ash free basis. So that means the energy yield ratio on as received basis is equal to energy yield ratio on dry basis, equal to the energy yield ratio on dry and ash free basis.

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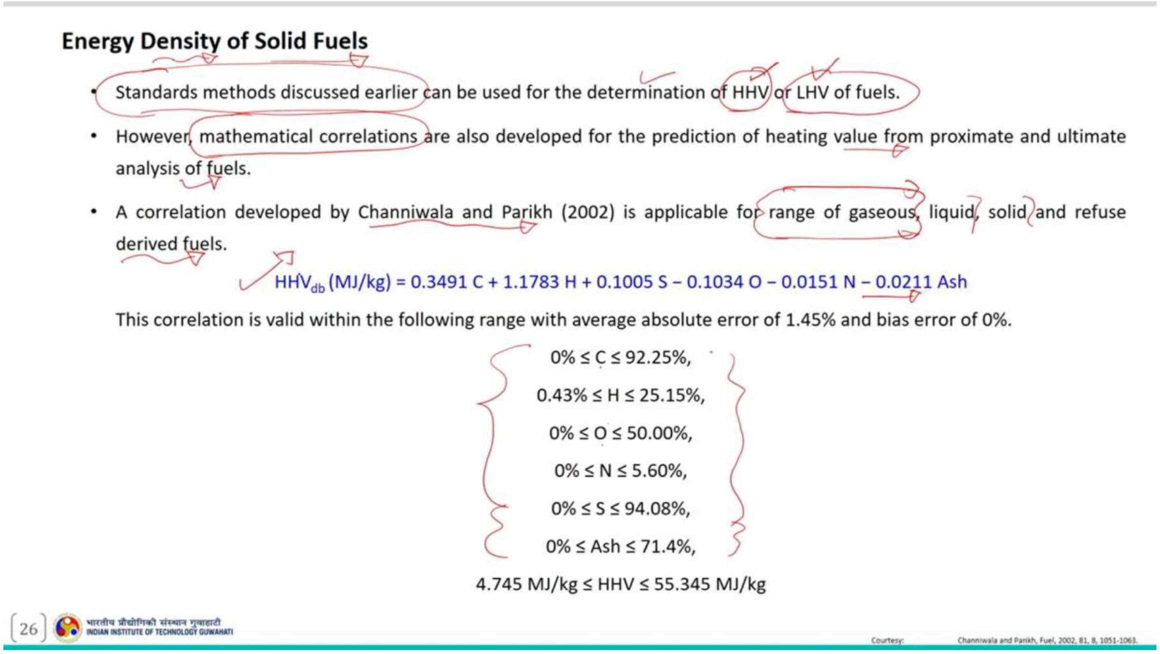

The next important topic in the thermochemical conversion process is the energy density of the produced solid fuels. And if you recollect we discussed this concept in one of the lectures, in the earlier module where we discuss about the standard methods which are available or can be used for the determination of high rating value or lower heating value of a fuels. However, some mathematical correlations are also developed for the prediction of heating value from proximate and the ultimate analysis of the fuel. And one such correlation which is developed by these two authors is applicable for range of gaseous, liquid, solid and the refuse derived fuel. And this is the equation which can be used for the determination of the fuels and the range of fuels which can be used for the estimation of this are mentioned here.

And this is the expression which can be used to estimate these values. However, this correlation is valid with a certain range with average absolute error or you can say the bias error. The list of components is given here along with their ranges and if it satisfies this particular range then this particular equation can be used to obtain the higher heating value on the dry basis.

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Comparison of Torrefied product with Wood, Carbonized Charcoal, and Coal

Parameter	Typical Wood	Torrefied Wood	Charcoal (Carbonization)	Bituminous Coal
Temperature (°C)		200–300	>300	
Moisture (%)(wb)	30-60	1–5	1–5	3–20
Volatile (%db)	70-80	55–65	10–12	28–45
FC (%db)	15-25	28–35	85-87	45–60
Mass yield		~80%	~30%	
Energy density (db)(MJ/kg)	~18	20–24	30–32	24–33
Volumetric energy density (GJ/m³)	~5.8	6.0–10.0	18.5–19.8	30–40
Apparent density (kg/m³)	350-680	300-500	600–640	1100–1350
Hydrophobicity	Hygroscopic	Hydrophobic	Hydrophobic	Hydrophobic

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Courtesy: Biomass gasification, pyrolysis and torrefaction: Practical design and theory, by P Basu, Academic Press, 2013.

This particular table here, it compares the torrefied product with wood, carbonized charcoal and coal sample. If you see here, the temperature range in the torrefaction process is between 200 to 300 °C. Whereas in case of carbonization it is more than 300 °C. The moisture is more or less same in the carbonized charcoal as well as the torrefied wood sample. But the volatile matter is relatively high in the torrefied wood compared to the charcoal. Similarly, the coal also has relatively higher amount of the volatile matter content but the native biomass has significantly high amount of the volatile matter content in its composition. The fixed carbon content is relatively low in the torrefied product but significantly high in the carbonized coal. Bituminous coal also has good amount of the fixed carbon content but the fixed carbon content in the native biomass feedstock is relatively less.

If you now compare the mass yield of the torrefied product and the carbonized product, so the mass yield here is significantly high. Because most of the volatiles are still remain in the material, because of that, the carbon content is more in the torrefied wood sample. Whereas in the carbonized sample here the mass yield is less because most of the volatiles are lost during the carbonization process. The energy density also it is quite good in case of torrefied wood but it is significantly high in case of charcoal and it is more or less compared to that of the coal. The charcoal and the coal value are more or less comparable at the upper end however in the lower end it is still good in case of the charcoal. Volumetric density it is quite high in case of the charcoal sample although the coal has significantly high volumetric energy density. But compared to the native biomass sample the charcoal has significant increase in the volumetric energy density. But the torrefied biomass, there is no such jump in the volumetric energy density value. And the remaining properties are more or less similar in case of the torrefied and the charcoal produced by the carbonization process.

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Comparing Carbonization and Torrefaction

Parameter	Torrefaction	Carbonization
Objective	Maximize energy and mass yields with reduction in (O/C) and (H/C) ratios.	Maximize Fixed Carbon and minimize Hydrocarbon content of the solid product.
Volatile matter	Retains most of material, driving away only the early volatilized low energy dense compounds and chemically bound moisture.	Drives away most of the volatiles, losing most of the mass.
Heating rate	Slow	Slow
Oxygen / air supply	Restricted / limited	Restricted / limited
Combustion	Avoided	Avoided
Temperature range	Narrow (200–300 °C)	Wide range (>300 – 900 °C)
Products	Less energy dense fuel than carbonization product.	More energy dense fuel than torrefaction, due to higher Fixed Carbon content.
Energy yield	Higher energy yield than carbonization.	Much lower energy yield due to the devolatization of most of the volatile matter.

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This last table, it compares the carbonization and the torrefaction process. Because the main objective of the torrefaction process is to maximize the energy and the mass yield with reduction in the O/C and the H/C ratio. Whereas the objective of the carbonization process is to maximize the fixed carbon content and minimize the hydrocarbon content in the solid product. Regarding the volatile matter torrefaction it retains most of the material driving away only the early volatilized low energy dense compounds and chemically bound moisture in the native biomass sample. Whereas in case of carbonization, it drives away most of the volatiles and losing most of the mass. And because of that, if you remember the mass yield in the carbonization is relatively low compared to that of the torrefied product.

The heating rate in both the cases is relatively slow heating rate is preferred in the carbonization as well as in the torrefaction process. Oxygen and the air supply, it is carried out in the restricted or the limited supply of oxygen. Or this process also tries to avoid oxygen as well as the combustion. Whereas in case of combustion it takes place at higher temperature but with certain oxygen deficient environment. Combustion it tries to avoid here also in the torrefaction process as I mentioned earlier. And same is the case in the carbonization process. Because then it will lose out most of the solid material. Temperature range is 200 to 300 °C here, but here there is a wide temperature range is used in the carbonization that is 300 to 900 °C. The product obtained from the torrefied product it is less energy dense fuel than the carbonization product. And here it is more energy dense fuel than the torrefaction due to the high fixed carbon content in the carbonized product.

Whereas the energy yield is higher in the torrefied product than the carbonized charcoal. And it is much lower energy yield obtained in the carbonized charcoal and that is due to the de-volatilization of the most of the volatile matter which is present in the feedstock material. So, this gives the details about the comparative analysis of the carbonization and the torrefaction process.

With this we will end our lecture here. In the next lecture we will practice few examples on the concept discussed in this module.

Thank you.