

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

Lecture - 26
Thermo-Chemical Conversion, Torrefaction and Combustion Processes

Good morning, everyone. Welcome to part 2 of the lecture 1 under module 8. So in this lecture, we will discuss about the thermo-chemical biomass conversion processes mainly to produce solid liquid and gaseous fuel.

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Module	Module name	Lecture	Content
08	Biocconversion of substrates into alcohol and Thermo-chemical conversion of biomass to solid, liquid and gaseous fuels	01 (Part II)	Thermo Chemical Conversion of Biomass to Solid, Liquid and Gaseous Fuels

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- Number of technological options are available to make use of a wide variety of biomass types as a renewable energy source to produce suitable product.
- Conversion technologies may release the energy directly, in the form of heat or electricity, or may convert it to another form, such as liquid biofuel or combustible gas.
- Depending on its source, these processes include: combustion, pyrolysis, gasification, liquefaction, torrefaction.
- *Thermo-chemical processes* convert biomass into higher-value or more convenient products.
 - ✓ The process releases a gas (~6 MJ/kg), a liquid (~17-22 MJ/kg) and/or a char (~18 MJ/kg), and depending on the technology one of these is the final product.

So, now, if you look at this particular slide here, there are a number of technological options are available to make use of this wide variety of the biomass types as a feedstock or renewable energy resource for the production of the fuels or chemical. The conversion technologies, if you see here, it may release the energy directly in the form of heat or electricity or it may convert the produced product in the form of either liquid or the combustible gas.

So, there are, options are available in this particular technology either to produce solid as a fuel, maybe liquid as a fuel or gaseous fuel, which is a combustible gas as well. So, depending on the source, the processes include here are combustion process, pyrolysis, gasification and liquefaction. Apart from that to produce the solid fuel also, one can use the torrefaction also as a process to convert the residual biomass into a solid field that is also called as a carbonised field.

And there is a slight difference between these 2 processes as well that is a torrefaction in the carbonization that we will discuss in the subsequent slide. So, depending on the composition of the material, which is available for the conversion purpose, for example, the carbonaceous material like a biomass, it can be converted into a convenient and the useful product.

And the process of conversion of this particular material into a suitable product is mainly depends on the severity of the process condition. That means the temperature range which has been used for the conversion of this biomass into a fuel. Apart from that the level of the oxygen

also during this process, it has a huge impact on the conversion of the residual biomass or we can say a biomass into a fuel that is either a solid liquid or the gas.

Why it is so? Because the thermo-chemical conversion of the biomass, it tends to shift the biomass component into a different material in the form of carbon, hydrogen and oxygen. If you just take a simple example of here the slow pyrolysis process, it maximise the conversion of the raw material that is the biomass as a feedstock to a solid char as a product. Whereas, in case of the fast pyrolysis or you can say the rapid pyrolysis process, it mainly produce hydrocarbon as a product.

So, there is a difference because of just slight change in the severity of the process condition or just by changing slightly the operating condition and then it can lead to a different kind of product as well. Similarly, the oxidation of the feedstock can produce combustible gas as a product just by converting the process condition and just supplying the excess oxygen to the system, it oxidises the feedstock to produce the gas and the mixture of this particular gas is say CO₂, H₂O and along with that it also releases significant amount of the heat.

So, this slight deviation in the process condition as well as the severity of the process condition, it leads to a different kinds of the product during the processing of the thermo-chemical conversion of the biomass. Similarly, the hydro gasification of the feedstock or the feed material, it tends to produce the gas with enrich hydrogen content. That means it can enrich the hydrocarbon ratio in the output of the product gas.

So, this is how the change in the product happens with a slight deviation in the process condition as well as the oxygen supply. Now, based on the thermo-chemical conversion processes, as we have just discussed, the conversion of biomass into higher value or more convenient product, it depends on the process condition either you can consider the combustion as a process for the conversion purpose, gasification or maybe the pyrolysis process as well.

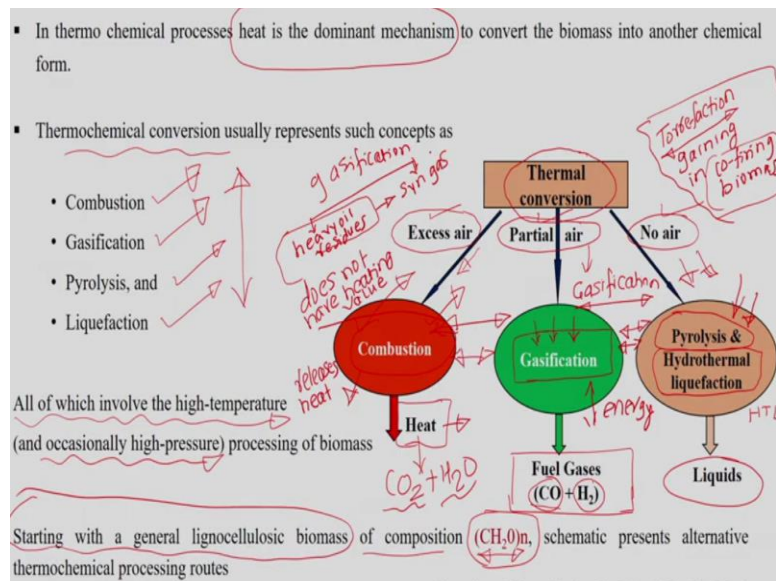
And this particular processes, it releases a gas which has the heating value of this, this is not a fixed value, it also vary between like 4 to 6 mega joule per kg and also produced a liquid with

the heating value of 17 to 20 mega joule. And this variation is mainly because of the carbonaceous content in the feedstock that is a raw biomass. And also produces a char, which also has a value 18 mega joule per kg.

It also varies between 16 to 18 mega joule per kg also in case of this thermo-chemical conversion processes, when the solid carbon is obtained as a product. And depending on the technology used, one of these is the final product. And that is what I just discussed, that just based on the severity of the process condition as well as the technology which is used, it all depends on the supply of the oxygen during the process.

And based on that, this particular concept of the thermo-chemical conversion procedures can be defined. And once you restrict the supply of oxygen or if you increase the supply of oxygen, one of these is the final product of this particular processes.

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So, based on the thermo-chemical conversion processes, if you look at the thermo-chemical processes and its conversion pattern, so heat is the dominant mechanism in the thermo-chemical conversion of biomass to a convenient product. And the thermo-chemical conversion processes, it usually represents such concept in the form of following processes like combustion, gasification, pyrolysis and liquefaction processes. So, this is how we can represent the thermo-chemical processes in the following way.

And all of these particular processes, it involves high temperature and as a result, the terminology itself you understand here the thermo-chemical processes that means thermal is nothing but the heat which is required for the production of the chemical. So, either the chemical or the fuel is a convenient product which can be obtained by the conversion of biomass using the thermo-chemical conversion processes.

And occasionally, it may require the high pressure processing of the biomass as well. It all depends on again the technology which is being used for the conversion purpose. So, if you just look at this simple chart, which is shown here, this talks about the thermal conversion of the biomass. So, in this case, we have specifically mentioned here the supply of the excess air then this is the supply of the partial air during the process and there is no air which is required for the conversion purpose.

Now, if you talk about the excess supply of air during the thermo-chemical conversion processes, then this particular concept is represented as a commercial process where the excess air or the oxidising agent is used for the oxidation reaction to happen and then it produces some gas that is in the form of CO₂, H₂O and some traces of other gases as well, along with the significant amount of the heat as the product.

As the result if you see here, it is represented as a heat as the product. Whereas, in case of the partial supply of the oxygen or the oxidising agent, in this case, what happens is like the feedstock material, it undergoes the partial oxidation and this particular process is represented as a gasification process. So, the concept of this particular process is based on the gasification of the raw material to produce the gas.

And that is the reason here the product obtained is the fuel gas in the form of H₂ and CO because, this particular process is carried out in the partial oxygen supply that is the externally supplied oxidising agent, but it is a partially supplied oxidising agent in the reaction and hence, as a result it produces CO as a gas, not as a CO₂. Whereas, in this case, it produces CO₂ plus H₂O as a gas along with a significant amount of it.

Although it also produces some traces of other gases as well, but its composition is in the trace amount. That is why these are considered as the major gases which are evolved during the combustion process. And another class of the conversion process which is discussed here. It is based on the no air supply concept means here the no air is supplied during the conversion process and there is no externally supplied oxidising agent is also used in this particular process.

And this particular process is termed as a pyrolysis process as well as the hydrothermal liquefaction process. It is also based on the type of the product which needs to be obtained during this particular process. That is why some time it is represented as a pyrolysis process or the liquefaction process. And there is one more concept which is gaining importance in this particular conversion technology is nothing but a hydrothermal liquefaction which is abbreviated as sometimes HTL, that is hydrothermal liquefaction of the biomass.

So, in this case, if you see, the product obtained is mainly the liquid. So, if you compare the pyrolysis process, the product of the pyrolysis process are mainly the liquid as a product, solid carbon as a residue and the gaseous product. So, once we try to restrict this particular product mainly to a liquid, then sometimes pyrolysis process is also represented as a liquefaction process. So, it all depends on the quality or the type of the product need to be produced during this conversion processes.

So, starting with the general lignocellulosic biomass of composition, which is shown here, once schematic has been prepared here just to understand the concept of the conversion of this lignocellulosic biomass to wide range of the product either fuel or the chemical. So, before we discuss in detail about that particular schematic, let us try to understand these 3 concepts as well as the solid production from the thermo-chemical conversion process very detailed.

So, before that let us discuss about this concept in detail. So, if you talk about the gasification as I mentioned the gasification process here. So, gasification is a chemical process that converts the carbonaceous material like type of the biomass into a convenient useful gas as a product or also

it can be converted into chemical feedstock as a product or it can also be converted into a value added chemical.

So, if we just compare this particular gasification process with the combustion process, so, combustion process also it converts carbonaceous material and it produce gas as the product. However, there is a slight or important difference between these 2 processes that is the gasification and the combustion process. Whatever in case of the combustion processes, the product gas obtained from the combustion processes, it does not have the heating value. Whereas, the gas produced from the gasification process, it does have the heating value.

So, this is a small difference between the gasification and the combustion process and which is very much important to understand that what is the exact difference between these 2 processes. And in case of the gasification what happens, it packs the energy in the form of chemical bond in the product gas. Whereas, in combustion process, it releases this particular energy. Moreover, the gasification process, it carried out in the reduced environment as I already discussed.

This particular process, it requires the reduced environment to convert into the suitable product and it requires energy during the process. Whereas, if you talk about the combustion process, it oxidises the material and it releases the heat. It releases the heat during the conversion process and this is what is the difference between these 2 processes. So, if you try to compare the gasification and the combustion process as well.

So, these are the important difference which need to be taken into consideration while selecting the biomass and by taking into account the concept of this particular technology to produce the suitable product. Now, the gasification and the pyrolysis processes, these are not only the processes to produce the energy. Apart from that the production of the chemical or the convenient product, it also the important aspect of this particular processes.

So, if you try to now understand the difference between the gasification and pyrolysis process, so, these particular processes these are not only restricted to just produce the energy, but these are also used to produce the convenient chemical out of valuable chemical from the resources.

That is the biomass resources, either it can be a MSW or rather it can be a lignocellulosic biomass.

So, gasification process nowadays is not only limited to you even in the solid feedstock, apart from the solid feedstock this particular process, it also handles the liquid as a feedstock. Apart from that, even it handles the gaseous feedstock to convert it into a convenient or high density fuel. For example, the partial oxidation of the methane to produce the gas is another example of the gasification of the gaseous to a high quality fuel.

So, during the partial oxidation of the methane as a gas, it releases the certain amount of synthetic gas in the form of H_2 and CO. And this is the very widely known example of the gasification of the methane to produce the gas. And hence, because of that, this particular process are widely being used even known for the conversion of gas into a high value fuel or as well as the given chemical using this particular technology.

Now, if you talk about another example of the thermo-chemical conversion processes as I mentioned, so, torrefaction is another example of the thermo-chemical conversion processes which is called as a torrefaction process and this is also gaining prominence due to its attractive use in co-firing biomass in the existing co-fired power station and this is the one of the best example of the solid fuel from the biomass.

So, the torrefaction is also one of the process which converts residual biomass into a high carbon containing solid fuel. So, it find its use in co-firing of the biomass in the existing co-fired power station as well. Apart from that, the pyrolysis also is one of the pioneering technique behind the conversion of transportable fuel in the form of clean fuel under biomass. Apart from that, this process also being used for the conversion of the biomass into liquid and gaseous field.

But the gaseous field which is obtained from the pyrolysis process is a low molecular rate and low heating value gas which can be obtained from the pyrolysis process that is what is the difference of the pyrolysis process again here and the gasification process. So, likewise, this particular processes are having slight difference based on the oxygen supply which is being used

during the conversion process and accordingly, it can lead to a suitable or the convenient product at the end of the process.

Apart from that, this particular gasification process is also used to convert heavy oil residues into syngas and this is another good example. And this particular process also is gaining much importance nowadays, because of the conversion of the heavy oil residues into syngas. And there are a number of technologies which have been dedicated for the conversion of this particular coal as a feedstock into a chemical.

Apart from that, some other hydrocarbons are also being used for this conversion purposes, but mainly the process is the gasification process, which can convert the coal or other hydrocarbon into a suitable or convenient chemical. Apart from that, the hydro gasification of the feed material to produce gas with higher hydrogen to carbon ratio is also gaining more popularity. In this particular process, the steam is used as a gasifying medium.

As a result, it adds hydrogen to the feedstock to produce the gas with higher hydrogen to carbon ratio and that is what is the advantage of this particular processes. Now, instead of using oxygen or the air as the oxidising agent, steam also can be used, so that it can add up hydrogen to the feedstock. So, that the product is also having the higher hydrogen to carbon ratio. And this is what is the advantage of the hydro gasification process as well.

Apart from that, supercritical water gasification is also gaining popularity nowadays. The main advantage of this supercritical water distribution process is, it utilises even though biomass as a feedstock, because the supercritical water gasification process in this particular process, the water slurry is used as a feedstock. So, the biomass needs to be converted into a slurry first and then need to be gasified using this particular technique, that is called a subcritical or the supercritical water gasification technique.

Even the yield of the oil obtained from this particular process is relatively less than the pyrolysis process, but the quality of the oil obtained in this particular process is superior than that of the pyrolysis process. So, this is how this particular process differs from each other depends on the

supply of the oxygen level as well as the severity of the process condition which are used during the transformation of the biomass using thermo-chemical processes.

So, now, let us discuss in detail about the conversion pathway of these thermal-chemical conversion processes using biomass as a feedstock.

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Thermo chemical conversion processes

The following schematic represents the thermochemical conversion of biomass to other, more useful products.

- Thermal conversion technologies are robust, and they efficiently convert a wide range of biomass feedstocks
 - ✓ Addresses seasonal and regional variability issues
 - ✓ Utilizes the entire biomass feedstock
- Thermal conversion provides range of fuel opportunities
 - ✓ Ethanol, mixed alcohols, oxygenates
 - ✓ Hydrocarbons including gasoline, diesel.

So, before that, if you just try to understand the thermo-chemical conversion technologies and their pathways, so, as I mentioned, these particular processes are very robust and they efficiently convert wide range of biomass to a suitable product. So, these particular processes, it address the seasonal and the regional variation in the biomass. So, this particular processes it can handle biomass of any form.

Apart from that it utilises the entire biomass as a feedstock. To understand this concept of utilisation of the whole biomass as a feedstock, just try to take the simple example of the corn plant. So, in the corn plant, only the corn kernel is used during the biochemical conversion of the material into the ethanol. And remaining part of the plant that is called as a corn stover, corn stock, leaves as well as the roots of the plant are not getting utilised for the conversion purpose.

Whereas in case of thermo-chemical conversion processes, the entire plant part can be utilised effectively to convert into the convenient product or the chemical. Moreover, that bio-chemical

conversion process, as we already mentioned, it is a well established and commercially used processes. As a result, the process conversion pathway of this particular process is very defined. However, because of the batch operation of the biochemical conversion processes, it requires order of magnitude of time compared to the thermo-chemical processes.

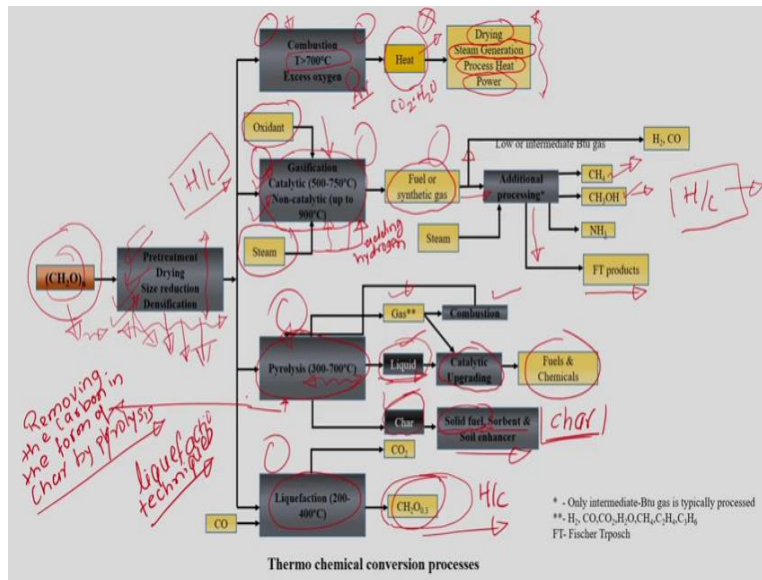
Whereas, the thermo-chemical process, it can convert the feedstock into the product in a lesser span of time compared to the biochemical conversion processes. And this is also one of the major advantage of the thermo-chemical conversion processes. Moreover, the thermo-chemical conversion processes typically have high throughput and in principle, can operate on any biomass form.

It is not necessary that it cannot be only a herbaceous plant, it is not only the dry material, even the MSW also can be handle effectively in the thermo-chemical conversion processes. Whereas, this may not be possible in the other biochemical processes to convert into a suitable product and the utilisation of such variability of the biomass, it also gives high process efficiency just by tuning the small properties before processing into the thermo-chemical conversion processes. So, this is all about the conversion of biomass using the thermo-chemical conversion processes.

And moreover, if you see here, the thermo-chemical process, it is not specific to a single one, it can also provide the wide range of the fuel opportunities in the form of say, ethanol. It can also provide the mixed alcohol and oxygenates, that is also possible in this case. Apart from that, the hydrocarbon including the gasoline and the diesel, the diesel here is nothing but is a green diesel, is not only a diesel, it is a green diesel, which can also be obtained using the thermo-chemical conversion of the biomass.

So, now, after understanding this small difference of the thermo-chemical conversion process as well as the biochemical conversion processes, let us discuss this particular schematic in more detail.

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Now, here if you see, these represent in general the lignocellulosic biomass and its composition. So, this particular biomass which is obtained, it needs to pass through a certain pre-processing stage and we have discussed this particular pattern of pre-processing of the biomass in detail in the one of the lectures also, if you remember. And this particular pre-processing stage, it includes either the pretreatment of the biomass, drying of the biomass, size reduction and the densification of the biomass.

Because this particular pre-processing of the biomass, it depends on the feedstock specification on the conversion system. So, just to understand the example of the feedstock specification on the conversion system, let us talk about the densification of the biomass first. So, biomass as it is an energy in fuel, so, this needs to be converted into a improved higher density material that is called as a densification process.

So, in the densification, the biomass is densified to increase its energy density and this is considered as a preferred feedstock for the combustion process as well as for the gasification process. So, this is a pre-processing stage which is required before utilising this particular material for the combustion and the gasification. Although it is not necessary, even the (()) (23:08) material can also be utilised for the combustion and gasification process.

But, to achieve the high process efficiency, it is better to densify the biomass first and then subject to either of this convergence system to get high process efficiency in the form of high heat output as well as higher convenient fuel output from the product. So, just talk about the combustion process first. In the process of combustion of the biomass, the temperature here is above 700 degrees C and it requires excess oxygen or air as a medium for the oxidation of the feedstock to produce the product.

And the product obtained from this process is a significant amount of it along with the CO₂ and H₂O as a gas as I already mentioned in the previous slide. So, these are the 2 gases which can be obtained from this particular process. And along with that, it also releases significant amount of the heat. So, the heat release from this particular process can be utilised for the drying purpose.

It can be also utilised for the steam generation and can be used as a process it in the manufacturing plant and can be subsequently converted into also in the power, that is the electricity. So, the heat produced from the combustion process as even the number of application here if you can see. Similarly, if you talk about the gasification process here, so, the gasification of the dried biomass or the densified biomass can be carried out using the catalytic gasification or the non-catalytic gasification process.

Whereas, in case of catalytic gasification procedure if you see here, the temperature requirement is little lower than that of the non-catalytic gasification process. And that is obvious because the catalyst is being used in the conversion system. So, as a result, it will lower the temperature requirement of the gasification process and the product obtained is in the form of the syngas or is also called as a fuel gas.

This particular gas which is obtained from the gasification process can be directly used as a heat source or further can be converted using the additional processing stages to produce either the methane or methanol. Apart from that the produced syngas can be used for the FT product synthesis as well. This particular gasification process can be carried out using oxidising agent

either in the form of air or the oxygen and can also be carried out using steam as a gasifying agent in the process.

But, the utilisation of steam as a gasifying agent as I mentioned earlier, it has also some advantages if you utilise the steam or the hydrogen as a gasifying agent in the gasification system compared to the use of oxidising agent as a gasifying agent in the gasifier. If you see the hydrocarbon ratio in the feedstock, which is used here, it almost get double when the feedstock that is a biomass is getting converted into methane and methanol.

Similarly, the hydrocarbon ratio, which almost remains unchanged, when the biomass is getting liquefied (()) (26:24) catalytic liquefaction technique and the hydrocarbon ratio of the product obtained from this particular technology, it remains unchanged. So, this can be evident from the composition of the product which is obtained from the conversion of the biomass using the liquefaction technique.

Similarly, as I mentioned, the hydrocarbon ratio in the gasification product also can be increased just by using steam as a oxidising agent, that is nothing but called as a by adding hydrogen into the gasification system in the form of steam and it can lead to increase in the hydrocarbon ratio. Similarly, by removing the carbon in the form of char by pyrolysis process, so, by removing the char from the pyrolysis process, it also can increase the hydrocarbon ratio of the fuel or the chemical which is obtained from the pyrolysis of the biomass.

So, this is how this particular variation in the hydrocarbon ratio can also be visualised here just by converting the suitable biomass into a convenient useful product. Now, one process which I mentioned here is again the pyrolysis process. So, the pyrolysis process also can convert the biomass into either the gas as a product liquid and solid char as a product. So, it all depends on the kind of product need to be converted in this particular process, this particular process also can be represented accordingly.

For example, if the option is to produce only the liquid as a product, then the pyrolysis process is regarded as a liquefaction process. So, in case of pyrolysis is where the temperature ranges varies

between the 300 to 700 degree C, it leads to the production of the gas and the gas produced during this process can also be combusted and can be provided as a heat which is required for the process itself. So, it can be recycled back into the same pyrolysis chamber, so that it can provided as a heat which is required for the pyrolysis process as well.

Apart from that, it also leads to a liquid as a product which can further be upgraded using a catalytic upgradation technique which is shown here to produce either fuel or chemicals as a product. This particular example we also discussed in the previous lecture, using (()) (29:12) technique, one can convert the bio-oil which is of low quality into a high quality fuel. Apart from that, it can be also converted into a suitable valuable chemical.

So, these all talks about the type of product, which can be obtained using the pyrolysis process. Apart from that, the pyrolysis process also can lead to a carbonaceous solid residue as a char. So, this particular solid fuel which is obtained from the pyrolysis process, it can also be used as a sorbent or soil enhancer. So, it also has a number of application.

So, the solid char which is obtained from the pyrolysis process, it can also be utilised as a solid fuel by converting into again the (()) (29:57) by the (()) (29:57) technique or can be densifying the solid char which is obtained from the pyrolysis process and can also be act as a fuel which is replacement of the fossil fuel that is the coal. And then it also act as a soil enhancer and conditioner because of the nutritional properties of this particular char.

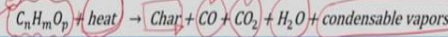
So, these all use the information about the thermo-chemical conversion pathway of the biomass to a suitable product. So, now after understanding this thermo-chemical conversion pathway of the biomass, now, let us discuss about this particular techniques and the reaction involved in this particular technique one by one.

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A brief description of reactions that take place in different thermal conversion processes of biomass are as follows

1. Torrefaction:

It is a process of production of carbon-rich solid fuels from biomass. So, gas and liquid parts of the conversion do not form a part of the product. Torrefaction has some similarity with the process of carbonization, but there are some important differences as mentioned below.



Torrefaction	Carbonization
Torrefaction retains most of it, driving away only the early volatilized low energy dense compounds & chemically bound moistures	Carbonization drives away most of the volatiles
The torrefaction process on the other hand tries to avoid oxygen as well as combustion	Carbonization takes place at higher temperatures with a certain level of oxygen that allows sufficient combustion to supply the heat for the process
Torrefaction is a thermal decomposition that takes place at low temperature & within a narrow temperature range of 200 to 300 C	<ul style="list-style-type: none"> Carbonization is a high temperature (300 to 600 °C) destructive distillation process Carbonization produces more energy dense fuel than torrefaction, but it has a much lower energy yield

So, let us first discuss about the torrefaction process. It is a process of production of the carbon rich solid fuel from the biomass. So, the gas and the liquid parts of the conversion processes do not consider as a part of the product. Apart from that this particular torrefaction process also has a similarity with that of the carbonization process. And there is a some important difference between these 2 processes as well.

And this torrefaction process is represented by this reaction. So, this is a general formula for the representation of the biomass. This particular biomass with some amount of heat is torrified to produce the char as a solid product. Along with that it also produce the CO, CO 2 and H 2 O as a product along with some condensable vapour that is also we term it here as a liquid product and that is what is the important difference between the torrefaction and the carbonization process here.

If you just try to compare the difference between the torrefaction and the carbonization process, in case of torrefaction process, it returns most of the volatile and driving away only the early volatilized low energy dense compound and the bound moisture which is present in the biomass. Whereas, in case of carbonization process, it drives away most of the volatiles which are present in the biomass. This is a small and very effective difference between the torrefaction and the carbonization process.

In case of torrefaction and the carbonization, in carbonization, the process is carried out at higher temperature with certain amount of level of the oxygen and as a result, it allows sufficient combustion to takes place during the process and it provides the energy which is required for this particular system as well. Whereas, in case of torrefaction if you see here, this particular process on the other hand, it tries to avoid the supply of the oxygen as well as the combustion process during the conversion of biomass into a char.

Apart from that the torrefaction process, it is the thermal decomposition of the biomass, which takes place at low temperature even and within a very narrow temperature range which is just 200 to 300 degree C. Whereas, in case of carbonization process, if you see here, the process is carried out in the high temperature range that is 300 to 600 degree Celsius. And this is regarded as a destructive distillation process as well.

And the carbonization process it produces more energy dense field than the torrefaction but it has much lower energy yield than that of the torrefaction process. So, this is one of the important difference between the torrefaction and the carbonization process, because of the utilisation of the oxygen level during the process, although it produces more energy dense fuel than that of the torrefied product.

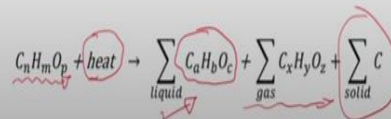
But the produced product, it has much lower energy yield than that of the torrefied product and because of that this particular process is gaining more prominence due to its attractive use of co-firing of biomass in the co-fired power station as well.

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2. Pyrolysis:

Pyrolysis is the thermal conversion of biomass at temperatures typically below 600 °C in the complete absence of oxygen to produce higher-energy density materials, including solid carbon as char, bio-oil, and gaseous products (CO, CO₂).

Pyrolysis works as the core reaction of thermal conversion processes since the irreversible degradation of the biomass (heavier hydrocarbon molecules into smaller hydrocarbon molecules) starts at temperatures of about 150–200 °C in the absence of O₂.



So, the another process which is effectively convert the solid fuel that is solid biomass into a convenient useful product is the pyrolysis process. So, in case of pyrolysis, it is the thermal conversion of biomass at typically higher temperature, but below 600 degree Celsius and the entire process is carried out in complete absence of oxygen. So that, it produces higher energy density material including solid carbon as a char, also it produces liquid and gaseous product during the pyrolysis process.

So, the pyrolysis process, it also works as the core of the thermal degradation of the biomass to produce the product. Since, the irreversible degradation of the biomass starts at a temperature range between 150 to 200 degrees C and in total absence of oxygen. So, because of that, it converts the higher hydrocarbon molecules into a low molecular weight compounds and can be effectively converted into either the liquid solid or the gaseous product as well.

So, the representative reaction of the pyrolysis of the biomass if you see here, these again represent the biomass composition and under thermal degradation of this particular biomass, it leads to a liquid as a product, it is represented in this particular form here, then the gas as a product and also provides solid char as a product at the end of the process. So, this is how is the difference of the pyrolysis process with the other thermochemical conversion process.

But, this particular process is considered as a core of thermo-chemical processes, because it allows the degradation of the material and start the degradation of the material at a temperature between 150 to 200 degree Celsius.

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3. Combustion:

Combustion is the oldest method of thermal conversion of biomass, which accounts for almost 97% of the world's bioenergy production (Demirbas et al. 2009).

In this process, the feedstock is subjected to high temperatures (typically above 700 °C) with an excess amount of air to produce gaseous products consisting mainly of CO₂, H₂O, N₂, and heat.

When 1 mol of carbon is burnt completely in adequate air or oxygen, it produces ~ 394 kJ heat and CO₂.

To explain the conversion process, consider the carbon as the feedstock and write the chemical reaction of the process as:

$$C + O_2 \rightarrow CO_2 + 393.77 \text{ kJ/mol of carbon}$$

+Q kJ/mol of the reaction equations implies that heat is absorbed in the reaction.
- Q kJ/mol indicates that heat is released in the reaction.

Now, let us discuss about the another important process in the thermo-chemical conversion pathway is the combustion process. So, the combustion process is the oldest method of thermo-chemical conversion of the biomass, which accounts for almost 97% of the world's bioenergy production. That is the reason I mentioned this is one of the technology which is commercially being used for the conversion of the biomass to a energy.

Although in this particular processes, instead of using the raw biomass as in the residual form, it can be converted into a first denser pellet or can be dried and then can be combusted to produce significant amount of the heat and as a result, it can also achieve the high process efficiency and the process heat obtained during this particular process can be used as a processed in the manufacturing plant or also can be converted into the electricity and that is why it is contributed to around 97% of the world's bioenergy production as well.

And this is the only technology which has significantly contributed to the energy production and that to the bioenergy production. In this process, the feedstock is subjected to a high temperature which is more than even 700 degrees C and also it goes up to around like 1200 degrees C as well

with an excess amount of air to produce gaseous product consisting mainly of CO₂, H₂O and significant amount of the heat.

So, for the representation purpose, just take the simple example of the conversion of carbon using a oxidising agent that is air or the oxygen. So, once the CO is getting oxidised in the combustion chamber with the adequate air or the oxygen as a supply, then it produces CO₂ as a main gas, along with that it also produces significant amount of heat per mole of the carbon. So, in this case, the plus Q in the reaction equation implies that the heat is absorbed in the reaction.

Whereas if it is a minus, then it implies that the heat is released during the reaction and that is what is the oxidation of the biomass reaction is which involves significant amount of energy during the oxidation of the biomass. Now, let us discuss about the another conversion pathway of the biomass that is gasification.

(Refer Slide Time: 38:11)

4. Gasification of carbon:

In restricted oxygen supply, carbon can be gasified into carbon monoxide. The carbon then produces 72% less heat than it would have in complete combustion, but the partial gasification reaction as shown below produces a combustible gas, CO

$$C + \frac{1}{2}O_2 \rightarrow CO \quad -110.53 \text{ kJ/mol of carbon}$$

The product of above reaction (gasification), CO, when burnt subsequently in adequate oxygen, then it releases the remaining 72% (283 kJ) of the heat. Thus, the CO retains only 72% of the energy of the carbon.

Apart from that, for complete gasification of a biomass the energy recovery is 75 to 88% due to the presence of hydrogen and other hydrocarbons.

The producer gas reaction is an example of gasification reaction, which produces H₂ and CO from carbon. This product gas mixture is also known as synthesis gas or syngas.

$$C + H_2O \rightarrow CO + H_2 \quad (131.00 \text{ kJ/mol})$$

* Gasification of biomass and hydrocarbons, in: P. Rao, 2nd Edition, 2013, Nelson & C^o

So, the gasification, it is carried out in the restricted oxygen supply and it also converts the carbonaceous material and gasifier into a carbon monoxide. Because the entire procedure is carried out in the restricted supply of the oxygen. As a result, it is not allowing the complete oxidation of the carbonaceous material in the gasifier. As a result, it only yield gaseous product in the form of carbon monoxide.

And the carbon then produces around 72% less yield than it would have in complete combustion process, but the partial gasification of the carbonaceous material, it leads to a combustible gas that is called as a CO. And along with that, it also releases significant amount of the energy during the partial combustion of the carbonaceous material in the gasifier.

And the produced gas as this is a combustible gas, this product of the above reaction that is the carbon monoxide, when it burns subsequently in an adequate oxygen supply, then what happens is like because of the combustion of the CO in the adequate oxygen supply, then it raises remaining that is 72% of the heat which is tapped in the molecule that is around 283 kilojoule of the heat get released during the combustion of this CO. As a result, the CO returns only 72% of the energy of the carbon.

So, if you just take the summation of this particular energy that is the heat released during the combustion of CO as well as the heat released during the conversion of the carbonaceous material into a carbon monoxide, these equivalents to a complete combustion of the carbonaceous material which is equivalent to a 393 kilojoule of heat which is releasing by burning the carbonaceous material that is per mole of burning of the carbon burnt in the gasification chamber.

So, this is how even the gasification process takes place that it first produces carbon monoxide as a gas and the produced gas can also be subsequently combusted in the adequate oxygen supply to produce the remaining amount of the heat that is a 72% of the heat which is remain in the carbon monoxide gas and the gas can subsequently be burned in the adequate oxygen supply to release remaining amount of the energy.

And that is how the gasification process also can be converted into a gas and subsequently produced gas can be converted into a further heat or the electricity or can be further used as a heat source for the process in a manufacturing plant and it can also be converted into the electricity. Apart from that for the complete gasification of the biomass energy source, the energy recovery in this particular processes is around 75 to 88% and this is due to the presence of hydrogen and the other hydrocarbon.

So, apart from that, for the gasification of the biomass, which is a complete gasification of biomass, the energy recovery is around 75 to 88% and that is due to the presence of hydrogen and the other hydrocarbon molecules in the carbonaceous material. And if you just try to see the representation of this particular reaction here, this particular process can also be carried out as I mentioned in the presence of steam as a gasifying agent.

And as a result, it gives the product gas in the form of H_2 and CO . And this particular product gas is termed as a syngas or the producer gas. Now, you see the reaction of this particular carbonaceous material. So, this shows even in the presence of steam, as a gasifying agent. So, once this carried out in the presence of steam as a gasifying agent, it produce CO and the hydrogen as a gas, but, there is an important difference between these particular reaction here, here it is a plus Q value. That means it requires the heat during the reduction process as well.

(Refer Slide Time: 42:07)

5. Liquefaction

Liquefaction of solid biomass into liquid fuel can be done through pyrolysis, gasification, and through hydrothermal process.

In the latter process, biomass is converted into an oily liquid by contacting the biomass with water at elevated temperatures (300 – 350 C) and high pressure (12 – 20 MPa) for a period of time. There are several other means including the supercritical water process for direct liquefaction of biomass.

Pyrolysis:
A pyrolysis process produces pyrolytic oil and gas. When the emphasis is on an oil rather than a gas yield, the process may be termed a liquefaction process.

Pyrolysis liquids can be used directly as heating oil.

- They have high water content
- The low pH of pyrolysis liquids make the liquid highly corrosive
- The HHV value of a pyrolysis liquid ranges from 17 to 20 MJ/kg.

* Courtesy: Biomass gasification, pyrolysis and liquefaction, by P. Menzies, 2011, p. 113, 114, 115, 116, 117.

So, another class of the thermo-chemical conversion process here is the liquefaction process. Liquefaction of the solid biomass into the liquid fuel can be carried out using a number of processes. First is the pyrolysis, gasification and through hydrothermal processes. But if you just talk about the hydrothermal processes first, so, in this case, the biomass is converted into a highly liquid product by contacting the biomass with water at relatively high temperature as well as high pressure.

So, the temperature required in this case is 300 to 350 degree Celsius, whereas, the pressure requirement in this particular reaction is 12 to 20 mega pascal for a period of time and during this particular process, the biomass is getting converted into a oily liquid kind of a product. Apart from that, there are several other techniques or means of conversion of solid biomass into a liquid phase are also available that is a supercritical technique by which also the biomass can be converted into a suitable liquid product.

Now, if we just try to differentiate these hydrothermal techniques with the pyrolysis and gasification, so let us discuss about the pyrolysis process to produce the liquid as a product. So, in case of pyrolysis process also, it produces pyrolytic liquid oil and the gas as a product. But when the emphasis is on oil as a product rather than as a gas, then the pyrolysis process is represented as or termed as a liquefaction process.

The similar process now, just working in a different way just because of the output of the product as here the main product is a liquid rather than the gas now, hence, it is termed as a liquefaction process. So, the liquid which is produced from the pyrolysis process, it can be directly used as a liquid oil. This is one of the advantage of this particular process and they have high water content.

So, this is one of the disadvantage of this particular liquid oil which is produced from the pyrolysis process that it has a high water content, but the low pH of the pyrolysis liquid it makes these liquids highly corrosive. Apart from that, the HHV value of the pyrolysis liquid it ranges from 17 to 20 mega joule per kg of the material. So, this also talks about the pyrolysis process and the liquid product which is obtained from the pyrolysis process.

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Liquefaction through gasification:
 It involves the production of methanol from mixture of H_2 and CO (producer gas). The reaction takes place at $330^\circ C$ and 150 atm.

$$2H_2 + CO \rightarrow CH_3OH$$

The H_2 and CO required for the process can be produced by gasifying biomass.

- CO, and H_2S present in producer gas removed prior to methanol reactor.
- Methanol yield from woody biomass expected to be in the range 480-568 liters/tons.
- Methanol can be used as liquid fuel in petrol engines with an energy density of 23 MJ/kg.

Thermochemical conversion—hydrothermal liquefaction (HTL):
 HTL is a unique thermal conversion process that utilizes biomass and water slurries. This makes HTL particularly well suited for high moisture containing material, such as algae, municipal solid wastes, or grasses into bio-based oils.

HTL bio-oils tend to be higher quality than pyrolysis oils.

- HTL oils have less oxygen.
- But the oil yields for HTL are lower than pyrolysis and
- Oxygen content is still higher than crude oil.

Handwritten notes:
 HTL → 5-40 MPa
 200-275°C → Solid product
 275-350°C → Liquid product
 400°C → 90%

* Gasifying Biomass and Solids: Principles and Practice, 2nd Edition, 2013, Nicholas D.P.

So, now, if you just compare this pyrolysis process and the gasification in terms of production of the liquid fuel as a product, so, in case of the liquefaction through the gasification process, it involves the production of methanol from the mixture of the H_2 and the CO and the H_2 and CO which is produced from the gasification of the biomass as a feedstock.

So, this particular producer gas can be efficiently converted into a methanol as a liquid product and the H_2 and the CO which is required for this process can be produced by the gasification of the biomass and this particular reaction of H_2 and the CO takes place at around 330 degrees C and the pressure of around 150 atmospheric pressure. So, this is a reaction where 2 moles of hydrogens are reacting with the one mole of CO to produce the methanol as a product.

So, in this case, the H_2 and the CO required for the process can be obtained from the gasification of the biomass as I mentioned and the CO_2 and H_2S which is an unwanted gas which is present in the composition of the producer gas can be removed before allowing CO and the H_2O to enter into the methanol reactor. And the methanol yield from the woody biomass, it is expected to be in the range of 480 to 568 litres per tones of the biomass. So, this is significantly a good ethanol yield can be obtainable by liquefying the gas.

And the methanol can also be used as a liquid fuel in the petrol engines with an energy density of around 23 mega joule per kg. Similarly, other process which is a thermo-chemical conversion of

the biomass so, in this case what happens is like it is termed as a hydrothermal liquefaction of the biomass. HTL, it is a unique thermo-chemical conversion process that utilises biomass and water slurries.

And this makes the HTL particularly well suited for even high moisture containing material even MSW also can be utilised directly for the liquefaction purpose using the hydrothermal liquefaction techniques. And the product quality which is obtained from the HTL process if you see here the HTL bio-oil, it tends to be higher quality than the bio-oil obtained using the pyrolysis process.

Similarly, the HTL oil have less oxygen content than (()) (47:07) of the oil obtained from the pyrolysis of the biomass. Apart from that the oil yield of HTL is lower than the pyrolysis process, but if you see the oxygen content of the oil obtained using the HTL process, it is lower than that of the pyrolysis process, but it is still higher than that of the crude oil. If you just try to see the difference of this particular process with the pyrolysis and the gasification.

So, because of the utilisation of the watering media in the reaction, it also avoids the utilisation of the dried feedstock material for the conversion purpose. And this is also one of the advantage of this particular process. Apart from that, because of the heat transfer rate in the media is relatively high, it also reduces the requirement of reduced particle size in the reaction purpose. So, these are the 2 main benefits of this hydrothermal liquefaction process.

And if you see this particular process, it carried out in the wide temperature range that is from 200 to around 600 degree Celsius. Because the product of the particular process can also be specified according to the temperature severity of the process. For example, if the process is carried out between 200 to 275 degrees Celsius, so, during this particular stage what happens is like it suitably produce solid as a product.

If the process is carried out between 275 to 350 degree C, then it produce basically liquid as a product and if the process is carried out in the temperature which is above 400 degrees C, so, majorly produced product is nothing but the gas. So, suitably it produced the gas as a product.

So, this is how we can see the variation in the temperature is also suitably producing the required product from the hydrothermal liquefaction of the biomass.

So, this is what you also the another advantage of this particular processes as similar to the pyrolysis, if you see there, the variation in the temperature also lead to a different kind of product. So, similarly the hydrothermal liquefaction process also just by a small variation in the temperature can lead to a suitability different kinds of the product. Apart from that another advantage of the hydrothermal liquefaction process is as this particular process is carried out in the liquid medium and high temperature.

Therefore, to keep the reaction mixture in the liquid state, it also required certain pressure which is in the range of around 5 to 40 mega pascal. So, this particular pressure it also varies depending on the temperature requirement of the process. So, once this particular temperature requirement is increasing accordingly the pressure requirement of the process also will vary. But this pressure requirement in the particular process is essential.

So, that to maintain the liquid state of the reaction mixture. That is the liquid stage of the reaction mixture to have efficient content of the biomass with the water molecule to convert it into a suitable product. But apart from that if you see here this particular process also has certain disadvantages, because of the cost competitiveness. In case of this particular process, the capital cost which is required is relatively high, because of the high temperature and the high pressure requirement of the process.

But, the another advantage of this particular process is like, it also handles (()) **(50:32)** biomass for the conversion purpose. As a result, the drying and the size reduction of the biomass is not essentially required for the conversion of the biomass using the HTL process to a suitable product and this can be a beneficial aspect of this particular process as well.

So, now, after understanding the different thermo-chemical conversion processes, if you just try to compare this thermo-chemical processes, which are listed here that is a liquefaction process, pyrolysis, combustion and gasification.

(Refer Slide Time: 50:56)

Comparison of some major thermochemical conversion processes

Process	Temperature (°C)	Pressure (MPa)	Catalyst	Drying
Liquefaction	250 – 330	5 – 20	Essential	Not required
Pyrolysis	300 – 600	0.1 – 0.5	Not required	Necessary
Combustion	700 – 1400	> 0.1	Not required	Not essential, but may help
Gasification	500 – 1300	> 0.1	Not required	Necessary
Torrefaction	200 – 300	0.1	Not required	Necessary

Source: Shengqian et al., Process and Performance of Biomass Conversion, 2011, Elsevier

If you just try to compare these particular processes from this table, it can be visualised that for the liquefaction process the temperature requirement is relatively less as well as the pressure if you see here, but it requires sufficiently high pressure for the liquefaction of the biomass. But essentially, it requires the catalyst for the conversion purpose, but it does not require the drying step to dry the feedstock and convert it into the product.

Whereas, in case of pyrolysis, the temperature ranges 300 to 600 degrees C, but pressure range is relatively low. Also it does not require catalyst, but drying is necessary in this particular stage, because, if the material is not dried, then significant amount of the energy is required to dry off this particular moisture from the raw material first and then only the thermal degradation of the material will happen. As a result, if the significant amount of the moisture loss is not removed, then it will lead to the moisture content in the product as well.

Similarly, if we talk about the commercial process, now, the temperature requirement in this case is significantly high. Pressure is not so high, but the catalyst also it is not required in this case and it is not essential, but if the dried material is used for the combustion purpose, then it may help to improve the process efficiency. Now, if you talk about the gasification process, now, here, the temperature ranges 500 to 1300 degrees C, pressure requirement is not essentially high in this case, even the catalyst is not required.

And as a result here, if you see in case of gasification process, it is necessary to have only the dried material for the conversion purpose. So, according to the material and the feedstock specification of the conversion system, the suitable feedstock that is the carbonaceous material or the biomass can be pre-processed and can be suitably converted into a useful product using either of these particular technologies.

Now, with this, I think it is very well understood that how thermo-chemical conversion of the biomass takes place and it leads to a suitable or the convenient useful fuel or chemical as a product. So, we will just end our lecture here.

(Refer Slide Time: 53:14)

(Overview of next lecture)

Module	08 (Bioconversion of substrates into alcohol and Thermo-chemical conversion of biomass to solid, liquid and gaseous fuels)
Lecture	02 (Part I)
Content	Thermo-chemical conversion processes Torrefaction, combustion, gasification, pyrolysis, <u>chemical conversion</u> processes

Thank you

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

So, in the next lecture, so, we will discuss individually about these particular processes in detail. Thank you very much. Regarding this lectur if you have any doubt, you just feel free to contact me at vvgoud@iitg.ac.in. Thank you.