Energy Conversion Technologies (Biomass And Coal)

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Lecture 18

Pyrolysis and Hydrothermal Liquefaction

Good morning everyone.

Welcome to first lecture of the module 4. In this lecture, we will discuss about the thermochemical conversion processes. In that, we will discuss about simultaneous biochar and bio-oil production, their applications, hydrothermal liquefaction of the bio-based feedstock, and comparison of biofuels with the conventional fuels.

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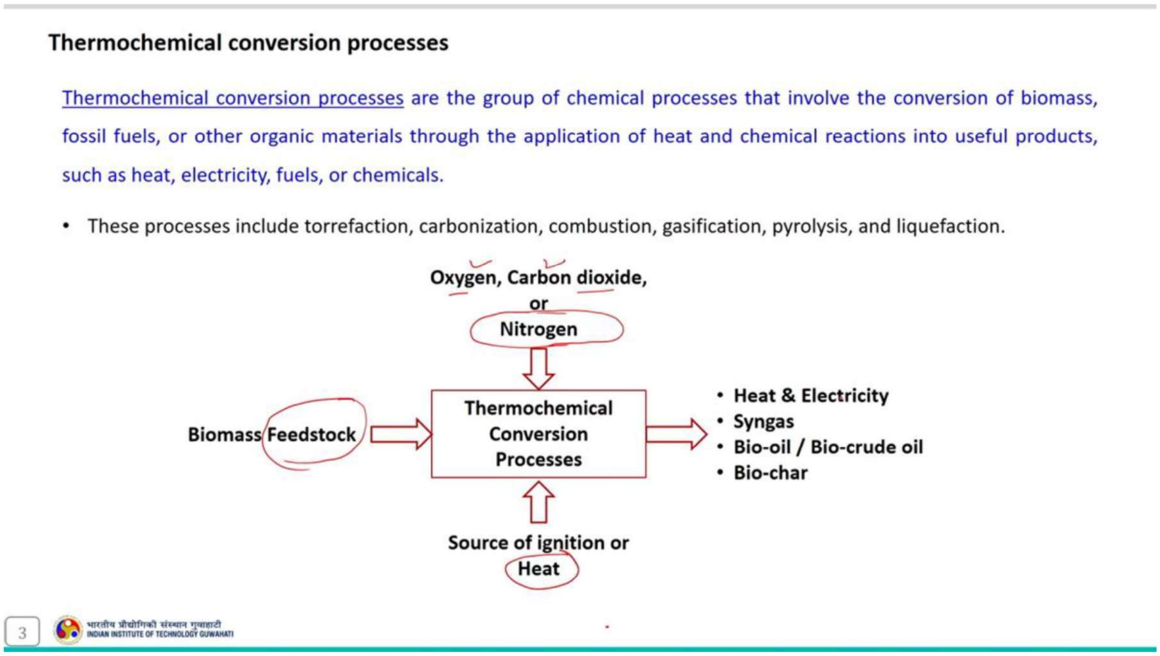

Thermochemical conversion processes are the group of chemical processes that involves the conversion of biomass, fossil fuels or other organic material through application of heat and chemical reaction into useful product such as heat, electricity, fuels or chemicals. These processes include torrefaction, carbonization, combustion, gasification, pyrolysis, and hydrothermal liquefaction process. This scheme here it represents the thermochemical conversion of bio-based feedstock, fossil fuel, and other organic materials using specific medium. So, some thermochemical conversion processes are carried out in oxygen, carbon dioxide, or other steam as a medium, while some chemical conversion processes carried out in absence of oxygen using suitable heat source. And the product obtained from the thermochemical conversion processes include heat and electricity, syngas, bio-crude oil, and solid product as a biochar.

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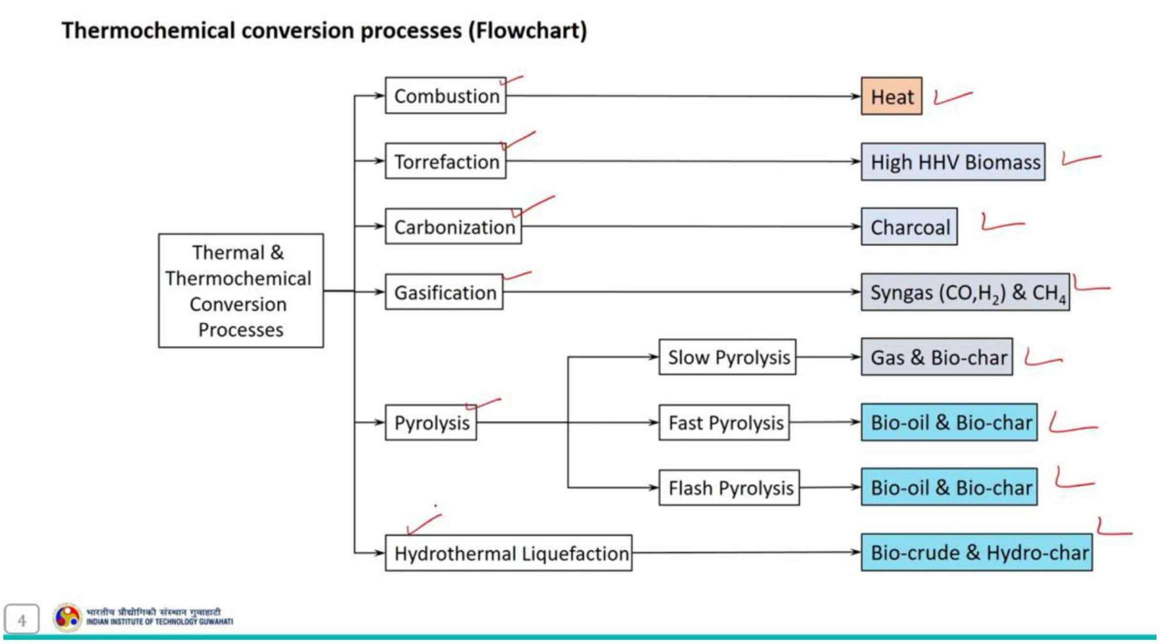

This flowchart here, provides the visual representation of different thermochemical conversion processes and their respective products. Among these thermochemical conversion processes, torrefaction and carbonizations are already discussed in the previous module. However, in this module the main focus is on combustion, gasification, pyrolysis, and hydrothermal liquefaction process.

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Thermochemical Processes, Products & Applications

Process	Extent of Oxidation	Primary products	Application
Combustion	Complete	CO_2, Water vapor, Ash	Heat & Power
Gasification	Partial	Syngas (CO, H_2), Bio-char	Heat & Power, Synthetic Fuels, Chemicals
Pyrolysis	None	Bio-oil, Bio-char, Gases	Liquid biofuel, Chemicals, Heat & Power
Hydrothermal Liquefaction	None	Bio-oil, Aqueous products, Hydro-char, Gases	Liquid biofuel, Chemicals, Fertilizers

And this table here, it provides the details of these four thermochemical conversion processes which we would be discussing in this module as well as the oxidizing medium used during these thermochemical conversion processes, their primary products, and application.

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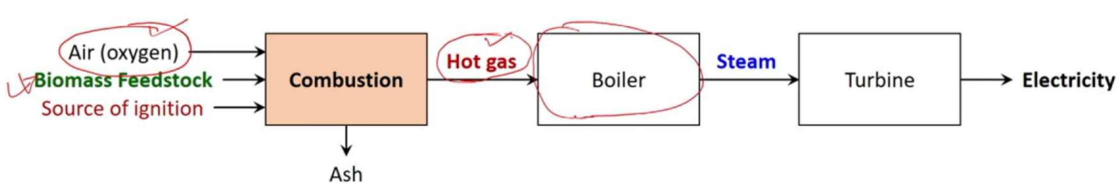
Combustion

- Combustion is the process of burning a fuel in the presence of oxygen, which produces heat and combustion gases, such as carbon dioxide and water vapors.
- This process is commonly used to generate electricity in power plants.



So, let us first discuss about the combustion process. In combustion, it is the process of burning a fuel either it is a bio-based feedstock, fossil fuel, or any other organic material in presence of oxygen which produces heat and combustion gases such as carbon dioxide and water vapor as a product. This process is commonly used to produce heat and the produce heat is further used for the electricity generation in power plant. So, for example here, the hot gases obtained after the combustion processes are sent to the boiler for the steam generation and the produced steam is used in the turbine to generate the electricity.

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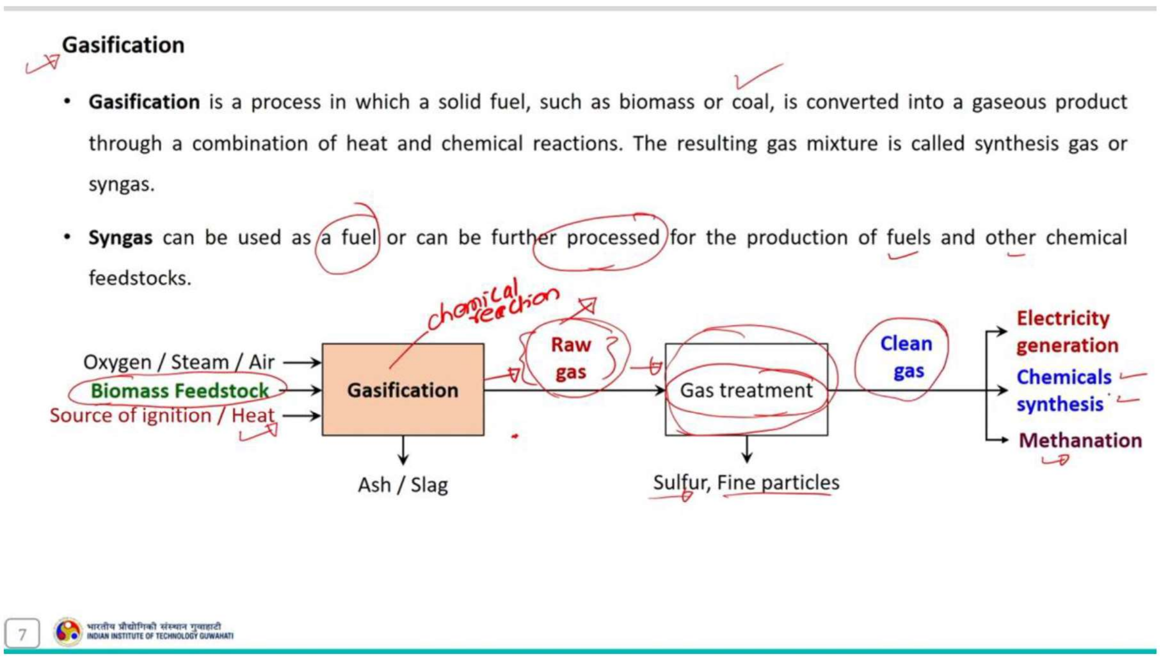

So, another important thermochemical conversion process is the gasification and a gasification it is a process in which again the solid fuel such as biomass or coal is converted into a gaseous product through a combination of heat and the chemical reaction. And the resulting gas mixture is called synthesis gas or syngas. And this produce synthesis gas can directly be used as a fuel or can further be processed for the production of fuels and another chemical feedstock. So, here we need to learn two things specifically, because the raw gas which is produced after the gasification process is used for the combined heat and power production, co-firing, or production of high temperature heat. And while using this raw gas for this operation the cleaning process is less demanding. However, when the gas is used for the production of fuels and chemicals then the more precise cleaning and the conditioning of the gas is necessary. And for that purpose, a gas treatment unit need to be used in the gasification process, where it can remove the fine particles and sulphur present in the raw gas. So, the clean gas can be used for the production of the fuels and chemicals.

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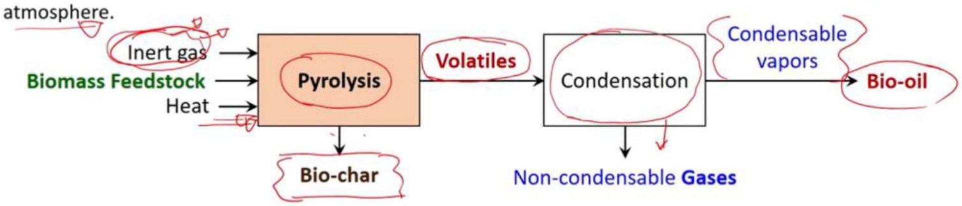
Pyrolysis

- In the 18th century, pyrolysis process was used to produce tar and pitch from woody biomass for shipbuilding and waterproofing. This process became popular over the time for various industrial application.
- Pyrolysis is the process of heating a solid fuel in the absence of oxygen, which produces a liquid or gaseous product, as well as a solid residue.
- This process is commonly used to produce bio-oil (a liquid fuel), that can be further upgraded to produce a liquid fuel for heating or transportation.
- Pyrolysis of biomass is typically carried out at medium (300–800°C) to high temperatures (800–1300°C) in an inert atmosphere.



Simultaneous bio-char and bio-oil production using pyrolysis process

Courtesy: Gahane et al., BioEnergy Research 2022, 15, 1987.

So, next important process in the thermochemical conversion processes is pyrolysis. The use of pyrolysis process for thermal application dates back to 18th century. And in 18th century the pyrolysis process was used to produce tar and pitch from woody biomass for ship building and waterproofing application. And thereafter this process become very popular for various industrial applications. This scheme here it represents the pyrolysis process which involves the heating of solid fuel in absence of oxygen. So, mostly this pyrolysis process is carried out in inert environment which produces a liquid or gaseous product as well as the solid residue. The volatiles which are produced during the pyrolysis process mostly contains the condensable and the non-condensable gases. So, for that purpose a condensation unit is required after the pyrolysis process to condense the condensable vapors which eventually results in the production of the bio-oil. And the non-condensable gases can further be recycled back into the process to provide the thermal energy which is required for the pyrolysis operation. And this particular process commonly produces bio oil that is a liquid fuel as a product that can further be upgraded to produce a liquid fuel for heating and the transportation. And this particular process is carried out at a medium temperature range of 300 to 800 °C, or even to a high temperature range that is 800 to 1300 °C in an inert environment. And that is the difference between the gasification and the pyrolysis process. If you remember, in the gasification an oxidizing medium is required in the form of oxygen or carbon dioxide for the gasification process to takes place. Whereas in case of pyrolysis, it is carried out in an inert atmosphere that is in absence of oxygen.

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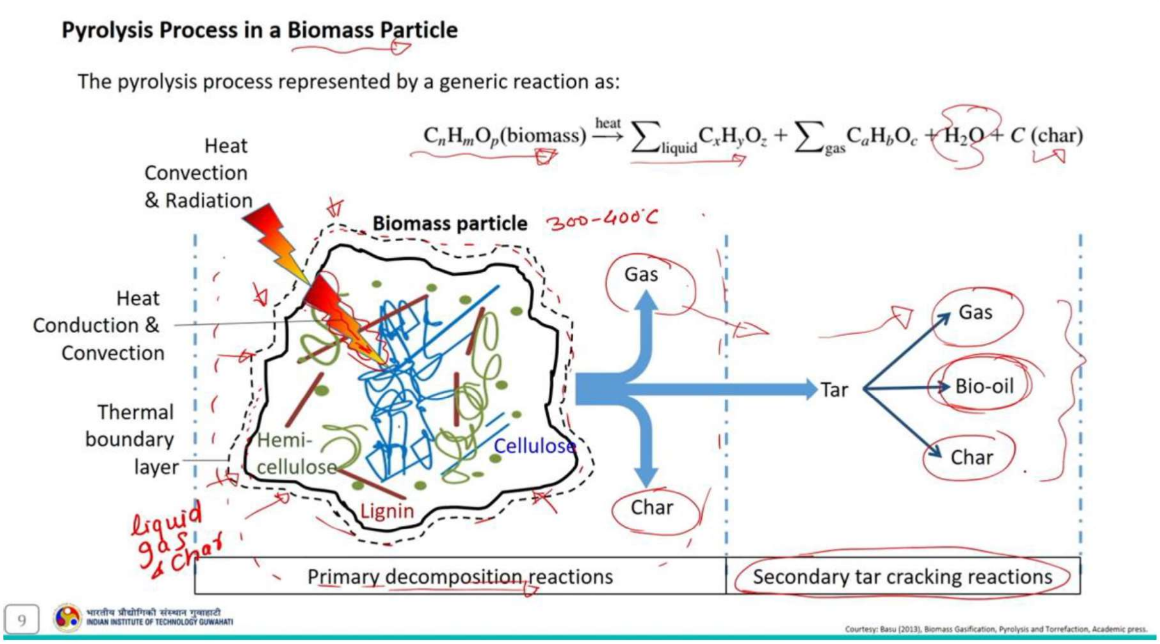

So, let us discuss about this pyrolysis process in a biomass particle. This schematic here, it provides the visual representation of biomass particle which undergoes the pyrolysis process. And here the pyrolysis process is represented by a generic reaction, which shows a biomass particle here. And once it undergoes the pyrolysis process then it produces the liquid gas and solid char as a product along with the water. Unlike combustion the pyrolysis is not an exothermic reaction and it occurs in absence of oxygen. But, sometime the partial combustion is allowed to provide the thermal energy which is required for the pyrolysis process. And if you recollect, we just discussed this concept of recycling of the combustible gases to provide the thermal energy, which is required for the pyrolysis process. For that those gases need to be recycled back into the pyrolysis process, so that it can be burnt to provide the thermal energy which is required for the pyrolysis operation. So, if you look at this particular biomass particle here the transport of heat in the pyrolysis process, it is assumed that the heat or mass transfer is too high to offer any resistance to overall rate of the pyrolysis process. but this is only true in a low temperature range of say 300 to 400 °C. But at higher temperature the transport of heat and mass is influenced by the rate of pyrolysis. So, we need to neglect this stage in case of high temperature pyrolysis operation. But if you look at this particular biomass particle here, so during the pyrolysis stage the heat is transferred from high temperature gas to the outer surface of particle here through the radiation and the convection mechanism. And once it reaches to the outer particle surface thereafter it is transported to the interior of the particle like this way, by conduction and by convection inside this pore of the biomass particle. So, this mode of heat transfer normally occur in the pyrolysis process and the sample is heated using a suitable heat source in case of pyrolysis operation. And during this process it decomposes the biomass particle into liquid, gas, and char as a product.

First if you look at this particular phase of the schematic, so here it represents the primary decomposition reaction. In this case once the sample undergoes the pyrolysis process, so it undergoes the thermal decomposition and it produces the condensable gases and char as a product. Once this produced gases and char undergoes the secondary char cracking reaction here, then it produces liquid char and then these non-condensable gases. So, because of the secondary char cracking these condensable gases further broke down into a non-condensable gas. And which eventually results in decreasing the bio oil yield. And this nature of the product during the pyrolysis process, it mostly depends on the temperature and the heating rate used during the pyrolysis operation. So, the product of the pyrolysis process is classified into three main types that is bio-oil which is a liquid product, gaseous product and bio char as a solid product. So, let us discuss about these three products one by one.

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Products of Pyrolysis Process

Pyrolysis products are classified into three main types:

1) Bio-oil (tars, heavier hydrocarbons, and water)
2) Bio-char (mostly char or carbon)
3) Gases (e.g., CO_2, H_2O, CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6).

1. Bio-oil

- Primary decomposition of biomass produces condensable vapors and non-condensable (permanent) gases.
- The vapors made of heavier molecules condense upon cooling to produce liquid product, known as pyrolytic oil, bio-oil, bio-crude or tar.
- Bio-oil is a mixture of complex hydrocarbons with large amounts of oxygen and water.
- The water content ranges from 15–35%. The oxygen content ranges from 35–40%.

Courtesy: Rasaq et al. *Energies* 2021, 14, 5426 / Basu. Biomass Gasification, Pyrolysis and Torrefaction. 2013. Academic press.

So, here the bio oil is basically produced by the primary decomposition of the biomass. and it mainly produces the condensable vapors and the non-condensable gases. And the vapour which are made of heavier molecules, this condense upon the cooling to produce the liquid as a product which is known as a pyrolytic-oil and bio-oil or even it is termed as a bio-crude or tar. And this bio oil it is a mixture of complex hydrocarbons with a large amount of oxygen and water in its composition. And the water contained in this bio-oil it ranges from around 15 to 35 percent. And the oxygen content it ranges from around 35 to 40 percent in the bio oil produced using the pyrolysis process.

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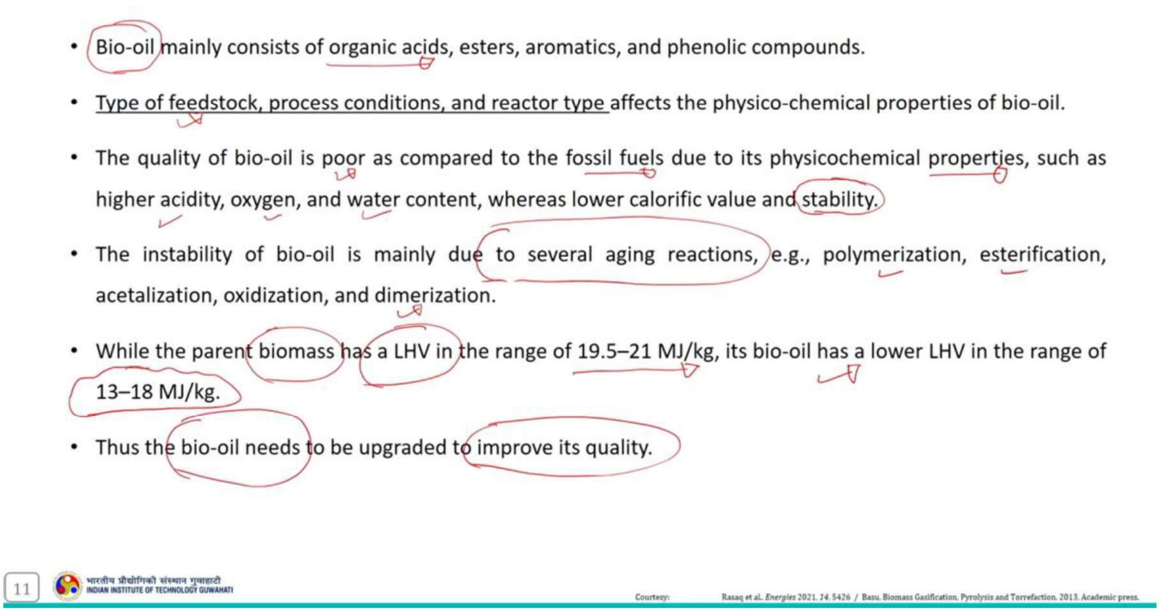

The bio oil produced from the pyrolysis process it mainly consists of the organic acids, esters, aromatics, and the phenolic compounds. And the composition of the bio oil it mainly depends on the process condition as well as the feedstock which is used for the pyrolysis operation. As well as the reactor type also affects the physicochemical properties of the bio oil produced during the pyrolysis process. And this quality of the bio oil, it is poor as compared to that of the fossil fuels and that is mainly due to its physicochemical properties such as higher acidity, oxygen and the water content, whereas lower calorific value and the stability. The bio oil produced from the pyrolysis process is relatively unstable compared to that of the conventional fuel because of several aging reactions that is polymerization, esterification, acetalization, oxidation, and the dimerization reaction which occurs during its storage for a prolonged period. If you compare the calorific value of parent biomass which is used for the pyrolysis process with that of the bio oil produced from the pyrolysis process. So, the bio oil produced from the pyrolysis process, it has relatively lower calorific value than that of the original material that is biomass which is used for the pyrolysis process. And that is mainly because of the high amount of oxygen and water content in its composition. And because of that the up gradation of the bio oil is necessary to improve its quality.

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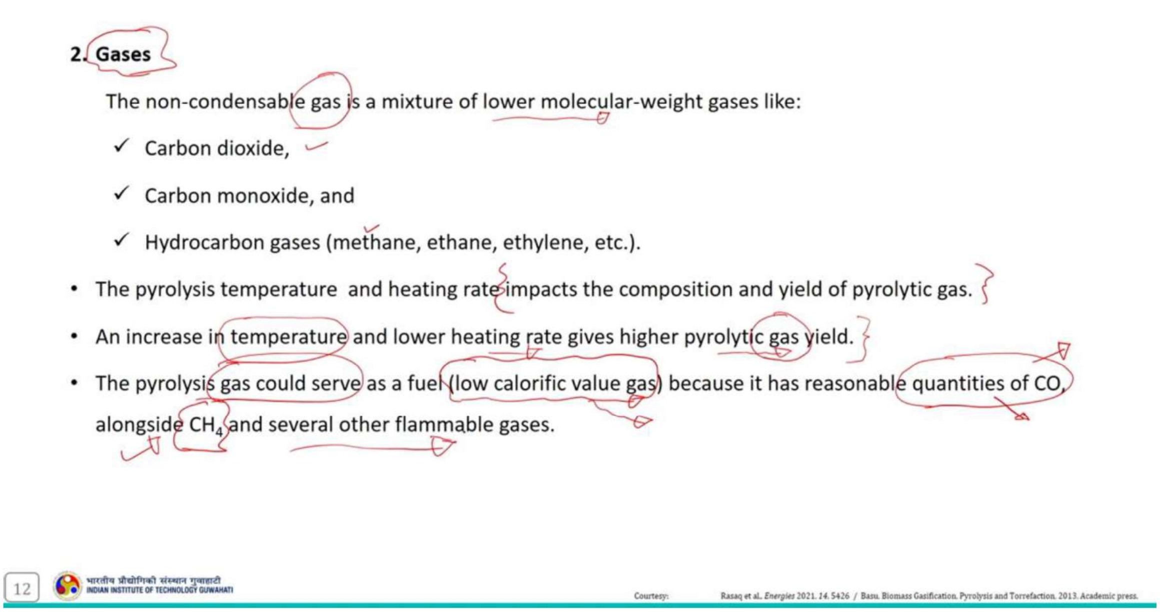

So, another important product which obtained from the pyrolysis process is a gas. And it is mostly the non-condensable gas which is a mixture of lower molecular weight gases like carbon dioxide, carbon monoxide, and the hydrocarbon. And in the hydrocarbon also it includes mostly the methane, ethane and the ethylene. And the pyrolysis temperature and the heating rate, it impacts the composition as well as the yield of pyrolytic gases. And with an increase in this pyrolysis temperature and lower heating rate, it gives relatively higher pyrolytic gas yield. And that is the issue if the operating conditions are not maintained properly then the most of the volatiles will get converted into a pyrolytic gas instead of the pyrolytic oil. The pyrolysis gas could serve as a fuel that is also termed as a low-calorie value gas. Because of its composition, as it has a reasonable quantities of carbon monoxide alongside the methane and several other flammable gases. And hence this particular type of gas can be used, as a low-calorie value gas for the heating application. Because if you recollect, in one of the lectures, we discuss about the heating value of the carbon monoxide. Since it contains relatively good amount of the heat, so the gas which is produced during the pyrolysis process can be used as a low-calorie value gas for the thermal application. Alongside carbon monoxide, it also contains methane and some other flammable gases so this combination of the gases can be used as a low-calorie value gas for the thermal application.

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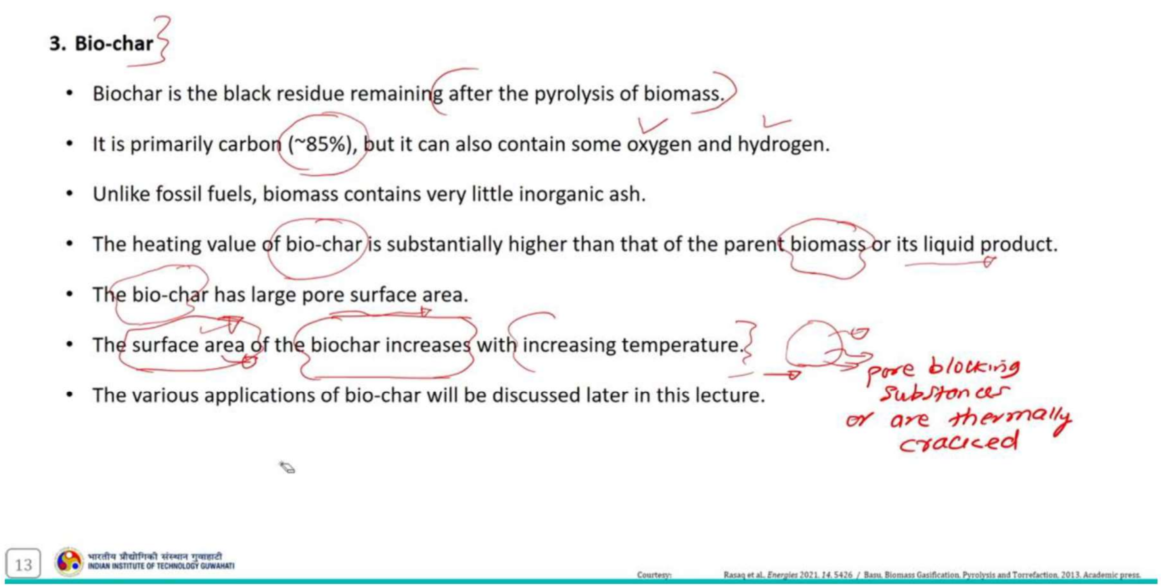

And next important product from the pyrolysis process is the biochar, which is a black residue remaining after the pyrolysis of biomass. And it primarily a carbon but along with the carbon, it also contains some amount of oxygen and the hydrogen in its composition. And the heating value of this biochar is substantially higher than that of the biomass, which is used to produce this biochar. As well as it is higher than the even liquid product which is obtained from the pyrolysis process. And the biochar it has a large pore surface area and this surface area of the biochar even can be increased with increasing the temperature during the pyrolysis operation. And it is also proven that with increasing the temperature, the surface area of the biochar also increases. Because with increasing temperature pore blocking substances are driven off or are thermally cracked, increasing the externally accessible surface area. And that is what is the reason for increasing the surface area of a biochar with increasing the temperature.

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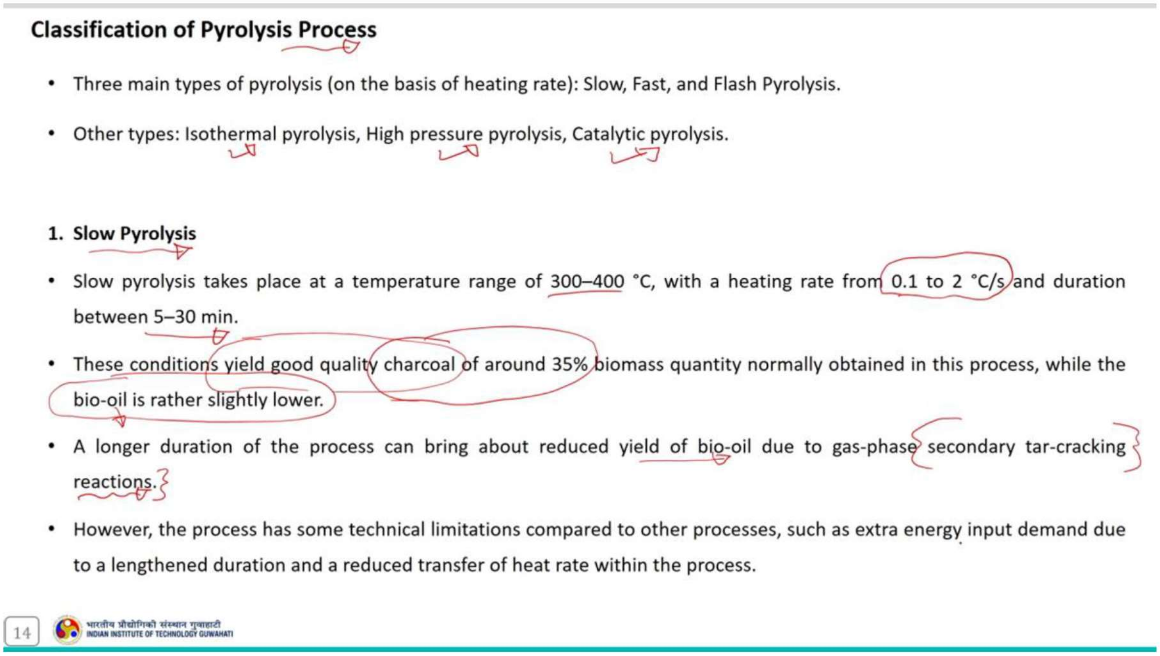

So, after learning about the product of the pyrolysis process let us discuss in detail about the different pyrolysis process. The pyrolysis process is mainly classified into three main type based on its heating rate that is slow pyrolysis process, fast pyrolysis process, and the flash pyrolysis process. Apart from that the other pyrolysis process includes isothermal pyrolysis, high pressure pyrolysis and catalytic pyrolysis operation. So, let us first discuss about the slow pyrolysis process, it mainly takes place at a temperature range of around 300 to 400 °C with a heating rate here is maintained in the range of 0.1 to 2 °C per second. And the duration of this slow pyrolysis operation is between 5 to 30 minutes. And at this condition this process yield good quality charcoal of roughly around 35%, while the bio oil is rather low in case of slow pyrolysis process. The longer duration of the process can bring about the reduced yield of the bio oil that is mainly because the secondary tar cracking reactions occur in this particular slow pyrolysis process. And which eventually results in decreasing the yield of bio oil. And this particular process also has some technical limitation compared to that of the other processes such as it requires extra energy input due to the lengthy process operation and a reduced heat transfer is observed in this process.

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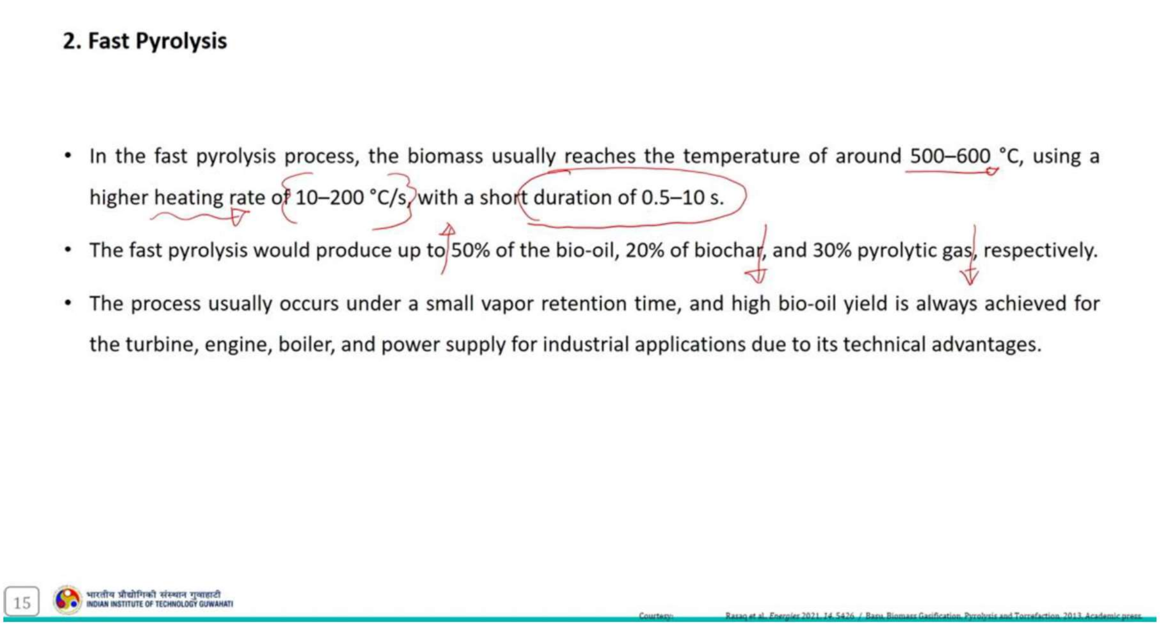

The fast pyrolysis process is carried out in the temperature range of around 500 to 600 °C using a heating rate of 10 to 200 °C per second. So, here it is basically carried out at higher heating rate and even the duration of the fast pyrolysis process is relatively very short between 0.5 to 10 second. And as a result, this process gives relatively high amount of bio oil yield with respective biochar and the pyrolytic gas yield. And that is what is the advantage of the fast pyrolysis process here. Because it gives relatively high amount of the bio oil yield, compared to that of the slow pyrolysis process. Because this particular operation carries out for short duration of the time that is as mentioned here. And even the heating rate which is used for the fast pyrolysis process is relatively high. As a result, it gives relatively good amount of the bio oil yield.

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3. Flash Pyrolysis

- The flash pyrolysis can produce biochar, bio-oil, and gases with respective shares of ~12%, 75%, and 13% of initial biomass weight.
- Particles are usually heated for a very short time of about <0.5 s and with a very high rate of heating, greater than 1000 °C/s, with a high-temperature level in this process between 550–1000 °C.
- Despite the catalytic activity of the biochar, bio-oil become viscous when it contain some solid particles.
- This process still provides a high potential of good quality bio-oil at minimum water content .

Pyrolysis type	Heating rate (°C/s)	Pyrolysis duration (s)	Temperature (°C)	Bio-oil yield (%)	Bio-char yield (%)	Gas yield (%)
Slow	0.1 – 2	450 – 550	300 – 400	~30	~35	~35
Fast	10 – 200	0.5 – 10	400 – 550	~50	~20	~30
Flash	> 1000	< 0.5	550 – 1000	~75	~12	~13

Courtesy: Rasaq et al. *Energies* 2021, 14, 5426 / Basu. Biomass Gasification, Pyrolysis and Torrefaction. 2013. Academic press.

And the next is the flash pyrolysis operation. And if you look at the bio oil yield which can be obtained from the flash pyrolysis process, it is significantly high compared to that of the fast pyrolysis and the slow pyrolysis process. And this particular operation is also carried out for a very short span of time even which is less than 0.5 second. And heating rate used here it is around 1000 °C per second. As a result, most of the volatiles are getting converted into a condensable vapor and which eventually results in the higher yield of the bio oil in the flash pyrolysis operation. And this particular process also has a high potential of producing good quality bio oil at minimum water content. Even the water content which is obtained at the end of this pyrolysis process is relatively low compared to that of the fast and the slow pyrolysis process. And this table here, it gives the information about these three-pyrolysis process. Now if you see here, the bio oil yield which is obtained in the flash pyrolysis process is significantly high than that of the fast and the slow pyrolysis process. Similarly, the heating rate which is used for the flash pyrolysis process is significantly higher compared to that of the fast and the slow pyrolysis process.

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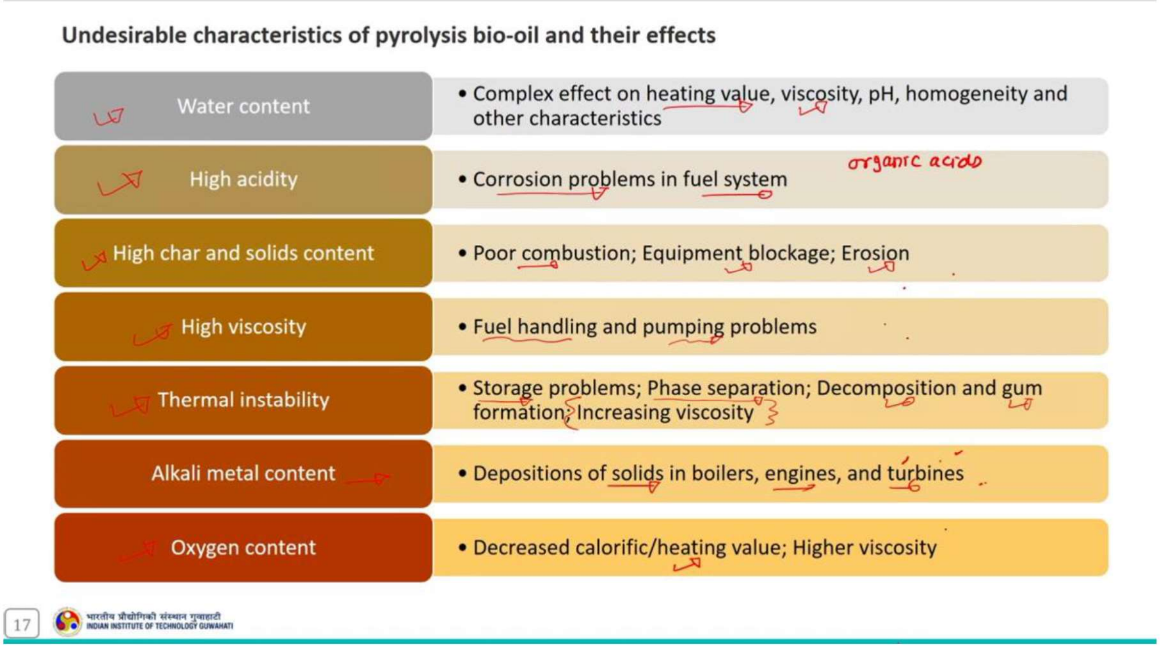

So, now let us discuss about the undesirable characteristics of the pyrolytic bio oil. As discussed before, the bio oil which is produced from the pyrolysis process has certain undesirable characteristics and which includes water content. The water content in the pyrolysis oil affects the viscosity and stability of the bio oil. And also lowers the heating value and flame temperature which eventually results in the ignition difficulties. High acidity which is another undesirable characteristic of the bio oil. The presence of organic acids such as carboxylic acid, acidic acid, and the formic acid makes bio oil more acidic in nature. And the pH of the bio oil varies in the range of say 2-3. And this low pH makes bio oil corrosive to some material and which mainly impede the bio oil application as an engine fuel. So, another undesirable characteristic includes the high chair and the solid content, which cause poor combustion, equipment blockage and erosion while it is used. Even the high viscosity is also one of the undesirable characteristics of the bio oil that is because it may cause fuel handling and the pumping problems. That is because higher viscosity is another undesirable characteristic of the bio oil and it may lead to fuel handling and the pumping problems. Thermal instability as just we discussed few slides before, is another undesirable characteristic. of the bio oil. Because the fresh bio oil contains many reactive components and its percentage is subjected to change during the storage. And this secondary reaction including polymerization make bio oil unstable which eventually results in the phase separation, decomposition, formation of gum, and also results in increasing the viscosity of a bio oil. Alkali metal content in bio oil produces inevitable problems such as poor deposition of solids in boilers, engines, and turbines, and blockage of the engine parts. Similarly, the high oxygen content in the bio oil makes bio oil significantly differ from the conventional fuel. It reduces the heating value of the bio oil and makes bio oil unsuitable during the storage and the transportation and also results in the increased viscosity.

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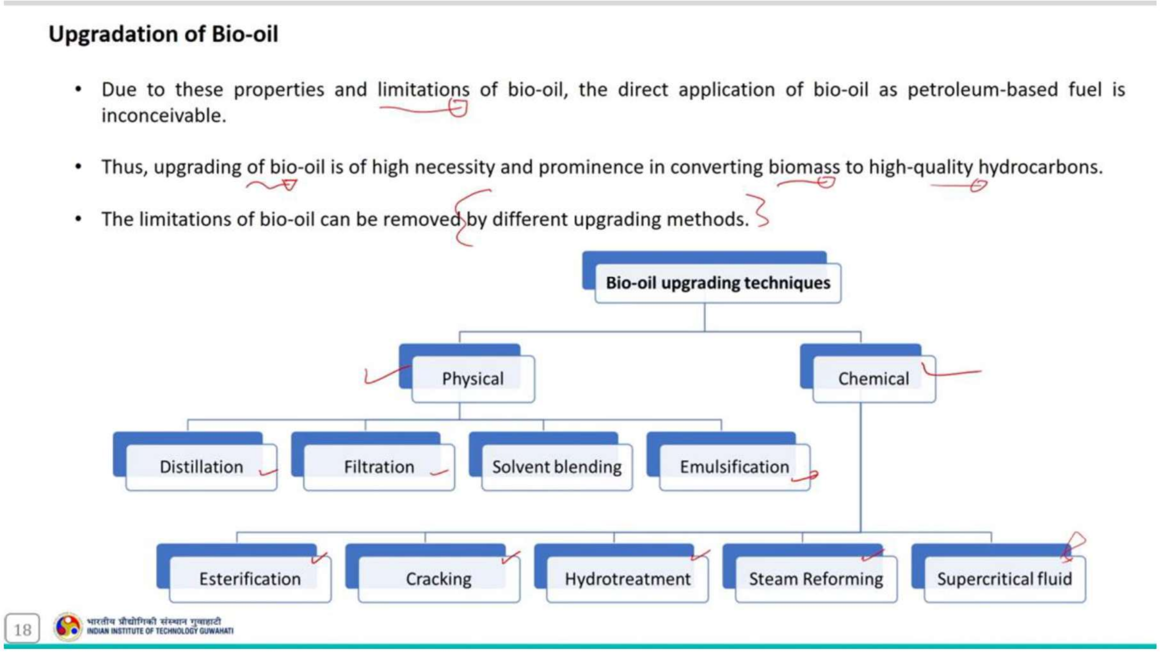

Due to these properties and the limitation, the direct application of bio oil as a fuel is inconceivable. Thus, the upgrading of bio oil is of high necessity and prominence in converting the biomass into high quality hydrocarbons. And this limitation of the bio oil can be removed by different upgrading methods such as physical and the chemical. The physical upgrading method includes the distillation, filtration, solvent blending, and emulsification whereas the chemical upgrade method includes esterification, cracking, hydrotreatment, steam reforming, and supercritical fluid treatment. So, with the help of this technique, the bio oil produced from the pyrolysis process can be upgraded to a high-quality fuel.

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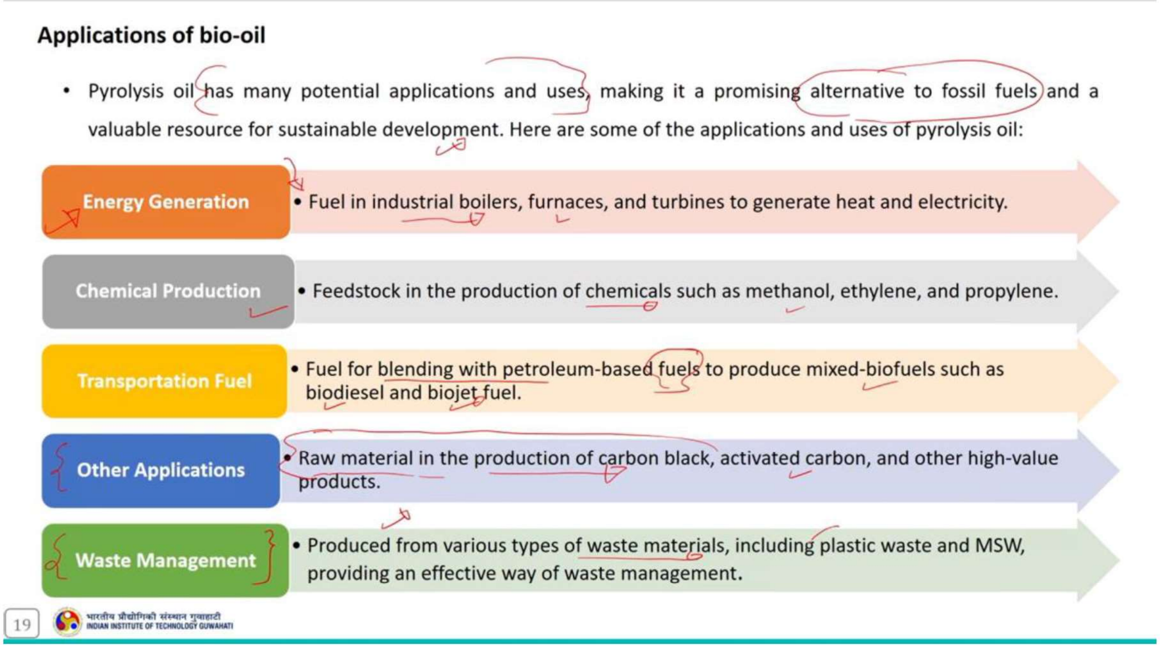

Applications of the produced bio oil. The produced bio oil has many potential applications and uses which making it a promising alternative to fossil fuels and a valuable resource for the sustainable development. So, the application of the bio oil includes the energy generation. The produced bio oil after the upgradation technique can be used as a fuel in the industrial boilers, furnaces, and turbine to generate heat and electricity. Similarly, it can be used as a feedstock in the production of the chemicals such as methanol, ethylene, and propylene. The bio oil produced after the upgradation method can be used as a fuel for blending with the petroleum-based fuel to produce mixed bio fuel such as biodiesel and biojet fuel. Apart from that, the biochar is also one of the products produced during the pyrolysis process, which can act as a raw material in the production of carbon black, activated carbon, and other high value products. And this particular process is also considered as one of the most efficient process for the waste management because it produces bio oil from various waste material including the plastic waste and MSW providing an effective way of solid waste management.

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Applications of bio-char

Biochar has several applications in agriculture, environmental remediation, and energy production. Some of the applications of biochar include:

1. **Soil amendment:** Biochar is a highly porous material that can retain nutrients and water in the soil, making it a useful soil amendment. When added to soil, biochar can improve soil fertility, increase crop yields, and reduce the need for chemical fertilizers.
2. **Carbon sequestration:** Biochar is a form of carbon that is stable and does not decompose easily. When added to soil, biochar can sequester carbon for hundreds or even thousands of years, helping to mitigate climate change.
3. **Water filtration:** Biochar is highly porous and has a large surface area, which makes it an effective filter material. Biochar can be used as a filter medium to remove contaminants such as heavy metals, pesticides, and organic compounds from water.

Another important product which can be obtained from the pyrolysis process is biochar and this produced biochar has several applications in agricultural, environmental remediation and energy production. And some of these applications of the biochar are included here that is soil amendment agent. So, biochar which is a highly porous material, can retain nutrients and water in the soil, thus making it a useful soil amendment agent.

And when added to the soil the biochar can improve the soil fertility also increase the crop yield and reduce the need for chemical fertilizers. Since, the biochar is a form of a carbon that is stable and does not decompose easily. And hence when it is added to the soil the biochar can sequester carbon for hundreds or even thousands of years and helping to mitigate the climate change. Another important application of the biochar it includes in the field of water filtration. Because the biochar is highly porous material and it has a very large surface-area as just discussed before few slides back. As a result, it acts as an effective filter material and biochar can also be used as a filter medium to remove the contaminants such as heavy metals, pesticides and organic compound from water. That is one of the most important application of the biochar produced from the pyrolysis process.

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4. **Livestock feed:** Biochar can be used as a feed supplement for livestock. When added to animal feed, biochar can improve digestion, reduce odors, and increase nutrient retention.
5. **Energy production:** Biochar can be used as a renewable energy source. When burned, biochar releases energy in the form of heat and can be used to generate electricity or heat.
6. **Environmental remediation:** Biochar can be used to remediate contaminated soils and mine tailings. When added to contaminated soil, biochar can reduce the bioavailability of contaminants and prevent them from leaching into groundwater.

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Similarly, the biochar can be used as a food supplement for the livestock, but in certain percentage. And when it is added to the animal feed, the biochar can improve the digestion, can reduce the odors and increase nutrient retention as well. Biochar can also be used for the energy production. Because of its high energy content, it can be used to generate the heat and the produce heat further can be used to generate electricity. And another important application of biochar is in the field of environmental remediation. As just mentioned before, the biochar can be used to remediate the contaminated soil, the mining, tails. And when it added to the such contaminated soil the biochar can reduce the bioavailability of the contaminants and prevent them from reaching into the ground water. So, this is also one of the important applications of the biochar obtained during the pyrolysis process. So, the biochar produced from the pyrolysis process has a wide number of applications. It can be used in the area of soil amendment, carbon sequestration, water filtration, even the livestock feed, energy production and the environmental remediation. This is all about the pyrolysis process. So, the next process in the thermochemical conversion of the bio-based feedstock is a hydrothermal liquefaction process.

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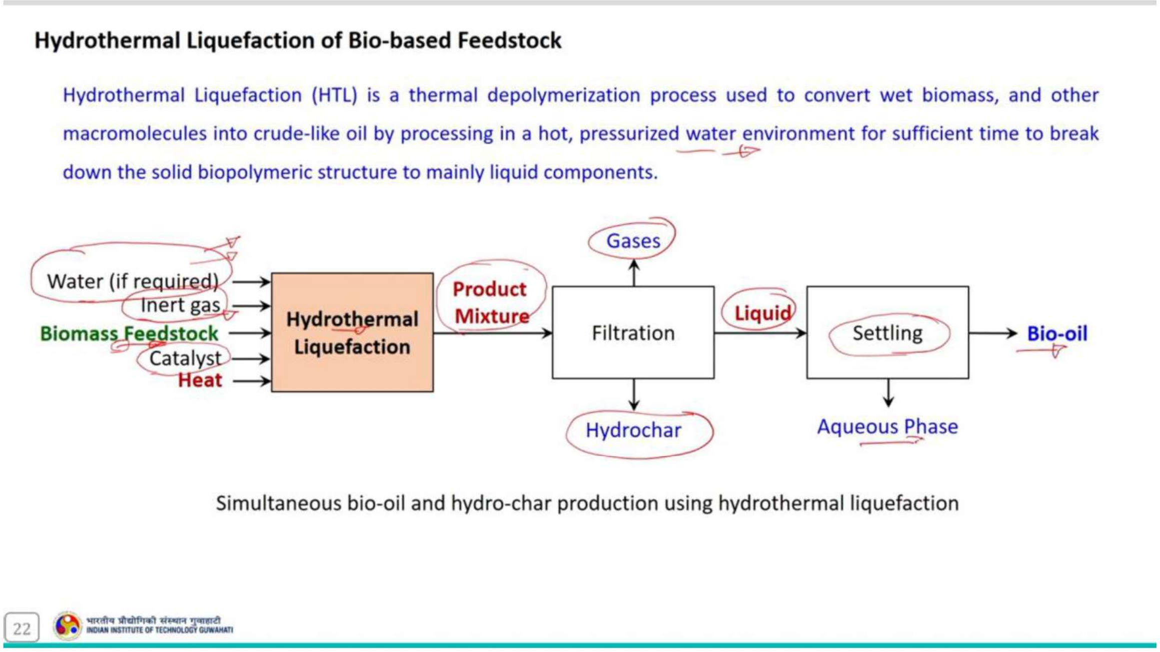

Hydrothermal liquefaction is a thermal depolymerization process which is used to convert the wet biomass and other macromolecules into crude like oil, by processing in a hot and pressurized aqueous medium for sufficient time to break down the solid biopolymeric structure into liquid components. This scheme here it represents the hydrothermal liquefaction of bio-based feedstock which carried out in an aqueous medium as well as in the inert condition. Sometimes, the catalyst is used during the hydrothermal liquefaction of biomass to increase the efficiency and the selectivity of the HTL process. The product mixture obtained at the end of the hydrothermal liquefaction process undergoes the filtration to separate out gases, liquid and hydro char as a product. The liquid obtained from the filtration unit is allowed to settle to separate the bio-oil and the aqueous phase. So this is about the hydrothermal liquefaction process.

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- HTL is an imitation (or simulation) of the geological processes of formation of fossil fuels within the Earth's crust, but at greatly increased speed.
- HTL require heating the biomass, with water and possibly catalysis to temperatures around 300 – 350 °C and pressures ~10 – 25 MPa.
- At these T & P conditions the chemical properties of water catalyze the thermochemical conversion of biomass into oils and residues.
- HTL is also termed as hydrous pyrolysis process, because HTL shares some similarities with conventional pyrolysis, but it takes place under a high-temperature and high-pressure aqueous (hydrous) environment.

Mechanism of Hydrothermal Liquefaction of Biomass

- Understanding the chemistry and mechanism is essential to optimize the HTL process to produce high-quality biofuels, chemicals, and other value-added products.

So hydrothermal liquefaction is an imitation of the geological process of formation of the fossil fuel under the earth crust. But, only difference in the hydrothermal process is it carries out at accelerated rate. The hydrothermal process it requires heating the biomass with water and possibly catalyst to temperatures around 300 to 350 °C and pressure around 10 to 25 mega Pascal. And at this condition the chemical properties of water it catalyzes the thermochemical conversion of biomass into the oil and solid residues. The HTL process it also termed as the hydrous pyrolysis process because the HTL process shares some similarities with the conventional pyrolysis process. But, only difference is it carries out at high temperature, high pressure and in the aqueous environment. That is the only difference between the conventional pyrolysis and the HTL process. Therefore, the understanding of the chemistry and the mechanism of the HTL process is essential, to optimize the HTL process to produce high quality biofuels, chemicals and other value-added products. The chemistry of the HTL process is quite complex and it involves range of the chemical reaction including the hydrolysis of biomass.

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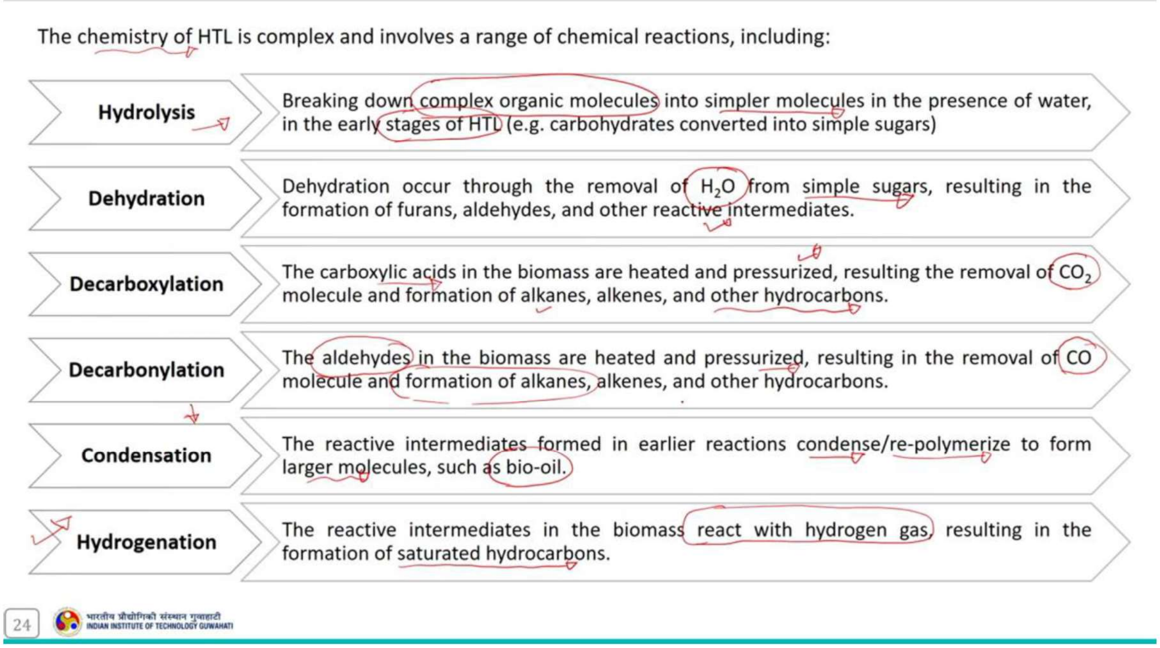

So, during this stage in the HTL process the complex organic molecules are broken down into simpler molecules in presence of water and that is in the early stage of HTL process. Example here, the carbohydrates are converted into the simple sugars followed by the dehydration stage in the HTL process. So, dehydration it occurs through the removal of water from simple sugars resulting in the formation of furans, aldehydes and other reactive intermediates. Followed by dehydration is the decarboxylation and decarboxylation reaction. So, first in the decarboxylation stage, the carboxylic acid in the biomass is heated and pressurized resulting in the removal of carbon dioxide molecule and the formation of alkanes, alkenes and other hydrocarbons. While in the decarboxylation stage, the aldehydes in the biomass are heated and pressurized resulting in the removal of carbon monoxide. So, this is the difference between these two stages in the HTL process. And it forms alkanes, alkenes and again other hydrocarbon compounds. Followed by this is the condensation operation in the HTL process. Here, the reactive intermediates which are formed earlier in the reaction condenses and repolymerize to form larger molecule that is bio oil. Similarly, the reactive intermediates which are formed in the earlier reaction reacts with the hydrogen gas and resulting in the formation of saturated hydrocarbon and that stage is termed as a hydrogenation reaction in the HTL process. This gives the details about the different reaction occurs in the HTL process. Since, the chemistry of the HTL process is complex proper designing and operation of the HTL process is essential to increase the efficiency and selectivity of the HTL process.

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HTL Process Design Aspects

The design of a hydrothermal liquefaction (HTL) process depends on several factors, including:

1. **Reactor type:** HTL reactors can be designed as batch, semi-continuous, or continuous reactors. Batch reactors are the simplest to operate but are limited in terms of throughput, while continuous reactors can handle larger volumes of feedstock but are more complex to operate.
2. **Operating conditions:** The operating conditions of an HTL reactor include temperature, pressure, residence time, and feedstock-to-water ratio. These parameters can be adjusted to optimize the yield and quality of the desired product(s).
3. **Catalyst:** The catalyst can have a significant impact on the efficiency and selectivity of the HTL process.
4. **Heat transfer:** The reactor should be designed to ensure uniform heating of the feedstock and to prevent hot spots that can cause fouling and degradation of the product. MoC: SS, CS, and Ni alloys (Inconel, Monel, Hastelloy, etc.) are commonly used for efficient heat transfer in HTL reactor.

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So, now let us discuss about the HTL process and its design aspects. So, the design of the hydrothermal reaction process it depends on the several factors including the reactor type. HTL reactors can be designed as batch, semi-continuous or continuous reactor. The batch reactors are easy to operate but are limited in terms of throughput. While continuous reactor can handle large volume of feedstock but are complex to operate. Another important factor which need to be considered while designing the HTL process as well as a HTL reactor is the operating condition. The operating condition of HTL reactor include temperature, pressure, residence time and feedstock to water ratio. And this parameter can be adjusted to optimize the yield and quality of the desired products. Sometimes, the catalyst is also used in the HTL process because the use of catalyst can have a significant impact on the efficiency and the selectivity of the HTL process. Apart from that, the heat transfer is also one of the important factors that need to be taken into consideration while designing the HTL reactor. The reactor should be designed to ensure uniform heating of the feedstock and to prevent hot spot that can cause fouling and degradation of the product. In most of the cases the reactors are made up of stainless steel, carbon steel and nickel alloys. And these are the material of construction which are commonly used for the efficient heat transfer in the HTL reactor.

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5. **Safety:** HTL involves high-temperature and high-pressure reactions, which can be hazardous if not properly designed and operated. The reactor should be designed to ensure safe operation and to prevent the release of hazardous gases.

6. **Separation:** The separation of the liquid products from the solid residue and water is a critical step in the HTL process. The reactor design should consider the methods for separating the products and how to recycle the water and residue.

By optimizing the reactor design, the efficiency and selectivity of the HTL process can be improved, leading to the production of high-quality biofuels, chemicals, and other value-added products.

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Another important factor while designing the HTL process as well as the reactor is safety. Because, the HTL process involves relatively harsh condition that is high temperature and high pressure which can be hazardous if not properly designed and operated. The reactor should be designed to ensure safe operation and to prevent the release of hazardous gases from the process. And separation is also one of the most important factors in the HTL process because the separation of the liquid product from the solid and the water is the critical step in the HTL process. And the reactor should have provision or the method for separating the product and how to recycle the water and residue. So, that the water and residue of the previous cycle can be recycle into the next stage of operation in the HTL process. Thus, by optimizing this reactor design, the efficiency and the selectivity of the HTL process it can be improved. And that may lead to the production of high-quality biofuels, chemicals and other value-added products.

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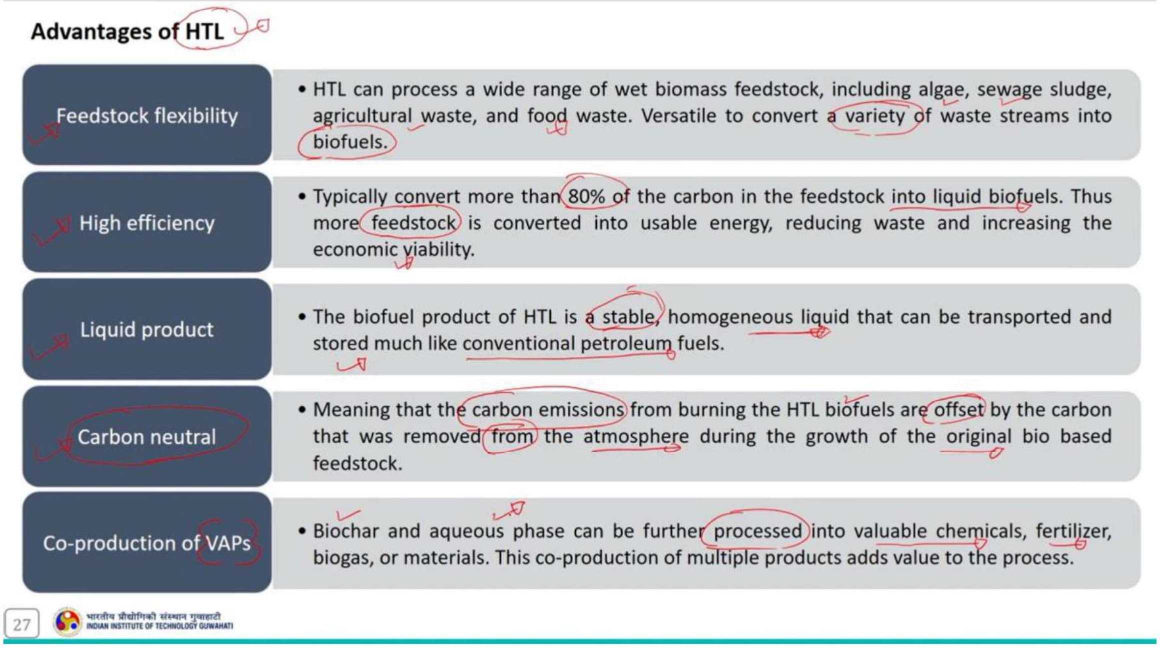

Let us discuss on the advantage of the HTL process. So, the first advantage of the HTL process is feedstock flexibility. That means the HTL can process wide range of the wet biomass feedstock including algae, sewage sludge, agricultural waste and food waste. The HTL process is versatile to convert variety of waste stream into biofuels. High efficiency is another advantage of the HTL process because this process typically converts more than 80 percent of carbon in the feedstock into liquid biofuels. Thus, more feedstock is converted into the usable energy reducing the waste and increasing the economic viability. The liquid product obtained from the HTL process is stable homogeneous liquid that can be transported and stored much like a conventional petroleum fuel. That means, the liquid product obtained after the HTL process after certain upgradation method can be converted into a stable HTL product and homogeneous liquid that can be transported and stored much like a conventional petroleum fuel. Carbon neutral is another advantage of the HTL process and if you recollect we discussed this concept in one of the lectures in module 1.

So, carbon neutral meaning here, the carbon emission from the burning of HTL biofuel are offset by the carbon that was removed from the atmosphere during the growth of this original bio-based feedstock. That is why it is called as a carbon neutral or CO2 neutral. Co-production of the value-added products the biochar, aqueous product can further be processed into valuable chemicals. Or may act as a fertilizer because of the good amount of the nutrient contained in this aqueous phase. It can also be used as a feedstock material for the biogas production and this co-production of multiple products adds value to this HTL process. Apart from the bio-oil, HTL process also produces varieties of the products that is products in the form of aqueous liquid phase product, hydrochar and gaseous product. Let us discuss about these different products and their application in the field of energy as well as in the field of environmental remediation.

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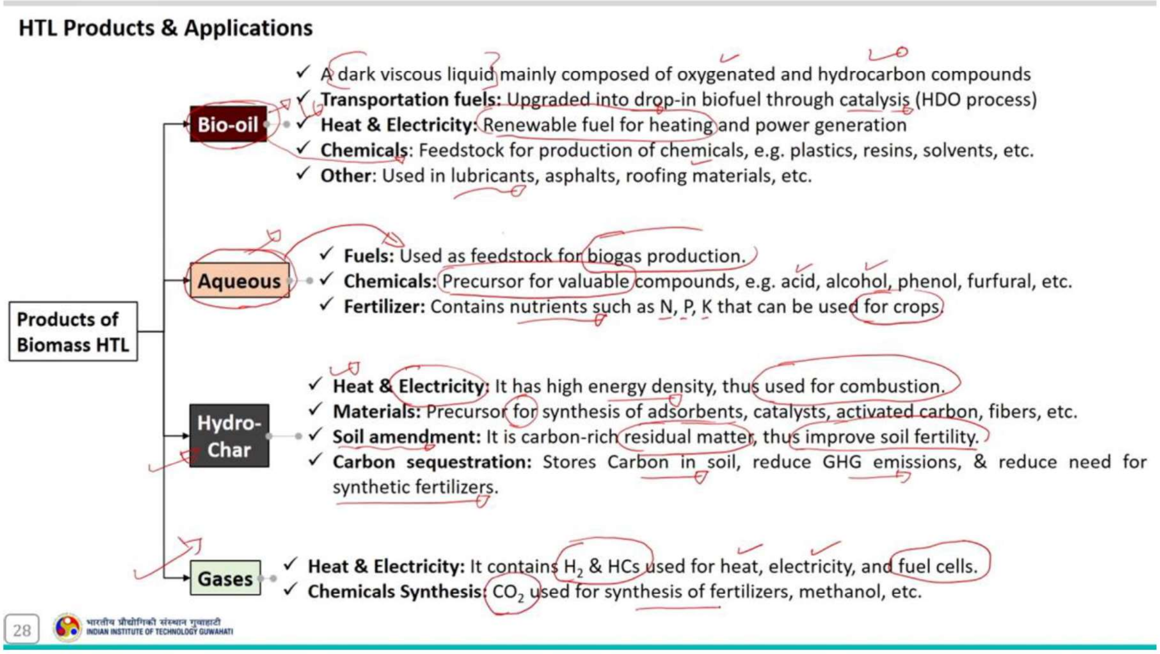

The bio-oil which is a major product of the HTL process is a dark viscous liquid mainly composed of oxygenated and hydrocarbon compounds. The bio-oil produced from the HTL process can be upgraded into drop-in fuel through catalysis so that it can be used as a transportation fuel. It can also be used as a renewable fuel for heating and power generation. The produced bio-oil can also act as a feedstock for the production of chemicals example plastics, resins and solvent. Apart from that, the other application of the bio-oil includes in lubricants, asphalt, roofing material etc. The aqueous product, because of its high nutrient content as well as good amount of the hydrocarbon content can be used as a feedstock for biogas production. It may act as a precursor for valuable compounds example - acid, alcohol, phenol and perfural. Because of its high nutrient content such as N, P and K, the aqueous product can also be used as a fertilizer for crops. Hydrochar is the solid product obtained during the HTL process and since it has a high energy density, it can be used for the combustion purpose to produce the heat. And the produced heat further be processed to generate the electricity. Even the hydrochar may act as a precursor for the synthesis of adsorbents, catalyst, activated carbon and fibers. The produced char is carbon rich residual matter hence it can be used for the soil amendment to improve the soil fertility. The produced char has relatively high surface area and hence it can be used as a carbon sequester which store carbon in the soil reduces greenhouse gas emission and reduce the need for synthetic fertilizers. The gaseous product obtained from the HTL process contains hydrogen and hydrocarbon which can be used for the heat electricity and fuel cell applications. Apart from that, the CO_2 produced during this process can be used for the synthesis of fertilizer and methanol. So, this covers the wide range of application of different HTL products. The bio oil is the major product obtained during the HTL process but the produced bio oil has certain undesirable characteristics and properties which need to be upgraded to improve its fuel quality. The properties of the HTL produced bio oil includes its composition, viscosity, water content, oxygen content, heating value, acidity and instability. So, let us discuss about the undesirable characteristics of HTL produced bio oil, one by one.

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Properties of HTL Biocrude oil

1. **Composition:**
   - ↦ HTL bio-oil is a complex mixture of oxygenates, alkanes, alkenes, aromatics, and heterocyclic compounds.
   - ↦ Exact composition depends on the type of biomass feedstock and the reaction conditions used.
2. **Heating value:**
   - ↦ HTL biocrude oil has a HHV of approximately 10-38 MJ/kg, which is lower than conventional fossil fuels.
3. **Viscosity:**
   - ↦ HTL bio-oil has a high viscosity, which can make it difficult to handle and transport.
   - ↦ Viscosity reduction methods, such as dilution with a solvent or thermal cracking, can improve the fluidity of the bio-oil.
4. **Water content:**
   - ↦ HTL bio-oil typically contains a significant amount of water, which can range from 10-50% by weight.
   - ↦ The presence of water can affect the stability and shelf life of the bio-oil.

Courtesy: Ravichandran et al., Fuel 313 (2022) 122679

So here, so first is the composition. So, HTL produced bio oil is a complex mixture of the oxygenates, alkanes, aromatics and the heterocyclic compounds. And the exact composition of the HTL produced bio oil, it depends on the quality or the type of feedstock which is used during the HTL process as well as the operation conditions and the reaction condition used during the HTL process. So, next important property of the bio oil is the heating value. The HTL bio crude oil has a heating value approximately in the range of 10 to 38 mega joule per kg and it is lower than the conventional fossil fuels high heating value. The viscosity of the HTL produced bio oil is relatively high which make it difficult to handle and transport. HTL produced bio oil also need to be upgraded using the suitable upgradation technique to improve its fuel quality. So, the viscosity reduction method such as dilution that is also termed as a upgradation technique with a solvent or the thermal cracking, need to be implemented to improve the fluidity of the bio oil. The water content in the HTL produced bio oil range from around 10 to 50 percent by weight. And this is because the HTL process is carried out in the aqueous medium. And this results in the increase in the water content in the bio oil. And this presence of water content in the bio oil can affect the stability and the shelf life of the HTL produced bio oil.

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5. **Acidic nature:** HTL bio-oil is typically acidic, with a pH range of 2 – 7. The acidity can cause corrosion and other issues in the downstream processing of the bio-oil.
6. **Instability:** HTL bio-oil is unstable and prone to degradation and polymerization. The stability of the bio-oil can be improved by upgrading the bio-oil into more stable products.
7. **High oxygen content:** HTL bio-oil has a high oxygen content, typically ranging from 35 – 50% by weight. The presence of oxygen can make the bio-oil prone to oxidation and can limit its use as a transportation fuel.

The properties of HTL bio-oil depend on the specific biomass feedstock and the reaction conditions used. HTL biocrude oil has the potential to be a valuable feedstock for the production of high-value chemicals and other products.

The HTL produced bio oil is also acidic in nature and the pH of this bio oil varies in the range of 2 to 7. And this increase acidity can cause corrosion and other issues in the downstream processing of the bio oil. And this is also one of the undesirable characteristics of the HTL produced bio oil which need to be upgraded using the suitable upgradation technique to improve its fuel quality. The next is the instability. The HTL bio oil is unstable and it is prone to degradation and the polymerization. And this stability of the bio oil it can be improved by upgrading the bio oil into more stable product. And high oxygen content is one of the most undesirable property or characteristics of bio oil. Because the HTL produced bio oil has a high oxygen content which is similar to that of the bio oil produced using a conventional pyrolysis process. And typically, it ranges from 35 to 50 percent by weight. And the presence of oxygen it can make the bio oil prone to oxidation and can limits its used as a transportation fuel. And since this property of the HTL bio oil are mostly depends on the feed stock and the reaction condition used. Therefore, large variation can be seen in the HTL produced bio oil. The HTL bio crude oil has the potential to be valuable feed stock for the production of high value chemicals and other products.

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Comparison of bio-oil with conventional fuels

Property	HHV	Water	Ash	C	H	N	O	S
Unit	MJ/kg	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%
Pyrolysis Bio-oil	16.5–19	15–35	0.01–0.5	50–64	5–7	0.05–6	35–40	0–0.05
HTL Bio-oil	30–38	2–13	0.1–4.5	67–80	6–10	0.5–4	5–23	0.3–0.5
Fossil crude oil	42–45	0.1–1.5	0.03–0.07	84–87	12–15	<0.004	–	0.002–4
Diesel (EN590)	44–46	<0.02	<0.01	87	13	–	–	<0.0015

Property	Density (15 °C)	Kin. Viscosity (40 °C)	Flash point	Acidity	TAN	C - Residue
Unit	kg/dm^3	mm^2/s	°C	pH	mg KOH/g	wt%
Pyrolysis Bio-oil	1.10–1.30	15–35	70–150	2–3	60–140	11–13
HTL Bio-oil	0.8–1.1	110–350	100–150	2–7	7–100	17–24
Fossil crude oil	0.75–1	0.5–130	–	–	0.01–3.0	0–12
Diesel (EN590)	0.842	2–4.5	67	NA	–	<0.3

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Courtesy: Chiaramonti et al., Applied Energy 2017, 185, 963 / Haarlemmer et al., Fuel 2016, 174, 180–188

This table here it depicts the comparison of pyrolytic bio oil with that of the HTL produced bio-oil, fossil crude oil and the conventional fuel. So, from this table, it appears that the higher heating value of the pyrolytic bio oil is relatively low compare to that of the other bio oils as well as the crude oil from the fossil source. Even the carbon content in the pyrolytic bio oil is lower than that of the HTL produced bio oil as well as the crude oil from the fossil source. While the oxygen content and the water content are relatively higher in the pyrolytic bio oil compare to that of the HTL produced bio oil as well as the fossil based crude oil. Similarly, in terms of the property, the density of the pyrolytic oil is relatively higher than that of the HTL produced bio oil as well as the fossil based crude oil. And in terms of the acidity, the acidity of the pyrolytic oil is quite low compare to that of the HTL produced bio oil. However, the residual matter contained in the HTL produced bio oil is relatively higher than that of the pyrolytic bio oil. This gives the details about the pyrolysis process and the HTL process.

So, in the next lecture, which is the second lecture of the module 4, we will discuss about the gasification upstream and downstream processing, comparison of the conventional gasification with the sub- and supercritical water gasification and plasma gasification processes.

Thank you.