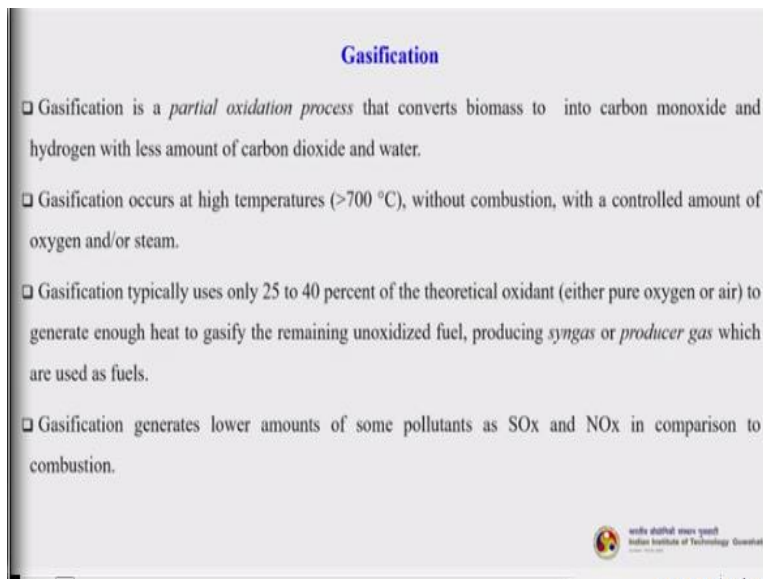


Biomass Conversion and Biorefinery
Prof. Kaustubha Mohanty
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Module 05
Lecture-14
Gasification and Pyrolysis


Good morning students this is lecture 2 under module 5. And as you know that we are discussing biomass physicochemical and thermochemical conversion in this module. And today's class is an important one in which we will be discussing about 2 most important thermochemical conversion processes, one is gasification and another is pyrolysis, so let us begin.

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Gasification

- ❑ Gasification is a *partial oxidation process* that converts biomass to into carbon monoxide and hydrogen with less amount of carbon dioxide and water.
- ❑ Gasification occurs at high temperatures ($>700\text{ }^{\circ}\text{C}$), without combustion, with a controlled amount of oxygen and/or steam.
- ❑ Gasification typically uses only 25 to 40 percent of the theoretical oxidant (either pure oxygen or air) to generate enough heat to gasify the remaining unoxidized fuel, producing *syngas* or *producer gas* which are used as fuels.
- ❑ Gasification generates lower amounts of some pollutants as SO_x and NO_x in comparison to combustion.

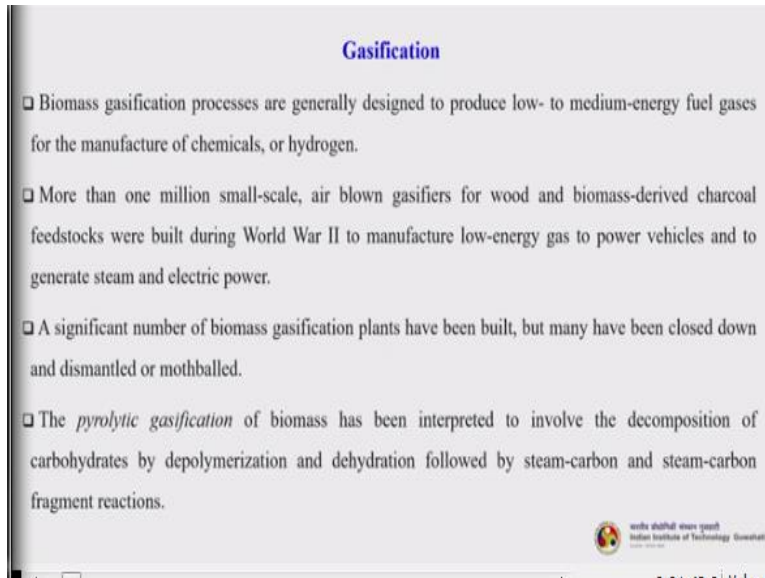
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So, gasification is a partial oxidation process that converts biomass into carbon monoxide and hydrogen with less amount of carbon dioxide and water. Now this process occurs at high temperatures (above 700 degrees centigrade) without combustion, with a controlled amount of oxygen and/or steam. Gasification typically uses only 25 to 40% of the theoretical oxidant - it can be either pure oxygen or air - to generate enough heat to gasify the remaining unoxidized fuel producing syngas or producer gas which are used as fuels.

Gasification generates lower amounts of some pollutants such as SO_x and NO_x in comparison to combustion. Now basically combustion is a full oxidation process in which all the biomass is


completely oxidized, whereas in gasification, we use less than theoretical oxygen that is required, for the partial oxidation process.

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Gasification

- Biomass gasification processes are generally designed to produce low- to medium-energy fuel gases for the manufacture of chemicals, or hydrogen.
- More than one million small-scale, air blown gasifiers for wood and biomass-derived charcoal feedstocks were built during World War II to manufacture low-energy gas to power vehicles and to generate steam and electric power.
- A significant number of biomass gasification plants have been built, but many have been closed down and dismantled or mothballed.
- The *pyrolytic gasification* of biomass has been interpreted to involve the decomposition of carbohydrates by depolymerization and dehydration followed by steam-carbon and steam-carbon fragment reactions.

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So, biomass gasification processes are generally designed to produce low or medium energy fuel gases for the manufacturer of chemicals or hydrogen. More than one million small scale, air blown gasifiers for wood and biomass derived charcoal feedstocks were built during World War II to manufacture low energy gas to power vehicles and to generate steam and electric power.

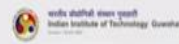
A significant number of biomass gasification plants have been built but many have been closed down and dismantled or mothballed. The pyrolytic gasification of biomass has been interpreted to involve the decomposition of carbohydrates by depolymerization and dehydration followed by steam carbon or steam carbon fragmentation reactions. So, pyrolytic gasification is a type of gasification process.

I would like to say during this discussion is that, pyrolysis, though it is a separate thermochemical conversion process, but whenever gasification is actually happening, so the second step is the pyrolysis reaction. So, before the gasification reaction really begins, so pyrolysis happens. We will discuss in our subsequent discussion today, when we will talk about the reaction mechanisms, then it will be a little more clear.

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Gasification

- Some of the coal gasification processes are also suitable for biomass feedstocks. Since the conditions required for coal gasification are more severe than those needed for biomass, some coal gasifiers can be operated on biomass or biomass-coal feedstock blends.
- Indeed, some gasifiers that were originally designed for coal gasification are currently in commercial use with biomass feedstocks.
- The chemistries of coal and biomass gasification are quite similar in terms of the steam carbon chemistry and are essentially identical after a certain point is reached in the gasification process.
- Note, however, that *biomass is much more reactive than most coals*. Biomass contains more volatile matter than coal, and the pyrolytic chars from biomass are more reactive than pyrolytic coal chars.



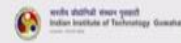
So, some of the coal gasification processes are also suitable for biomass feedstocks. Since the conditions required for coal gasification are more severe than those needed for biomass, some coal gasifiers can be operated on biomass or biomass-coal feedstock blends. Indeed, some gasifiers that were originally designed for coal gasification are currently in commercial use with biomass feedstock because coal is being depleting day by day.

The chemistries of coal and biomass gasification are quite similar in terms of the steam carbon chemistry, and are essentially identical after a certain point is reached in the gasification process. Note, however, that biomass is much more reactive than most of the coals. Biomass contains more volatile matter than coal, and the pyrolytic chars from biomass are more reactive than pyrolytic coal chars.

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Gasification

- The thermodynamic equilibrium concentrations of specific gases in the mixture depend on the abundance of carbon, hydrogen, and oxygen, the temperature, and the pressure.
- Biomass is gasified at lower temperatures than coal because its main constituents, the high-oxygen cellulose and hemicellulose, have higher reactivity than the oxygen-deficient, carbonaceous materials in coal.
- The addition of co-reactants to the biomass system, such as oxygen and steam, can result in large changes in reaction rates, product gas compositions and yields, and selectivity as in coal conversion.
- Biomass feedstocks contain a high proportion of volatile material, 70 to 90% for wood compared to 30 to 45% for typical coals.



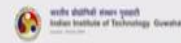
The thermodynamic equilibrium concentrations of specific gases in the mixture depend on the abundance of carbon, hydrogen and oxygen, the temperature, as well as the pressure. Biomass is gasified at lower temperatures than coal because its main constituents, the high-oxygen cellulose and hemicellulose, have higher reactivity than oxygen-deficient carbonaceous materials in the coal.

In addition of co-reactants to the biomass system, such as oxygen and steam, can result in large changes in reaction rates, product gas compositions and yields and selectivity as in coal conversion. Biomass feedstocks contain a high proportion of volatile materials 70 to 90% for wood, compared to 30 to 45% for typical coals.

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Gasification

- ❑ A relatively large fraction of most biomass feedstocks can be devolatilized rapidly at low to moderate temperatures, and the organic volatiles can be rapidly converted to gaseous products.
- ❑ The chars formed on pyrolytic gasification of most biomass feedstocks have high reactivity and gasify rapidly.
- ❑ For biomass and waste biomass, steam gasification generally starts at temperatures near 300 to 375 °C.
- ❑ Undesirable emissions and by-products from the thermal gasification of biomass can include particulates, alkali and heavy metals, oils, tars, and aqueous condensates.



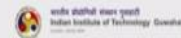
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Undesirable emissions and byproducts from the thermal gasification of biomass can include particulates, alkali and heavy metals oils, tars and some aqueous condensates.

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Gasification

- ❑ It is important to avoid gas turbine blade erosion and corrosion by removing undesirable particulates that may be present.
- ❑ The removal of tars and condensable gases may also be necessary. Furthermore, utilization of the sensible heat in the product gas improves the overall thermal operating efficiencies. Non-turbine applications of the gas may also be able to take advantage of processes that provide clean, pressurized hot gas, such as certain downstream chemical syntheses and fuel uses.
- ❑ Research on thermal biomass gasification in North America has tended to concentrate on medium-energy gas production, scale-up of advanced process concepts that have been evaluated at the PDU scale, and the problems that need to be solved to permit largescale thermal biomass gasifiers to be operated in a reliable fashion for power production, especially for advanced power cycles.

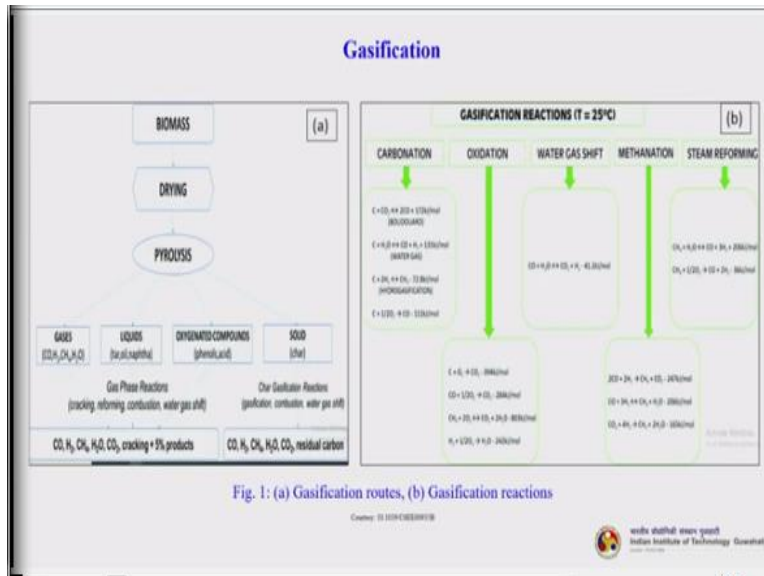


It is important to avoid gas turbine blade corrosion and corrosion by removing undesirable particulates that maybe present. The removal of tars and condensable gases may also be necessary. Furthermore, utilization of the sensible heat in the product gas improves the overall thermal operating efficiencies. Non turbine applications of the gas may also be able to take advantages of the process that provide clean, pressurized hot gas such, as certain downstream chemical syntheses and fuel uses.

So, what happens, basically when the gasification is happening in a gasifier any type of gasifier we will also discuss in our class today, what are the different types of gasifiers available and of course, pyrolysis reactors are pyrolysis. So, there are many obnoxious byproducts that actually getting formed including some of the tar also. So, these needs to be removed frequently otherwise it will create a problem inside the reactor.

So, the reactor vessel will corrode if there are some corroding elements present and if you do not take it out from for a prolonged time and they keep on presenting then there cannot be a proper reaction will proceed basically. So, research on thermal biomass gasification in North America has tended to concentrate on medium energy gas production, scale-up of advanced process concepts that have been evaluated at the PDU scale, and the problems that need to be solved to permit large scale thermal biomass gasifiers to be operated in a reliable fashion for power production, especially for advanced power cycles. So, PDU means the power distribution unit.

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So, this is a typical scheme please have a look. The first one here, it talks about the gasification routes, the second one is about the gasification reactions, we will discuss that in detail in our next slide. So, let us understand this is what I was telling you that pyrolysis is a part of the entire gasification process if you stop here and do only pyrolysis then it becomes a pyrolysis reaction and then subsequent products.

But then if you go on for the next step, that step is basically the gasification process, let us understand. So, biomass needs to be dried for any thermochemical conversion process, we have discussed last class in one of the pretreatment classes, we have discussed that biomass needs to be dried to a particular moisture level otherwise the reaction may not proceed in a proper direction, so it is dried then it goes for pyrolysis.


So, after pyrolysis there may be so many different types of things you can see that gases, liquids, oxygenated compounds and solid is basically the char. So, if you go for a gas phase reactions like cracking, reforming, combustion, water gas shift reactions, you get carbon monoxide, hydrogen, methane, water, carbon dioxide and some other smaller components. If you go for the char gasification reactions, so you get carbon monoxide, hydrogen, methane, water carbon dioxide, residual carbon.

So, if you talk about the product, the product from the gasification is mostly the syngas/synthesis gas or maybe producer gas. So, these are some of the reactions that happen actually the carbonation reaction, oxidation reaction, water gas shift reaction - water gas shift reaction takes place at very high temperature, then methanation and steam reforming. So, this is given in detail we will see in the next slide the reactions.

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Gasification Reactions

- 1) The first reaction is *dehydration or drying process* that occurs at around 100 °C. The resulted steam is then mixed into the gas flow and may be involved with subsequent chemical reactions, predominantly the water-gas reaction if high temperature exists.
- 2) The second step is *pyrolysis (or devolatilization)* that occurs at around 200–300 °C. This process releases the volatiles thereby producing char as an effect almost 70% weight loss. The process is dependent on the properties of the biomass which eventually determines the structure and composition of the char.
- 3) The char then undergoes *combustion reactions* to primarily form carbon dioxide and small amounts of carbon monoxide, that provides heat for the subsequent gasification reactions.
- 4) The *gasification process* occurs as the char reacts with steam and carbon dioxide to produce carbon monoxide and hydrogen.
- 5) The reversible gas phase *water-gas shift reaction* reaches equilibrium very fast at higher temperatures thereby balancing the concentrations of carbon monoxide, steam, carbon dioxide and hydrogen.



The diagram illustrates the gasification process. It starts with biomass (represented by a pile of wood) being converted into char (represented by a pile of black material). From the char, three arrows point to the products: H₂, CO, and CO₂. Above the char, there are labels for H₂O and O₂, indicating the reactants. The diagram also shows a cloud of gases containing H₂, CH₄, and Tar, which are released from the biomass. The process is labeled 'Gasification Reactions' and includes a logo for the Indian Institute of Technology Guwahati.

So, 4 to 5 different types of reactions happen. The first one is the dehydration or the drying process as I have shown you here, the drying process. So, that occurs at around 100 degrees centigrade, so the resulted steam is then mixed into the gaseous flow and maybe involved with subsequent chemical reactions predominantly the water gas reaction if high temperature actually exists.

So, after that the biomass or whatever the vapor that is getting generated actually that goes to the pyrolysis step, which is called as devolatilization state. So that occurs between 200 to 300 degrees centigrade, sometimes up to 350 degrees also. This process releases the volatiles, thereby producing char as an effect almost 70% weight loss. So, char is getting produced because there is severe weight loss almost approximately up to 70%.

The process is, however dependent on the properties of the biomass which eventually determines the structure and composition of the char. Then in the next step it goes to the combustion

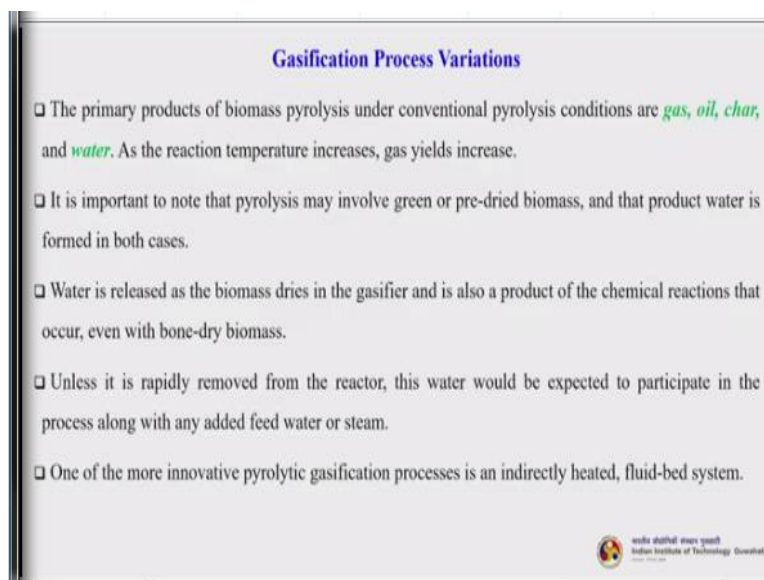
reaction. So, the char then undergoes the combustion reactions to primarily form carbon dioxide and small amounts of carbon monoxide that provides heat for the subsequent gasification reactions.

So, you can see that here the fuel, let us understand it is a dry fuel or after the drying fuel, then when the devolatilization or the pyrolysis reaction is proceeding we get char. And some of the tars and hydrogen, some methane, some gases - you can trap it or you can leave it depending upon how much you are producing. Then this char subsequently goes for the combustion reaction and gasification reactions.

So, the gasification process occurs as the char reacts with steam and carbon dioxide to produce carbon monoxide and hydrogen. Now there is a reversible gas phase water shift reaction which we talked in the step one also. And this happens at very high temperatures, and this reaction, water gas shift reaction reaches equilibrium very fast when the temperature is very high thereby balancing the concentrations of carbon monoxide, steam, carbon dioxide and hydrogen.

The major product of syngas or synthesis gas is of course carbon monoxide and hydrogen, and if certain amount of carbon comes into contact with a proper amount of oxygen and get combusted then it will result in some amount of carbon dioxide.

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Gasification Process Variations

- ❑ The primary products of biomass pyrolysis under conventional pyrolysis conditions are *gas, oil, char,* and *water*. As the reaction temperature increases, gas yields increase.
- ❑ It is important to note that pyrolysis may involve green or pre-dried biomass, and that product water is formed in both cases.
- ❑ Water is released as the biomass dries in the gasifier and is also a product of the chemical reactions that occur, even with bone-dry biomass.
- ❑ Unless it is rapidly removed from the reactor, this water would be expected to participate in the process along with any added feed water or steam.
- ❑ One of the more innovative pyrolytic gasification processes is an indirectly heated, fluid-bed system.

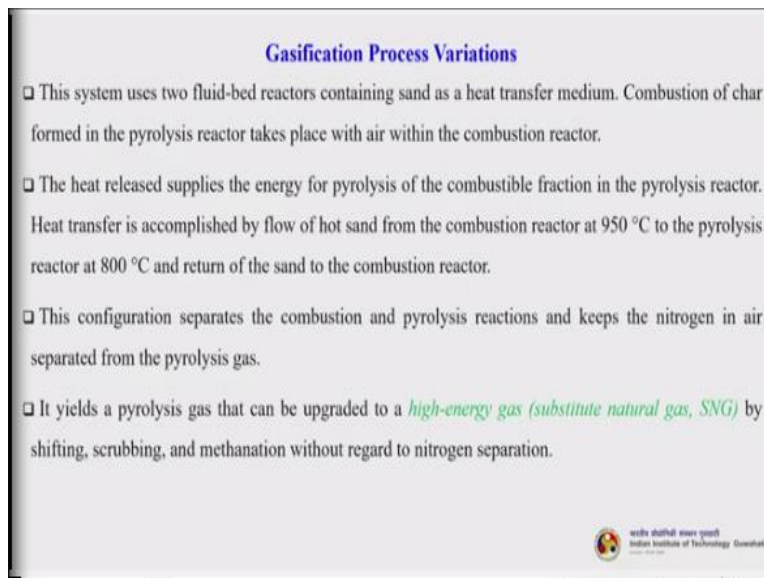
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So, let us understand the different types of gasification process variations. So, the primary products of biomass pyrolysis under conventional pyrolysis conditions are gas, oil, char and water. As the reaction temperature increases, gas yield increases. That means what predominantly it means, when you stop during pyrolysis - at the pyrolysis reaction that the entire thermochemical conversion process becomes pyrolysis process.

Then you will get gas, oil, char and water, that is what we get from the pyrolysis reaction. But when we are proceeding in a gasifier and doing the gasification reactions, so then we will get the gases - there will be more gaseous product yield. So, it is important to note that pyrolysis may involve green or pre dried biomass and that product water is formed in both cases.

Water is released as the biomass dries in the gasifier and is also a product of a chemical reaction that occur even with bone dry biomass, even if the dry biomass is almost close to 95, 98% or close to 99% dry. So, unless it is rapidly removed from the reactor, this water would be expected to participate in the process along with any added feed water or steam. One or one of the more innovative pyrolytic gasification process is an indirectly heated fluid bed system, we will discuss about that later.

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Gasification Process Variations

- This system uses two fluid-bed reactors containing sand as a heat transfer medium. Combustion of char formed in the pyrolysis reactor takes place with air within the combustion reactor.
- The heat released supplies the energy for pyrolysis of the combustible fraction in the pyrolysis reactor. Heat transfer is accomplished by flow of hot sand from the combustion reactor at 950 °C to the pyrolysis reactor at 800 °C and return of the sand to the combustion reactor.
- This configuration separates the combustion and pyrolysis reactions and keeps the nitrogen in air separated from the pyrolysis gas.
- It yields a pyrolysis gas that can be upgraded to a *high-energy gas (substitute natural gas, SNG)* by shifting, scrubbing, and methanation without regard to nitrogen separation.

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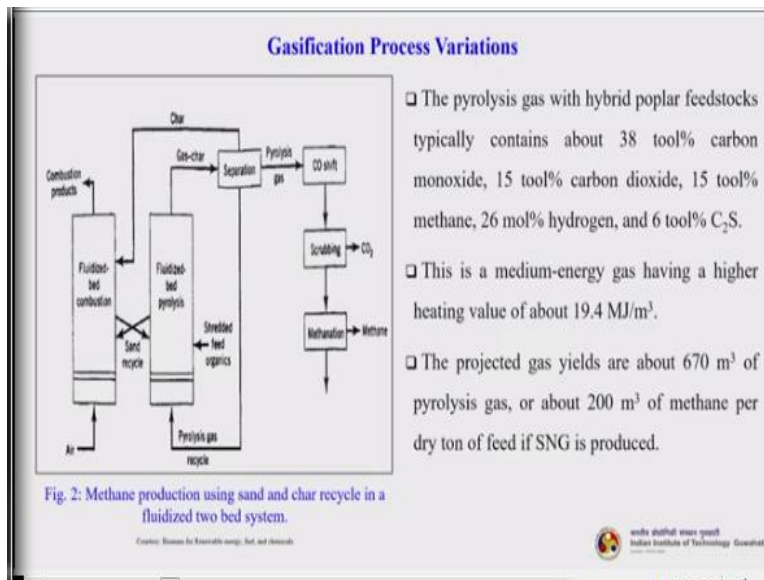
Now this system uses two fluid bed reactors containing sand as a heat transfer medium. Now sand holds the heat for a long time and it is a good medium for doing the heat transfer. So, that is

why it is being used and it is low cost readily available can be recycled back. So, combustion of char formed in the pyrolysis reactor takes place with air within the combustion reactor. The heat released supplies the energy of pyrolysis of the combustible fraction in the pyrolysis reactor.

Heat transfer is then accomplished by flow of hot sand from the combustion reactor at 950 degrees centigrade to the pyrolysis reactor at 800 degree centigrade and then the sand can be returned back or recycled back to the combustion reactor. So, this configuration separates the combustion and pyrolysis reactions, that means predominantly instead of a single gasifier under which drying pyrolysis, gasification, combustion everything is happening you have 2 different reactors.

In which in one reactor pyrolysis is happening and another reactor combustion is happening. And it yields a pyrolysis gas that can be upgraded to a high energy gas, which is a *substitute natural gas* is called **SNG** by shifting, scrubbing and methanation with regard to nitrogen separation. So, there are certain the shifting, scrubbing, methanation are the polishing steps.

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So, let us have a look at this particular 2 bed fluidized reactor system which is being used to produce methane. So, you can see this, this is the fluidized bed combustion process, this is the fluidized bed pyrolysis process, both are using the sand. The sand is as a heating medium and the

sand is getting interchanged or recycled between these 2 beds. So, when the air is supplied to combustion reactor, whatever you get is the combustible products.


Then this one, under the pyrolysis reaction, the shredded feed organics are being actually fed your feedstock, so and whatever you get is basically the gas and char. Now under there is a separator, the separator actually separates that char and the gas phase, so the gas phase means the pyrolysis gas phase. Then it goes to the some shifting reactions, carbon monoxides, scrubbing to remove carbon dioxide, then methanation reaction to get methane, pure methane, you have to purify it and part of the pyrolysis gas is being recycled to maintain the reaction conditions inside the pyrolysis reactor. And the char is getting fed to the combustion reactor where it is undergoing the gasification reaction. So, the pyrolysis gas with hybrid popular feedstocks typically contains about 38% carbon monoxide, 15% carbon dioxide, 15% methane, 26 mole percent of hydrogen and 6% of C_2S .

Now this is a medium energy gas having a higher heating value of about 19.4 mega joule per meter cube. The projected gas yields are about 670 meter cube of pyrolysis gas or about 200 meter cube meter of methane per dry ton of feed is SNG is produced, substitute natural gas. It is a very nice process.

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Gasification (Partial Oxidation)

- ❑ Many thermal conversion processes can be classified as *partial oxidation processes* in which the biomass is supplied with less than the stoichiometric amount of oxygen needed for complete combustion.
- ❑ When the oxygen is supplied by air, low energy gases are formed that contain higher concentrations of hydrogen, carbon monoxide, and carbon dioxide than medium-energy gases. When pure oxygen or oxygen-enriched air is used, gases with higher energy values can be obtained.
- ❑ In some partial oxidation processes, the various chemical reactions may occur simultaneously in the same reactor zone.
- ❑ In others, the reactor may be divided into zones: *A combustion zone that supplies the heat to promote pyrolysis in a second zone, and perhaps to a third zone for drying*, the overall result of which is partial oxidation.

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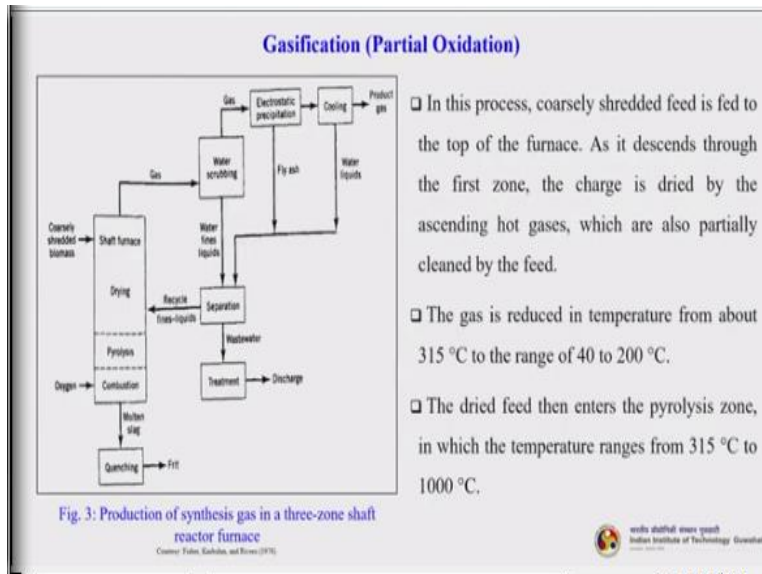
So, many thermal conversion processes can be classified as partial oxidation processes in which the biomass is supplied with less than the stoichiometric amount of oxygen needed for complete combustion. When the oxygen is supplied by air, low energy gases are formed that contain higher concentrations of hydrogen, carbon monoxide and carbon dioxide than medium energy gases.

When we use pure oxygen or oxygen enriched air or even air also gases with higher energy values can be obtained. In some or certain partial oxidation processes, the various chemical reactions may occur simultaneously in the same reactor zone. Most of the time you will understand that the gasification process is being done in a single gasifier, in a single reactor let us called it single reactor all sorts of reactions are happening there are different zones.

But what we have discussed is just before this last slide about the 2 fluidized bed systems that has essentially done to produce when you look for 2 different things, one is this syngas, producer gas whatever it is and one is the pure methane. So, that was particularly aimed to produce methane as well as the usual syngas, so then you go for a 2 bed systems.

Otherwise if you are looking for a syngas whether high quality energy carrier or low energy carrier gas whatever it is depending upon the feedstock and other process conditions a single gasifier is more than enough. So, in others the reactor maybe divided into zones that is what I was just telling - a combustion zone that supplies the heat to promote the pyrolysis in a second zone, and perhaps a third zone for drying, the overall result of which is partial oxidation.

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- In this process, coarsely shredded feed is fed to the top of the furnace. As it descends through the first zone, the charge is dried by the ascending hot gases, which are also partially cleaned by the feed.
- The gas is reduced in temperature from about 315 °C to the range of 40 to 200 °C.
- The dried feed then enters the pyrolysis zone, in which the temperature ranges from 315 °C to 1000 °C.

So, this is another example of the partial oxidation process, so here the production of synthesis gas in a three zone shaft reactor furnace. Please understand that it is a three zone shaft reactor, but it is a single reactor. Now let us understand, so the three zone, so here you feed the biomass. So, the biomass is being feed, this is that zone which is responsible for the first reaction that is that drying zone.

Then comes the second zone that is the pyrolysis zone, then it comes to the third zone where oxygen or air enriched with oxygen is being fed to do the combustion process in a of course less than theoretical demand. So, whatever you get is basically the molten slag, then it goes to feed quenching and the gas will be recovered here on the top of the reactor.

Then it goes to water scrubbing and you get a downstream part of that or the bottom product is being separated and recycled. So, this is the fine liquid that is getting recycled, the wastewater is again treated and then discharged. And whatever is coming here is the almost pure gas after the water scrubbing, then it goes to electrostatic precipitation to remove fly ash and other certain components.

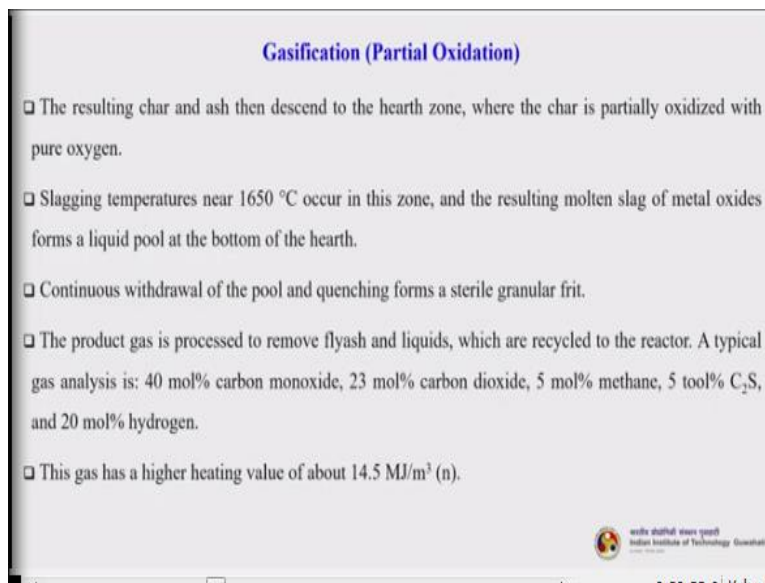
Then you cool it and you get product gas and whatever during the cooling process certain amount of moisture whatever it is actually still remains in the gas phase will condense and then that can be fed back to the separation unit. So, in this process, coarsely shredded feed is fed to

the top of the furnace. As it descends to the first zone the charge is dried by the ascending hot gases which are partially cleaned by the feed.

So, please try to understand what is happening here, you feed it, so when you feed initially here drying is happening. So, the drying is happening then pyrolysis combustion, when the pyrolysis and combustion reaction is happening at the bottom portion, the gas is moving upward. So, this gas is also doing the drying process, correct, do you understand this? So, that means in a single thing you do not have to supply extra energy or heat to take care of the drying process.

The product gas whatever is producing that is doing the drying. So, the gas is reduced in temperature from about 315 degrees centigrade to the range of 40 to 200 degrees centigrade. The dried feed then enters the pyrolytic zone in which temperature ranges from 315 to 1000 degrees centigrade. Again depending on what feed you are using, for different feedstocks the temperature may vary.

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Gasification (Partial Oxidation)

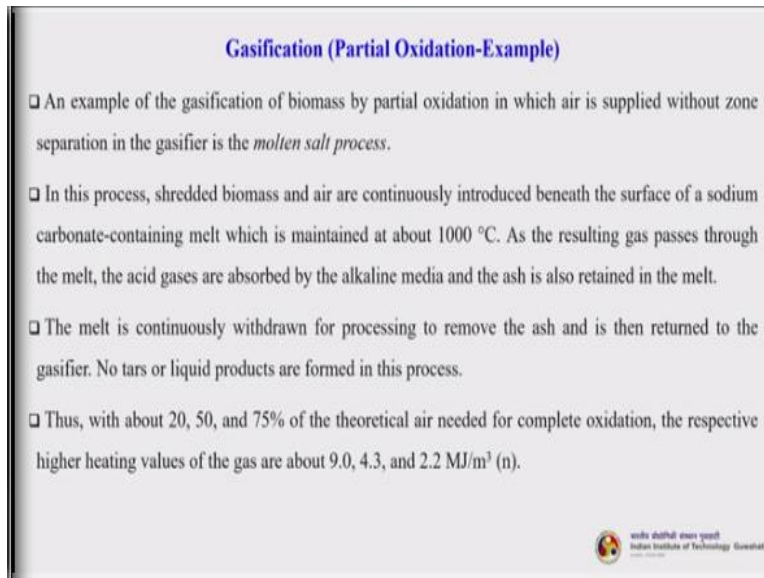
- The resulting char and ash then descend to the hearth zone, where the char is partially oxidized with pure oxygen.
- Slagging temperatures near 1650 °C occur in this zone, and the resulting molten slag of metal oxides forms a liquid pool at the bottom of the hearth.
- Continuous withdrawal of the pool and quenching forms a sterile granular frit.
- The product gas is processed to remove flyash and liquids, which are recycled to the reactor. A typical gas analysis is: 40 mol% carbon monoxide, 23 mol% carbon dioxide, 5 mol% methane, 5 mol% C₂S, and 20 mol% hydrogen.
- This gas has a higher heating value of about 14.5 MJ/m³ (n).

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So, the resulting char and ash then descend to the hearth zone, where the char is partially oxidized with pure oxygen, the hearth is that the bottom zone basically. Slagging temperatures near 1650 degrees centigrade occur in this zone, and the resulting molten slag of metal oxide forms a liquid pool at the bottom of the hearth. Continuous withdrawal of the pool and quenching forms a sterile granular frit.

The product gas is processed to remove fly ash and liquids, which are recycled to the reactor. A typical gas analysis is almost 40 mole percent of carbon monoxide, 23 mole percent of carbon dioxide, 5 mole percent of methane, 5 mole percent of C_2S and 20 mole percent of hydrogen. This gas has higher heating value of about 14.5 mega joule per meter cube.

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Gasification (Partial Oxidation-Example)

- An example of the gasification of biomass by partial oxidation in which air is supplied without zone separation in the gasifier is the *molten salt process*.
- In this process, shredded biomass and air are continuously introduced beneath the surface of a sodium carbonate-containing melt which is maintained at about 1000 °C. As the resulting gas passes through the melt, the acid gases are absorbed by the alkaline media and the ash is also retained in the melt.
- The melt is continuously withdrawn for processing to remove the ash and is then returned to the gasifier. No tars or liquid products are formed in this process.
- Thus, with about 20, 50, and 75% of the theoretical air needed for complete oxidation, the respective higher heating values of the gas are about 9.0, 4.3, and 2.2 MJ/m³ (n).

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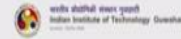
An example of the gasification of biomass by partial oxidation in which air is supplied without zone separation in the gasifier is the molten salt process. In this process, shredded biomass and air are continuously introduced beneath the surface of a sodium carbonate containing melt which is maintained at about 1000 degrees centigrade. As the resulting gas passes through the melt the acid gases are absorbed by the alkaline media and the ash is also retained in the melt.

The melt is continuously withdrawn for processing to remove the ash and is then returned to the gasifier. No tars or liquid products are formed in this process. Thus, with about 20, 15, 75% of the theoretical air needed for complete oxidation, the respective higher heating values of the gas are about 9, 4.3, 2.2 mega joules per meter cube.

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Biomass Gasifier Design

- Basically, biomass gasifiers can be categorized into several reactor design groups: a descending bed of biomass, often referred to as a *moving or fixed bed*, with counter-current gas flow (updraft); a descending bed of biomass with co-current gas flow (downdraft).
- A descending bed of biomass with crossflow of gas; a fluidized bed of biomass with rising gas; an entrained-flow circulating bed of biomass; and tumbling beds.
- The designs include *fixed-bed, moving-bed, suspended-bed, and fluid-bed reactors; entrained-feed solids reactors; stationary vertical-shaft reactors; inclined rotating kilns; horizontal-shaft kilns; high-temperature electrically heated reactors with gas-blanketed walls; single and multihearth reactors; ablative, ultrafast, and flash pyrolysis reactors*; and several other designs.
- There are clearly numerous reactor designs and configurations for biomass gasification, probably more than in the case of coal gasification systems because of the relative ease of thermal biomass conversion.



Basically, biomass gasifiers can be categorized into several reactor design groups. A descending bed of biomass often referred to as a moving or fixed bed with counter current gas flow updraft and a descending bed of biomass with counter current gas flow that is called downdraft. A descending bed of biomass with crossflow gas, a fluidized bed of biomass with rising gas and entrained flow circulating bed of biomass and a tumbling beds, there are various types of arrangements can be possible.

So, some of the designs that are being tested and are commercialized are fixed bed, moving beds, suspended bed, fluid bed reactors, entrained feed solid reactor, stationary vertical shaft reactors, inclined rotating kilns, horizontal shaft kilns, high temperature electrically heated reactors with gas blanketed walls, single and multi hearth reactors, ablative, ultrafast and flash pyrolysis reactors and several other designs.

You can see that there are so many different types of designs of the reactors that is already been tested. There are clearly numerous reactor designs and configurations for biomass gasification probably more than in the case of coal gasification systems because of the relative ease of thermal biomass conversion.

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Biomass Gasifier Design

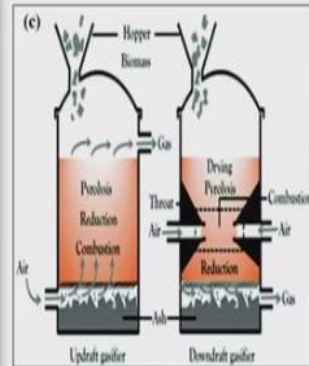


Fig. 4: Difference between updraft and downdraft fixed bed gasifiers

Courtesy: IS 1100/GEDD/0108



□ Briefly, a fixed-bed gasifier can be either *updraft* (fuel enters from the top, gasifying agent from the bottom) or *downdraft* (both fuel and gasification agent enter from the top), with the fuel coming in from a lock-hopper.

□ In updraft gasification, the char at the bottom of the bed meets the gasifying agent first, and complete combustion occurs, producing H_2 and CO_2 and raising the temperature to $\sim 1000^\circ C$.

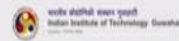
So, let us now understand the different biomass gasifier design, we will just try to understand in a glance, how this looks like. This you can see in this particular diagram, I have shown 2 different type of fixed bed gasifiers. One is the updraft gasifier another is the downdraft gasifier. Now a fixed bed gasifier can be either updraft, that means what is happening in the updraft.

The fuel is getting dropped from the top, gasifying agent from the bottom. And the downdraft, so both fuel and gasification agents occurs from the top, it is a co-current flow, here the flow is counter current. In updraft gasification, the char at the bottom of the bed meets the gasifying agent first and complete combustion occurs producing hydrogen and carbon dioxide and raising the temperature to almost 1000 degrees centigrade.

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Biomass Gasifier Design

- The hot gases percolate upwards through the bed, driving endothermic reactions with unreacted char to form H_2 and CO, with consequent cooling to ~ 750 °C.
- The gases pyrolyze the dry biomass which is descending, and also (near the top of the reactor) dry the incoming biomass. Updraft gasifiers typically produce between 10 and 20 wt% tar in the produced gas, which is far too high for many advanced applications.
- The allowable tar levels depend on the downstream application. These are around 0.05 g N/m³, 0.005 g N/m³, 0.001 g N/m³, for gas engines, gas turbines and fuel cells, respectively.
- In contrast to an updraft gasifier, in a downdraft gasifier (closed top) the gas flows co-currently with the fuel. A "throated" gasifier has a restriction part-way down the gasifier where air or O₂ is added, and where the temperature rises to 1200-1400 °C, and the fuel feedstock is either burned or pyrolyzes.



So, the hot gases percolate upwards through the bed driving endothermic reactions with unreacted char to form hydrogen and carbon monoxide with consequent cooling to 750 degrees centigrade. The gases pyrolyze the dry biomass which is descending and also of course near the top of the reactor and also dry the incoming biomass. Updraft gasifiers typically produced between 10 to 20 weight percent tar in the produced gas which is far too high for many advanced applications, it is not a good thing of course.

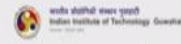
The allowable tar levels depend on the downstream application. These are around 0.05 grams normal per meter cube, 0.005 gram normal per meter cube 0.001 gram normal per meter cube, for gas engines, gas turbines and fuel cells applications respectively. In contrast to an updraft gasifier in a downdraft gasifier which is the closed loop, the gas flows co-currently with the fuel.

A throated gasifier has a restriction partway down the gasifier where air or oxygen is added and when the temperature rises to 1200 degree to 1400 degree centigrade, and the fuel feedstock is either burned or pyrolyses.

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Biomass Gasifier Design

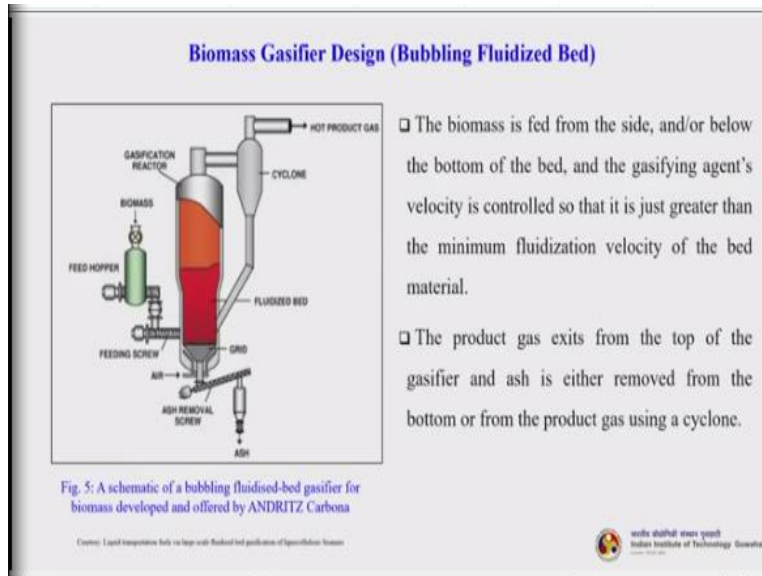
- The combustion gases then pass down over the hot char at the bottom of the bed, where they are reduced to H₂ and CO.
- The high temperature within the throat ensures that the tars formed during pyrolysis are significantly cracked (homogeneous cracking), with further cracking occurring as the gas meets the hot char on the way out of the bed (heterogeneous cracking), leading to a less tarry off-gas.
- Some disadvantages of a throated gasifier are:
 - 1) The constriction at the throat affects the types of biomass that can be successfully gasified. A low moisture content is required (25 wt%).
 - 2) Ash and dust are significantly present in the exhaust.
 - 3) Tar can still be up to 5 gN/m³, needing further clean-up.



The combustion gases then pass down over the hot char at the bottom of the bed where they are reduced to hydrogen and carbon monoxide. The high temperature within the throat ensures that the tar formed during pyrolysis are significantly cracked, that is the homogeneous cracking with further cracking occurring as the gas meets the hot char on the way out of the bed, heterogeneous cracking leading to a less tarry off-gas.

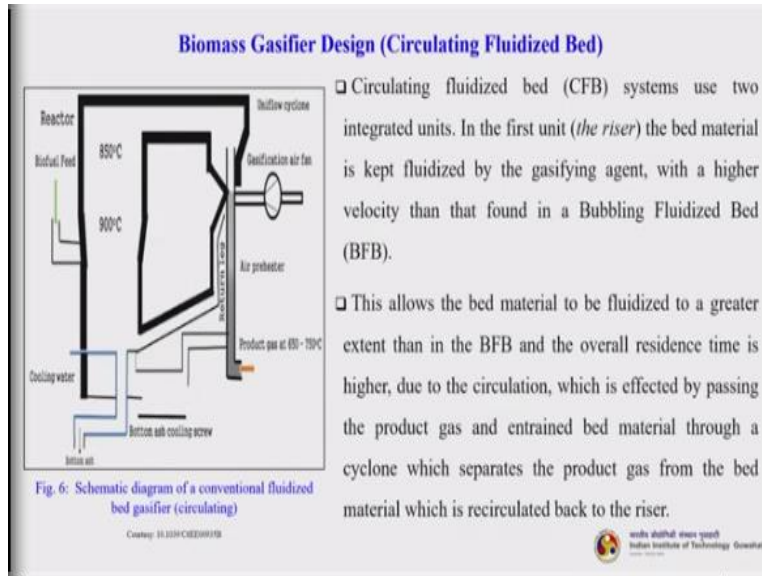
Some disadvantages of a throated gasifiers are, the constriction at the throat affects the type of biomass that can be successfully gasified, a low moisture content is required almost 25 weight percent. Ash and dust are significantly present in the exhaust; tar can still be up to 5 grams normal per meter cube needing further clean- up.

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Biomass gasifier designs. So this is a bubbling fluidized bed system. So, the biomass is fed from the side, you can see this is the main bubbling fluidized bed. Here the biomass is being fed using a hopper and a feeding screw, there is a screw system which is slowly actually feed in a particular rate. There are grids here, this is the fluidized bed, then whatever the gasification product is going basis the gas phase, that needs to be separated from the fly ash and other components. So, that will be done using a cyclone separator, then you get the hot product gas and whatever it is remain the solid fractions will again come down to the bottom of the reactor. So, either they will be burned again or they can be collected from the bottom. So, the biomass is feed from the side and/or below the bottom of the bed and the gasifying agent's velocity is controlled so, that it is just greater than the minimum fluidization velocity of the bed material, the product gas exits from the top of the gasifier and ash is either removed from the bottom or from the product gas using a cyclone.

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So, next design is a circulating fluidized bed. So, circulating fluidized bed known as CFB systems use 2 different integrated units. In the first unit, there are 2 systems you can see, this is one column there is another column here. So, the first unit is called the riser the second unit is called the downcomer. Now in the first unit, which is known as the riser the bed material is kept fluidized.

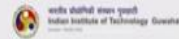
So, this is the main reactor where the fluidization is happening by the gasifying agent. So, you see that we feed the biofuel feed or the feedstock is being fed here somewhere and from the bottom you collect the ash. And then when the gas goes out and there is a downcomer here, here you basically do some processing some other things are also there, you collect the product gas here.

So, there is air pre heater and then part of that gas is also being recycled back. So, in the riser, the biomass is fluidized by the gasifying agent with a higher velocity that then found in the bubbling fluidized bed the BFB, which we discussed. Now this allows the bed material to be fluidized to a greater extent than the BFB and the overall residence time is higher due to the circulation, which is effected by passing the product gas and entrained bed material through a cyclone which separates the product gas from the bed material which is re-circulated back to the riser.

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Special Gasification Technique : Super Critical Water Gasification

- Water above its critical point ($T = 374.12\text{ }^{\circ}\text{C}$ and $P = 221.2\text{ bar}$) is termed as supercritical. Under these settings, the liquid and gas phases do not exist and supercritical water shows distinctive reactivity and solvency characteristics.
- Solubilities of organic materials and gases which are normally insoluble, are enhanced, with a decrease in solubility for inorganics.
- SCWG has been applied to *wet biomass* without the need for pre-drying, which is a major advantage over other more conventional gasification techniques.
- Product gas from SCWG mainly comprises H_2 , CO_2 , CH_4 and CO . The CO yield is comparatively low as CO transforms into CO_2 through the water-gas-shift reaction.



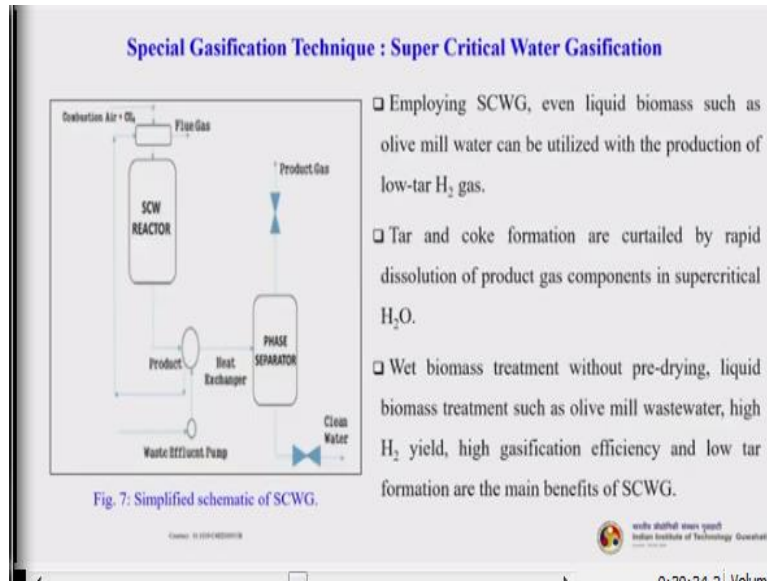
So, we will now discuss about a special gasification technique which is called supercritical water gasification. Water above its critical point which is 374.12 degree centigrade and a 221.2 bar is termed as supercritical. Now under these settings, the liquid and gas phase do not exist, it is a phase between a liquid and gas phase, it is called supercritical phase. And in that phase particularly the water shows distinctive reactivity and solvency characteristics.

So, the water in supercritical phase will have both the properties of a gas phase as well as a liquid phase. Solubilities of organic materials and gases which are normally insoluble are enhanced with a decrease in solubility for inorganics. So, supercritical water gasification has been applied to wet biomass without the need for pre drying. So, this technology is being actually developed to take care of the wet biomasses.

Please understand that when the biomasses are highly wet or has high moisture content, then you need a significant amount of energy to basically dry them before you feed them to a gasifier or a pyrolyser. So, if you go for a supercritical water gasification system, then whatever the water or moisture is present inside the biomass will actually behave like a reactant? So, this is the major advantage and this is the aim of developing the supercritical water gasification system.

So, product gas from this SCWG is mainly comprises hydrogen, carbon dioxide, methane and carbon monoxide. The carbon monoxide yield is comparatively low as carbon monoxide transforms into carbon dioxide through the water gas shift reaction.

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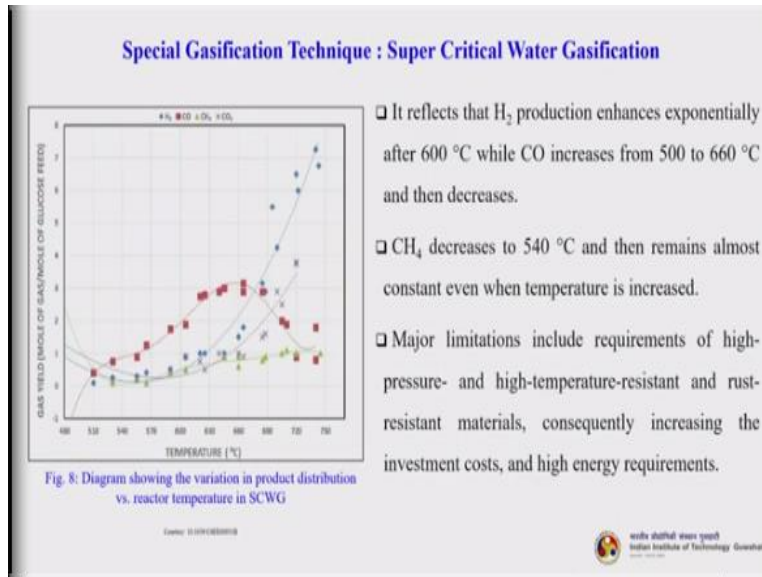


So, this is the unit. So, this supercritical water gasification the main reactor is of course very costly, you can think about the high temperature and high pressure required to make the water into the supercritical stage. So, here the main reaction is happening then whatever you are getting here the product it goes through some heat exchanger and there is a phase separator, you get clean water and you get the product gas.

And whatever portion from this is a combustion air and methane is recycled and being collected as a flue gas or maybe used for other purposes. So, by employing the supercritical water gasification process, even liquid biomass such as olive mill water can be utilized with the production of low tar hydrogen gas. It is a very nice technology, the only problem is the cost and special types of reactors of course, and that is why it leads to the extra or additional cost.

Tar and coke formation are curtailed by rapid dissolution of product gas components in supercritical water. Wet biomass treatment without pre drying, liquid biomass treatments such as olive mill wastewater, high hydrogen yield, high gasification efficiency and low tar formation are the main advantages of this particular technology.

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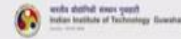
We are just further discussing about that particular technology only. If you look at this particular slide, you can see that hydrogen, this is the blue one is the hydrogen production. You can see that it enhances exponentially after the 600 degrees centigrade. So, up to 600 degrees centigrade it is almost in a saturated stage the production is happening. The moment we cross 600 degrees centigrade, there is an exponential increase in the hydrogen gas production.

While the carbon monoxide, the carbon monoxide is the red one, it decreases after 600 degrees centigrade, it is almost after 660 or 650 you can say that. So, methane decreases to 540 degrees centigrade and then remains almost constant when even the temperature is increased. Major limitations include requirements of high pressure, high temperature resistance and rust resistant materials, consequently increasing the investment cost and high energy requirements.

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Gasification

- The major motivation behind biomass gasification is to exploit a large variety of waste materials as feedstock, to increase resource efficiency and reduce adverse climate change via CO₂ mitigation.
- Although gasification is a key technology to utilize biomass waste, it poses many potential kinds of risks which have a significant impact on society and the environment at large.
- One of the main problems is the potential emissions of particulates (PM₁₀ or PM_{2.5}, dioxins, PAH), CO, SO_x, NO_x and volatile organics. These pollutants can interact with humans through inhalation, ingestion and dermal contact and thus pose a grave threat to human health.
- Ash and tars are noteworthy elements which have potential for environmental contamination.



The major motivation behind biomass gasification is to exploit a large variety of waste materials as feedstock, to increase resource efficiency and to reduce adverse climate change via carbon dioxide mitigation. Although gasification is a key technology to utilize biomass waste, it poses many potential kinds of risks, which have a significant impact on society and the environment at large.

One of the main problems is the potential emissions of particulates. Some are dioxins, PAH, carbon monoxide, SO_x, NO_x, and some volatile organics. These pollutants can interact with humans through inhalation, ingestion, and dermal contact and thus pose a grave threat to human health. Ash and tars are noteworthy elements which have potential for environmental contamination, should be properly disposed off.

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Gasification

- Gasification is a system which has an inherent risk for fire and explosion vulnerability, especially since the gasifiers operate at high temperature and pressure.
- This probability enhances significantly when H₂ is the desired product. It is highly flammable and, therefore, necessitates a great amount of caution.
- The waste streams formed require a suitable disposal system to be implemented that meets all legislative guidelines.
- Techniques like low-temperature CFB which can produce ash with negligible PAH impurity pose little threat to the environment, meaning that this ash can also be used as a fertilizer.



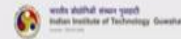
So, gasification is a system which has an inherent risk for fire and explosion vulnerability, especially since the gasifiers operate at high temperature and pressure. This probability enhances significantly when hydrogen is the desired product; it is highly flammable and therefore necessitates a great amount of caution. The waste streams formed require a suitable disposal system to be implemented that meets all the legislative guidelines, especially these environmental guidelines.

Techniques like low temperature circulating fluidized bed, which can produce ash with negligible PAH impurity pose little threat to the environment, meaning that this ash can also be used as a fertilizer or soil enhancer basically.

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Pyrolysis

- ❑ Biomass pyrolysis can be described as the *direct thermal decomposition of the organic components* in biomass in the absence of oxygen to yield an array of useful products - liquid and solid derivatives and fuel gases.
- ❑ Eventually, pyrolysis processes were utilized for the commercial production of a wide range of fuels, solvents, chemicals, and other products from biomass feedstocks.
- ❑ Knowledge of the effects of various independent parameters such as *biomass feedstock type and composition, reaction temperature and pressure, residence time, and catalysts* on reaction rates, *product selectivities, and product yields* has led to development of advanced biomass pyrolysis processes.
- ❑ The accumulation of considerable experimental data on these parameters has resulted in advanced pyrolysis methods for the direct thermal conversion of biomass to liquid fuels and various chemicals in higher yields than those obtained by the traditional long-residence-time pyrolysis methods.

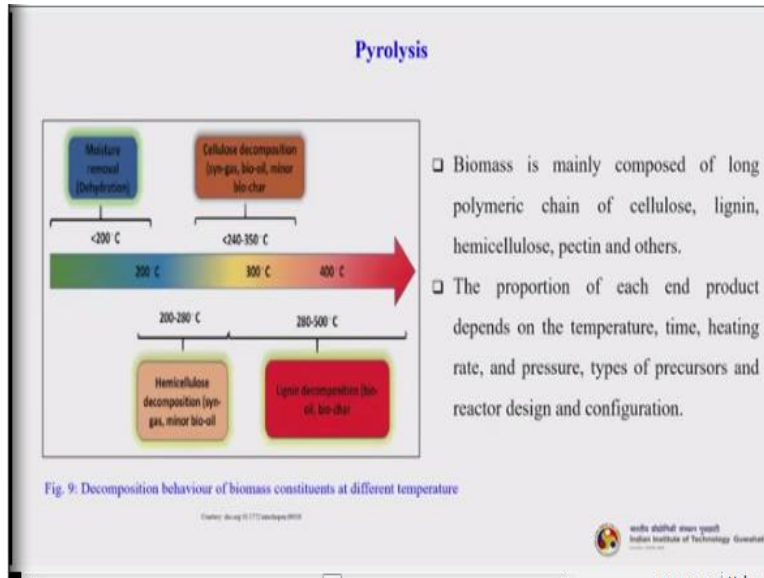


So, next is we will discuss about pyrolysis. So, biomass pyrolysis can be described as the direct thermal decomposition of the organic components in biomass in the absence of oxygen to yield an array of useful products, liquid or solid derivatives and fuel gases. Eventually, pyrolysis processes were utilized for the commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feedstocks.

Knowledge of the effects of various independent parameters such as biomass feedstock type, composition, reaction temperature and pressure, residence time and catalyst on reaction rates, product selectivities and product yields has led to the development of advanced biomass pyrolysis processes.

The accumulation of considerable experimental data on these parameters has resulted in advanced pyrolysis methods for the direct thermal conversion of biomass to liquid fuels and various chemicals in higher yields than those obtained by the traditional long residence time pyrolysis methods.

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So, the main product from pyrolysis, there is I already told you in the beginning of the class that pyrolysis is a step inside the gasification. However, when you only go for pyrolysis reaction, our main aim is mostly to produce the bio oil or pyrolytic oil, which can be further processed and can be blended as a transportation fuel and it can have several other users also.

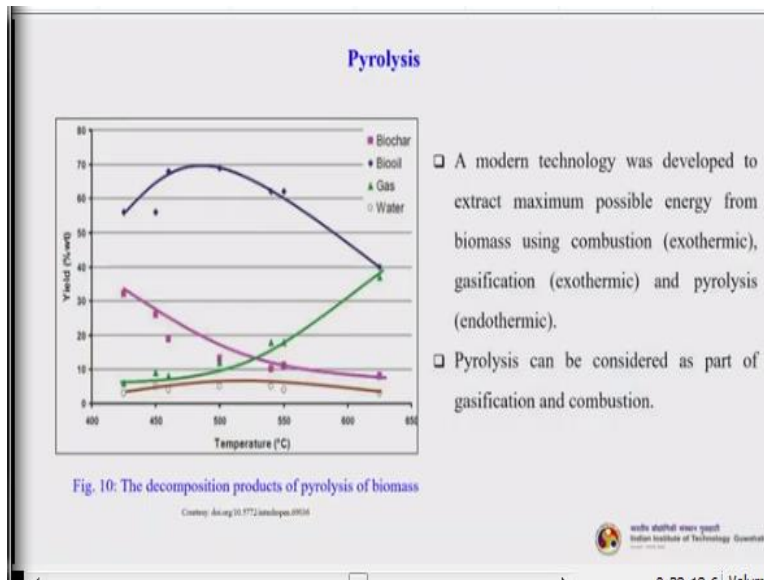
So, let us understand pyrolysis with different types of reaction conditions. So, a biomass is mainly composed of long polymeric chain of cellulose, hemicellulose and pectin and some other components - volatiles. Now the proportion of each end product depends on the temperature, time - residence time, heating rate and pressure, types of precursors that we are using, and the reactor design and configurations.

We can see how the reactions proceeds. So less than 200 degrees centigrade what is happening, that is called as dehydration, drying or removal of the moisture, we call it dehydration. The moment you proceed beyond 200 and within that 200 to 280 degrees centigrade you can see this first hemicellulose will start degrading, so hemicellulose decomposes. So, it will result in some amount of syngas and a minor quantity of bio oil, then we proceed further to beyond 280 degrees centigrade and in the range of almost 300 degrees centigrade.

The broad range of 240 to 350 degrees centigrade, the cellulose degrades, when the cellulose decomposes, it again produces some amount of syngas some more amount of bio oil, and minor

amount of the bio char, that is the solid residue that will be left out. You proceed further beyond 350 degrees centigrade up to 400 or 500 degrees centigrade here lignin decomposes, lignin decomposes mostly to the bio char and certain less amount of bio oil, so this is how the pyrolysis reaction happens.

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So, this is the yield of the pyrolytic products, you can see the yield of the bio char this decreases as and when we proceed with the pyrolysis reaction or we increase the temperature. So, this is the yield of bio oil, you can see that the most amount of the highest yield is about this 500 degrees centigrade you beyond that it decreases. Because beyond that lignin is decomposed, lignin is not resulting more into bio oil, it is getting converted more into your bio char.

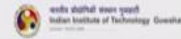
Then there is gas and water also. So, a modern technology was developed to extract maximum possible energy from biomass using combustion, which is exothermic reaction, gasification which is another exothermic reaction and pyrolysis which an endothermic reaction. Pyrolysis can be considered as part of gasification and combustion, this is what I already mentioned you.

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Pyrolysis

Temperature	Type of reaction	End products
Less than 350°C	Moisture loss, depolymerization, free radical generation	carbonyl and carboxyl group production, CO and CO ₂ gas liberation, biochar formation
Between 350°C and 450°C	Substitution for breaking of glycoside chain of polysaccharide	Tar production containing levoglucosan, anhydrides and oligosaccharides
Above 450°C	Dehydration, rearrangement and fission of sugar units	acetaldehyde, glyoxalin and acrolein production
Above 500°C	A mixture of all above processes	A mixture of all above products
Condensation	Unsaturated products condense and cleave to the char	A highly reactive char residue containing trapped free radicals

Course: Acryl 10 172 1400000000




So, these are some of the end products and the temperature and the type of reactions. So, less than 350 moisture loss, depolymerization we get carbonyl and carboxyl group production, this is what I have already described, but this is given in a tabular format for a better understanding. So, between 350 to 450, you get breaking up glycosides chain of polysaccharides. So, tar production begins that contains levoglucosan, anhydrides and oligosaccharides. Above 450 dehydration rearrangement and fission of sugar units happens, you get acetaldehyde, glyoxalin, acrolein production and some other components. Above 500 degree centigrade a mixture of all the processes reactions that is happening and mixture of all the above products also being produced. So then condensation reaction happens. So, unsaturated products condense and cleave to the char, a highly reactive char residue containing trapped free radicals is the end product.

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Pyrolysis (Fundamentals)

- ❑ *Conventional pyrolysis* (carbonization, destructive distillation, dry distillation, retorting) consists of the slow, irreversible, thermal degradation of the organic components in biomass, most of which are lignocellulosic polymers, in the absence of oxygen.
- ❑ *Slow pyrolysis* has traditionally been used for the production of charcoal. Short-residence-time pyrolysis (flash, rapid, ultra pyrolysis) of biomass at moderate temperatures can afford up to 70 wt% yields of liquid products.
- ❑ Pyrolysis conditions can be used that provide high yields of gas or liquid products and char yields of less than 5%.
- ❑ One configuration of an advanced biomass pyrolysis system, for example, involves an ablative, vortex reactor for pyrolysis at biomass residence times of fractions of a second coupled to a downstream vapor cracker.


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So, conventional pyrolysis consists of the slow irreversible thermal degradation of the organic components in biomass, most of which are lignocellulosic polymers, in the absence of oxygen. So, pyrolysis is happening without oxygen, whereas gasification is happening which happens after the pyrolysis with a less amount of theoretical oxygen, which is required for the combustion process.

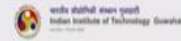
So, slow pyrolysis has traditionally been used for the production of charcoal. Short residence time pyrolysis which are flash pyrolysis, ultra pyrolysis of biomass at moderate temperatures can afford up to 70 weight percent yields of the liquid products. So, they are very good in producing higher amount of bio oil. Pyrolysis conditions can be used, that provides high yields of gas or liquid products and char yields of less than 5%.

One configuration of an advanced biomass pyrolysis system, for example, involves an ablative vortex reactor for pyrolysis at biomass residence times of fractions of a second coupled to a downstream vapor cracker.

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Types of Pyrolysis Processes

- ❑ Overall the pyrolysis process can be classified as *slow and fast* depending on the heating rate.
- ❑ In *slow pyrolysis* process, the time of heating the biomass substrate to pyrolysis temperature is longer than the time of retention of the substrate at characteristic pyrolysis reaction temperature.
- ❑ However in *fast pyrolysis*, the initial heating time of the precursors is smaller than the final retention time at pyrolysis peak temperature.
- ❑ Based on medium, pyrolysis can be of another two types namely *hydrous pyrolysis* and *hydro-pyrolysis*.
- ❑ Slow and fast pyrolysis is usually carried out in *inert atmosphere* whereas hydrous pyrolysis is carried out in presence of *water* and hydro-pyrolysis is carried out in presence of *hydrogen*.



Overall, the pyrolysis process can be classified as slow and fast depending upon the heating rate. In slow pyrolysis process, the time of heating the biomass substrate to pyrolysis temperature is longer than the time of retention of the substrate at characteristic pyrolysis reaction temperature. However, in fast pyrolysis, the initial heating time of the precursor is smaller than the final retention time at pyrolysis peak temperature.

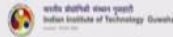
Based on medium, pyrolysis can be another 2 types namely hydrous pyrolysis and hydro pyrolysis, what medium is being used. So, a slow and fast pyrolysis is usually carried out in inert atmosphere, whereas hydrous pyrolysis is carried out in the presence of water and hydro pyrolysis occurred in the presence of hydrogen.

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Types of Pyrolysis processes with resultant products

Pyrolysis types	Retention time	Rate of heating	Final temperature (°C)	Products
Fast	<2 s	Very high	500	Bio-oil
Flash	<1 s	High	<650	Bio-oil, chemicals and gas
Ultra-rapid	<0.5 s	Very high	1000	Chemical and gas
Vacuum	2-30 s	Medium	400	Bio-oil
Hydro-pyrolysis	<10 s	High	<500	Bio-oil
Carbonization	days	Very low	400	Charcoal
Conventional	5-30 min	Low	600	Char, bio-oil and gas

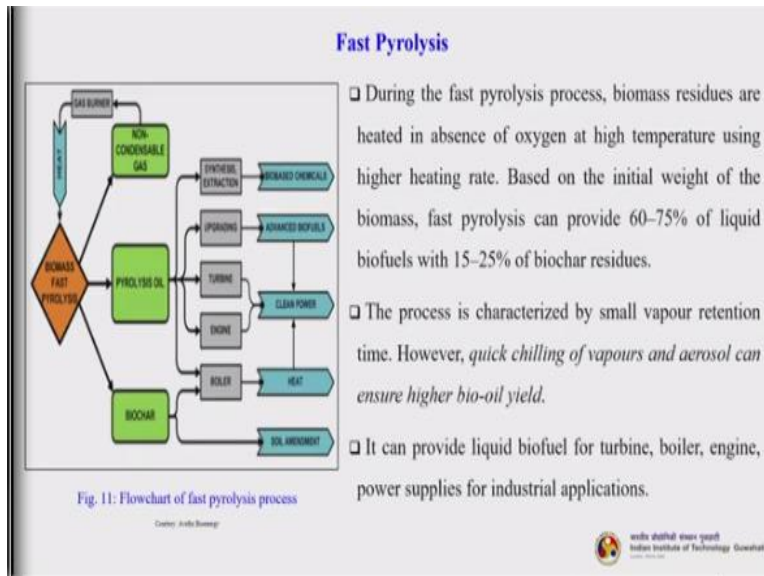
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So, this table gives you the types of pyrolysis process with resultant products. So, a fast pyrolysis the retention time is extremely low, less than 2 seconds, rate of heating is very high, final temperature is around 500 degrees centigrade and the major product that you get is the bio oil. The highest yield is of course bio oil. Flash pyrolysis less than one second extremely fast, high rate of heating less than around 650 degrees centigrade. And again the major product is bio oil and certain chemicals and maybe gas - less amount of gas. Ultra-rapid - less than 0.5 second, very high rate of heating; the temperature required is 1000 degrees centigrade, you get chemicals and gases. Vacuum pyrolysis, you get bio oil. Hydro pyrolysis less than 10 seconds, high rate of heating, temperature required is less than 500 and the major product is bio oil.

And carbonization - this is the slow pyrolysis which was initially used so many years before to produce that char - charcoal. So, the resultant product is charcoal and less than 400 degrees centigrade. Conventional is about 5 to 30 minutes, (heating rate) low, many times we can call it as an intermediate pyrolysis, so the maximum temperature we can go depending upon the type of feedstock is 600, you get so many different types of products in a certain proportion - char, bio oil and gas. However, again depending upon the type of feedstock, maximum yield is of course of the bio oil.

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- During the fast pyrolysis process, biomass residues are heated in absence of oxygen at high temperature using higher heating rate. Based on the initial weight of the biomass, fast pyrolysis can provide 60–75% of liquid biofuels with 15–25% of biochar residues.
- The process is characterized by small vapour retention time. However, *quick chilling of vapours and aerosol can ensure higher bio-oil yield.*
- It can provide liquid biofuel for turbine, boiler, engine, power supplies for industrial applications.

So, fast pyrolysis. So, during the fast pyrolysis process, biomass residues are heated in absence of oxygen at high temperature using higher heating rate. Based on the initial weight of the biomass fast pyrolysis can provide 60 to 75% of the liquid bio fuels with 15 to 25% of the biochar residues. So, the process is characterized by small vapor retention time, however quick chilling of vapors and aerosol can ensure higher bio oil yield, so this is another further step.

So, you get a pyrolysis oil here, non condensable gases - can be processed through the gas burner. And you get the heat - again that heat can be used in the pyrolysis here. So, the pyrolysis oil you can see that so many different types of processing here, synthesis and extraction to biobased chemicals. I can tell you again we have already discussed once, the major product from the fast pyrolysis or any pyrolysis of course, is the oil, that is the major aim.

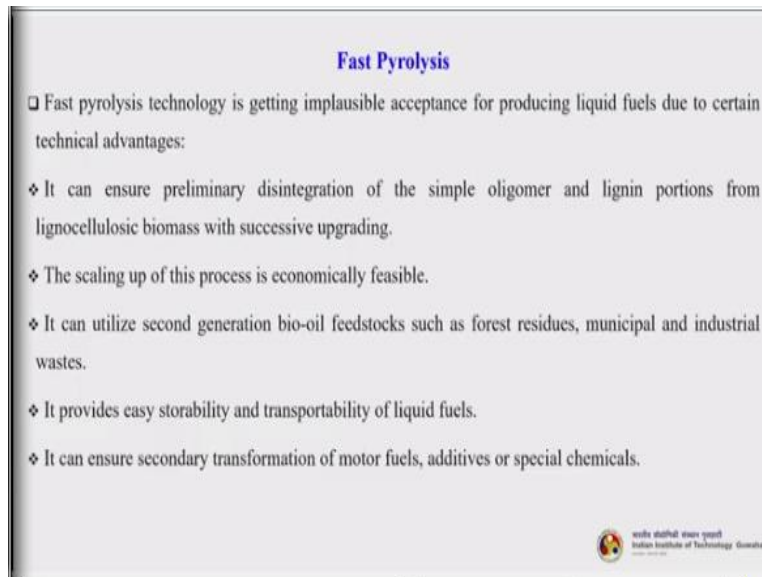
Whenever we generate oil, so you just leave it or settle it under gravity, allow it for some time, you see that 2 distinct phases, one top phase and bottom phase, there is phase separation. The one phase is containing the oil rich phase that is the organic components and that is if we decant it properly and take it out and further process that is the bio oil.

And there are other portion which is aquatic phase, that aquatic phase contains so many different types of chemicals and some of these chemicals can be of very high value depending upon what is the feedstock you are using, that can be processed. You get that type of platform chemicals

here. Upgrade you get advanced bio fuels, if you can go for some sort of distillation process. Feed to turbine engine you get a clean power here.

Boiler you get heat and whatever the biochar that leaves, it can either be burnt in a boiler to produce the heat - maybe steam at certain cases or if the quality of the char is poor it can be used as a soil enhancer.

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Fast Pyrolysis

- Fast pyrolysis technology is getting implausible acceptance for producing liquid fuels due to certain technical advantages:
- ◆ It can ensure preliminary disintegration of the simple oligomer and lignin portions from lignocellulosic biomass with successive upgrading.
- ◆ The scaling up of this process is economically feasible.
- ◆ It can utilize second generation bio-oil feedstocks such as forest residues, municipal and industrial wastes.
- ◆ It provides easy storability and transportability of liquid fuels.
- ◆ It can ensure secondary transformation of motor fuels, additives or special chemicals.

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Fast pyrolysis technology is getting implausible acceptance for producing liquid fuels due to certain technical advantages, so some of them are listed here. So, it can ensure preliminary disintegration of the simple oligomer and lignin portions from the lignocellulosic biomass with successive upgrading. The scaling up of this process is economically feasible. It can utilize second generation bio oil feedstock such as forest residues, municipal and industrial wastes.

It provides easy storability and transportability of liquid fuels. It can ensure secondary transformation of motor fuels, additives or special chemicals.

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Flash Pyrolysis

□ The flash pyrolysis process of biomass can give solid, liquid and gaseous products. The bio-oil production can go up to 75% using flash pyrolysis.

□ This procedure is carried out by *speedy devolatilization* under inert atmosphere using higher heating rate with high pyrolysis temperatures around 450 and 1000 °C.

□ In this process, the *gas residence time (less than 1 s)* is too little. Nevertheless, this process has poor thermal stability.

□ Due to catalytic effect of the char, the oil becomes viscous and sometimes it contains some solid residues also.

Fig. 12: Reactor for Flash Pyrolysis
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Then is flash pyrolysis. So this is a flash pyrolyser or flash pyrolysis reactor. So, flash pyrolysis process of biomass can give solid, liquid and gaseous products. The bio oil production can go up to 75% if you use this particular technology. This procedure is carried out by speedy devolatilization under inert atmosphere using higher heating rate with high pyrolysis temperature around 450 to 1000 degree centigrade.

So, in this process, the gas residence time is less than 1 second - is too little. Nevertheless, the process has poor thermal stability. Due to catalytic effect of the char, the oil becomes viscous and sometimes it contains some solid residues also which is not desirable but you can further process it to take out the solid part.


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Slow Pyrolysis

- ❑ Slow pyrolysis can yield good quality charcoal using low temperature and low heating rates.
- ❑ The vapour residence time can be around 5-30 min in this process. The volatile organic fractions present in vapour phase continue to react with each other to yield char and some liquid fractions.
- ❑ The *quality of bio-oil produce in this process is very low*. Longer residence time initiates further cracking to reduce the yield of bio-oil.
- ❑ The process suffers from low heat transfer values with longer retention time leading to enhance the expenditure by higher input of energy.
- ❑ The stoichiometric equation for production of charcoal is shown by

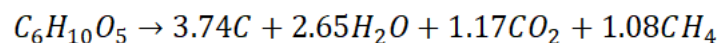
$$C_6H_{10}O_5 \rightarrow 3.74 C + 2.65 H_2O + 1.17 CO_2 + 1.08 CH_4$$

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Then slow pyrolysis. Slow pyrolysis can yield good quality charcoal using low temperature as well as low heating rates. The vapour residence time can be around 5 to 30 minutes in this process. The volatile organic fractions present in vapor phase continue to react with each other to yield char and some liquid fractions. The quality of bio oil produce in this process is very low.

So, if your aim is to produce bio oil it is recommended not to use slow pyrolysis, you can better go for an intermediate pyrolysis where you get a good amount of bio oil. And if you only want higher bio-oil yield then you can go for the fast pyrolysis or flash pyrolysis. So, the longer residence time in slow pyrolysis initiates further cracking to reduce the yield of bio oil.

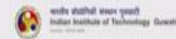
The process suffers from low heat transfer values with longer retention time leading to enhance the expenditure by higher input of energy. The stoichiometric equation for a production of charcoal is shown by this equation :



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Catalytic Pyrolysis

- ❑ A mixture of hydrocarbon was produced earlier from methanol over zeolites like ZSM-5.
- ❑ Another patent suggested passing the vapours from pyrolyzer over the bed of zeolite ZSM-5 to produce short chain hydrocarbon.
- ❑ It was reported that the catalyst of ZSM-5 can convert bio-oils generated from the pyrolyzer to *alkylated benzene*. The disadvantage of using ZSM-5 as catalyst was coke formation.
- ❑ However these disadvantages can be overcome by using *circulating fluid bed technology* where the fluidized bed can be prepared using different types of catalyst instead of sand.
- ❑ Catalysts can be mixed with the lignocellulosic substrate earlier to pyrolysis process or separately with the gaseous reactants to obtain desired products.
- ❑ It was revealed that parting of the catalyst and biomass was more operative for the transformation of the required products.



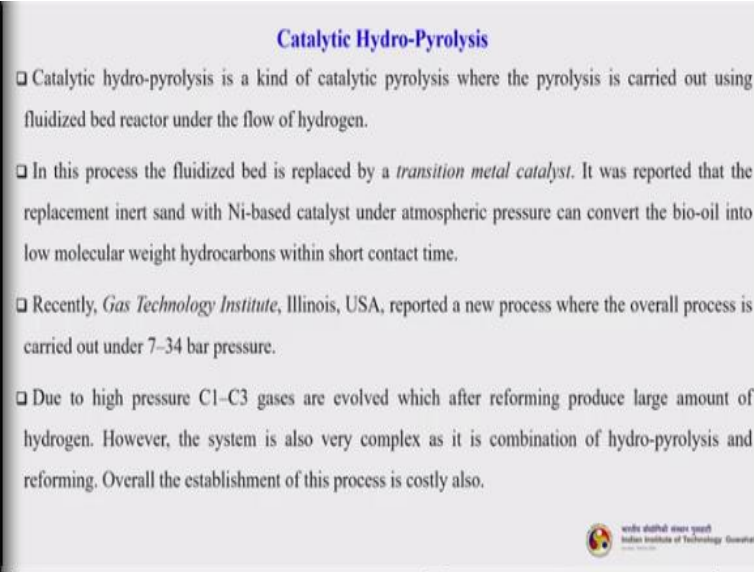
Then let us understand catalytic pyrolysis. A mixture of hydrocarbon was produced earlier from methanol over zeolites like ZSM-5. Another patent suggested passing the vapors from pyrolyzer over a bed of zeolite ZSM-5 to produce short chain hydrocarbons. It was reported that the catalyst of ZSM-5 can convert bio oils generated from the pyrolyzer to alkylated benzene. The disadvantage of using ZSM-5 as catalyst was coke formation.

However, these disadvantages can be overcome by using a circulating fluidized bed technology, where the fluidized bed can be prepared using different types of catalyst instead of sand. So, this CFB whatever we have discussed under the gasification, the same reactor can be used. Catalyst can be mixed with lignocellulosic substrate earlier to pyrolysis process or separately with the gaseous reactants to obtain desired products.

So, this statement you will see many times. You will come across 2 different terminologies, one is called ex-situ catalytic pyrolysis, one is called in-situ catalytic pyrolysis; where the in-situ catalytic pyrolysis the catalyst is physically mixed with the biomass, then we go for the pyrolysis reaction. In ex-situ pyrolysis reaction what happens that there is a fixed bed type of reactor, it can be fluidized bed also. There the biomass is not mixed with the catalyst, so the catalyst is kept in a separate section and **the** when the vapour is getting generated after the pyrolysis reaction from the feed biomass, that passes through a bed of catalyst. So, the catalytic cracking is happening for the vapor phase, so you can call it vapor phase catalytic cracking.

That is better because this catalyst can be regenerated and reused. Whereas, if you mix with the feedstock then you cannot separate the catalyst from the biomass and it will be waste basically. And you know the catalysts are extremely costly, most of the catalyst or commercial catalyst. So, it was revealed that parting of the catalyst and biomass was more operative for the transformation of the required products.

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Catalytic Hydro-Pyrolysis

- Catalytic hydro-pyrolysis is a kind of catalytic pyrolysis where the pyrolysis is carried out using fluidized bed reactor under the flow of hydrogen.
- In this process the fluidized bed is replaced by a *transition metal catalyst*. It was reported that the replacement inert sand with Ni-based catalyst under atmospheric pressure can convert the bio-oil into low molecular weight hydrocarbons within short contact time.
- Recently, *Gas Technology Institute*, Illinois, USA, reported a new process where the overall process is carried out under 7–34 bar pressure.
- Due to high pressure C1–C3 gases are evolved which after reforming produce large amount of hydrogen. However, the system is also very complex as it is combination of hydro-pyrolysis and reforming. Overall the establishment of this process is costly also.

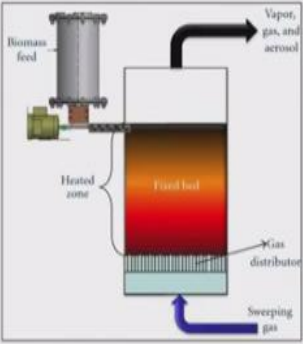
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So, catalytic hydro pyrolysis. So catalytic hydro pyrolysis is a kind of catalytic pyrolysis where pyrolysis is carried out using fluidized bed reactor under the flow of hydrogen. In this process the fluidized bed is replaced by a transition metal catalyst. It was reported that the replacement inert sand with nickel based catalyst under atmospheric pressure can convert the bio oil into low molecular weight hydrocarbons within short contact time.

Recently, Gas Technology Institute in Illinois, United States reported a new process where the overall process is carried out under 7 to 34 bar pressure. Due to high pressure C1 and C3 gases are evolved which after reforming produce large amount of hydrogen. However, the system is also very complex as it is a combination of hydro-pyrolysis and reforming. Overall the establishment of this process is very costly.

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Fixed Bed Reactor



The diagram illustrates a fixed bed reactor. On the left, a vertical shaft labeled 'Biomass feed' leads into a 'Heated zone' containing a 'Fixed bed'. Below the fixed bed is a 'Gas distributor'. A 'Sweeping gas' inlet is shown at the bottom right, with an arrow pointing upwards through the distributor. An outlet at the top right is labeled 'Vapor, gas, and aerosol'.

- This is a very simple technology that gives priority to the production of bio-oils, which are relatively uniform in size with low fines content.
- It is made up of two basic components, that is, the gas cooling compartment and the cleaning system by filtering through cyclone, wet scrubbers and dry filters.

Fig. 13: Generalized Fixed Bed Reactors

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So, we will see certain types of reactors. The first is the fixed bed reactor. So, this is a very simple technology that gives priority to the production of bio oils which are relatively uniform in size with low fines content. So, it is made up of 2 basic components; that is the gas cooling compartment and the cleaning system by filtering through the cyclone, wet scrubbers and dry filters.

So, here this is a gas distributor which is distributing the sweeping gas, here you feed your biomass through a feeder and it is a fixed bed pyrolysis reaction happens; the heat is being supplied and whatever the resultant is the vapor, gas and aerosol.

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Fixed Bed Reactor

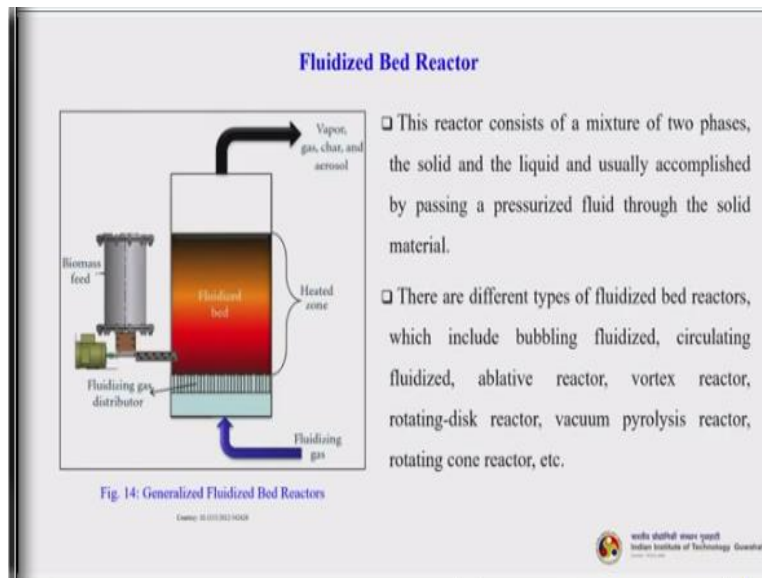
- During reaction, the solid sample is allowed to pass through a vertical shaft where it encounters an upwardly moving counter current gas stream product.
- This reactor can be made using either steel, firebricks or concrete and composed of the feeding unit (fuel), a unit for removing the ash and the gas escape unit.
- The reactor, which has its priority for applications involving small-scale heat and power, has high ability to conserve carbon and can operate for long time for solid residence, low gas velocity and of course with a low ash carry-over.
- It has its limitation in the problem usually encountered during tar removal.

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So, during reaction, the solid sample is allowed to pass through a vertical shaft where it encounters an upwardly moving counter current gas stream product. This reactor can be made using either steel, firebricks or concrete and composed of the feeding unit, a unit for removing the ash and the gas escape unit.

The reactor, which has it is priority for applications involving small scale heat and power, has high ability to conserve carbon and can operate for long time for solid residence, low gas velocity and of course with a low ash carry-over. It has it is own limitation in the problem is usually encountered during the tar removal.

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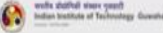
Then fluidized bed system, the unit looks like similar - it is a schematic. Here it can be little something conical like shape maybe, there are different designs available. But the bed is fluidized it is not a fixed bed, the remaining things are same, so this reactor consist of a mixture of 2 phases the solid and the liquid and usually accomplished by passing a pressurized fluid through the solid material.

Now there are different types of fluidized bed reactors which include bubbling fluidized, circulating fluidized, ablative reactor, vortex reactor, rotating disk reactor, vacuum pyrolysis reactor and rotating cone reactor, there are many different designs are available and this is the simplest schematic.

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Advantages of Fluidized Bed

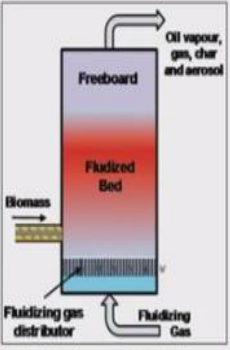
- A very popular reactor for fast pyrolysis, it has the following advantages:
- ❖ The provision of heat transfer is rapid.
- ❖ It has a good grip of pyrolysis reaction and vapour holding time control.
- ❖ It has a sufficiently high surface area for contact between the two phases in the mixture.
- ❖ The heat transfer in the system is exemplary, and
- ❖ The relative velocity between the phases is very high.



So, the advantages of fluidized bed are: The provision of heat transfer is very rapid. It has a good grip of pyrolysis reaction and vapor holding time control. It has sufficiently high surface area for contact between the 2 phases in the mixture, because, the biomass is in suspended medium. The heat transfer in the system is exemplary and the relative velocity between the phases is very high.


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Bubbling Fluidized Bed Reactor



- The high presence of solid density in the bed ensures a better temperature control, smooth contact between gas and solid, good transfer of heat and excellent storage capacity.
- The biomass is heated in an environment devoid of oxygen and decomposed into gas, vapour, aerosols and char and these components are finally collected from the reactor.
- While the charcoal is collected using the cyclone separator and stored, the vapour is cooled rapidly and condensed into high-quality bio-oil and stored with about 70% yield of biomass weight (dry weight).

Fig. 15: Bubbling Fluidized Bed Reactors
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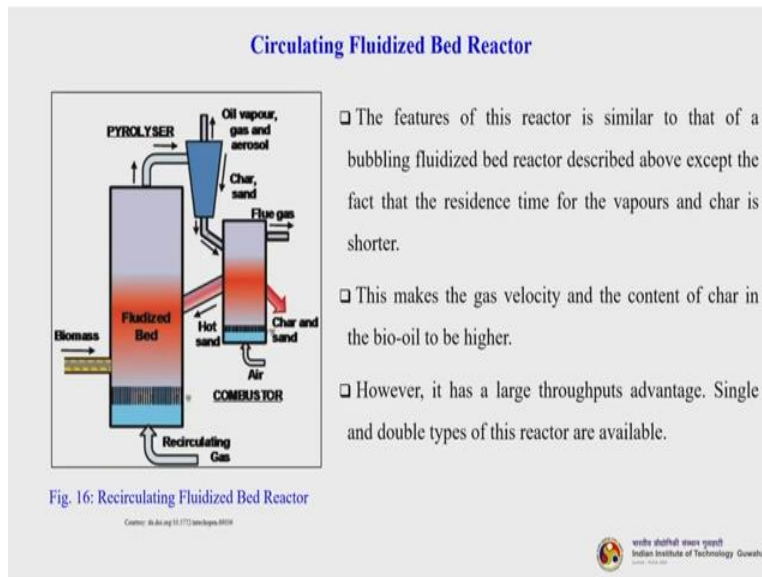


So, then the next is bubbling fluidized bed reactor. So, the high presence of solid density in the bed ensures a better temperature control, smooth contact between gas and solid, good transfer of heat and excellent storage capacity. The biomass is heated in an environment devoid of oxygen

and decomposed into gas, vapor, aerosols and char and these components are finally collected from the reactor.

While the charcoal is collected using the cyclone separator and stored, the vapour is cooled rapidly and condensed into high quality bio oil and stored with about almost 70% yield of the biomass weight - dry weight basically.

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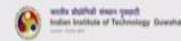


Then next is the circulating fluidized bed. So you can have a close look at the image, you can see that there are 2 different sections. The first one is the fluidized bed here, the main reactor here and this is the combustor. So the features of this reactor is similar to that of a bubbling fluidized bed reactor described above except the fact that residence time for the vapors and char is shorter. This makes the gas velocity and the content of char in the bio oil to be higher. However, it has a large throughputs advantage, single and double type of these reactors are also available.

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Vacuum Pyrolysis Reactor

- This is a slow pyrolysis reactor with heat transfer rate very low. This results in a lower bio-oil yield usually in the range of 35–50 wt%.
- The design is highly complicated and requirement for investment and maintenance is always high thereby making the technology uneconomically suitable.
- The biomass is conveyed into the vacuum chamber with a high temperature with the aid of a conveyor metal belt with periodical stirring of the biomass by mechanical agitation.
- The heat carrier is usually made of a burner while the biomass is melted by heating inductively using molten salts. It has the ability to process larger particle size biomass but requires special solids feeds, special discharging devices in order to have an effective seal all the time.



Then next is vacuum pyrolysis reactor. This is a slow pyrolysis reactor with heat transfer rate very low. This results in a lower bio oil yield usually in the range of 35 to 50 weight percent. The design is highly complicated and requirement for investment and maintenance is always high thereby making the technology uneconomically suitable. The biomass is conveyed into the vacuum chamber with a high temperature with the aid of a conveyor metal belt with periodical stirring of the biomass by mechanical agitation.

The heat carrier is usually made of a burner while the biomass is melted by heating inductively using molten salts. So, it has the ability to process larger particle size biomass but requires special solid feeds, special discharging devices in order to have an effective seal all the time.

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Rotating Cone Reactor

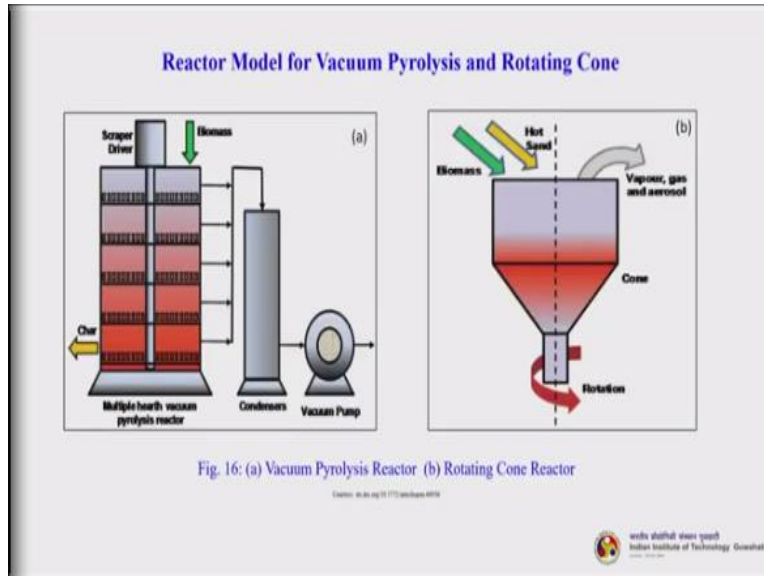
- Unlike the fluidized bed reactor, the rotating cone reactor requires the mixing of biomass and hot sand mechanically and does not require the use of inert gas.
- The feed and the hot sand are fed in from the bottom of the cone while they are transported to the lip of the cone during spinning using centrifugal force and as they get to the tip, the vapour generated is condensed by the condenser.
- The char and the sand are combusted with the sand being heated up again and reintroduced to remix with fresh feedstock at the bottom of the cone.
- Though the design of this reactor might be complex, its high bio-oil yield makes it desirable.



Then rotating cone reactor. Unlike the fluidized bed reactor the rotating cone reactor requires the mixing of biomass and hot sand mechanically and does not require the use of inert gas. The feed and the hot sand are fed in from the bottom of the cone while they are transported to the lip of the cone during spinning using a centrifugal force and as they get up to the tip, the vapour generated is condensed by the condenser and then you can collect the condensable part.

The char and the sand are combusted with the sand being heated up again and reintroduced to mix the fresh feedstock at the bottom of the cone. So you take out the char. And char if it is getting converted and fully combusted, so you basically end up with a certain ash and the ash is having a low density and it can be easily separated. And the sand which is already containing high amount of heat can be recycled back. Though the design of this reactor might be complex, its high bio oil yield makes it extremely desirable.

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So, the 2 different designs which we have already discussed - this is the vacuum pyrolysis reactor and that is the rotating cone reactor. So, you can have more different stages in the vacuum pyrolysis reactor, you can have a single stage also, you can have multiple stages also. Then whatever it is coming out - biomass is usually fed from the top or if it has different distinct stages, so you can feed from this side also.

There is a condenser which condenses the liquid and you get the liquid here and the char can be collected from the bottom. Again in the rotating cone reactor also biomass as well as the hot sand which is carrying the heat is being fed from the top and the cone is rotating.

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Advantages and Disadvantages of Different Pyrolysis Reactors

Reactor	Advantages	Disadvantages
Fixed Bed Reactor	<ul style="list-style-type: none"> Simplicity in design Reliable results Biomass size independent 	<ul style="list-style-type: none"> High carbon conservation Long solid residence time Low ash carry over Difficult to remove char
Bubbling fluidized bed	<ul style="list-style-type: none"> Simple design Easy operational procedures 	<ul style="list-style-type: none"> Good temperature control Suitable for large-scale application Small particle sizes are needed

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So, we will just summarize. So advantages and disadvantages of different pyrolysis reactor. If you look at fixed bed reactor, the advantages are simplicity in design, reliable results and biomass size is independent, no fixed biomass size is required. However, the disadvantages are high carbon conservation, long solid residence time, low ash carry-over and difficult to remove the char.

If you talk about bubbling fluidized bed, the advantages are the design is simple and easy operational procedures. However, it suffers from good temperature control and suitable for large scale application, small particle sizes are needed. There is a small mistake here actually the good temperature control will come to the advantages.

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Advantages and Disadvantages of Different Pyrolysis Reactors

Reactor	Advantages	Disadvantages
Circulating fluidized bed	Well-understood technology Better Thermal control Larger particle sizes can be processed	Large-scale production difficult Complex hydrodynamics Char is too finer
Rotating cone	Centrifugal force circulates hot sand and biomass substrate No carrier gas required	Difficult operational process Smaller particle sizes needed Large-scale application is difficult



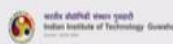
And for the circulating fluidized bed, the advantages are: well understood technology, better thermal control, large particle sizes can be processed, disadvantages large scale production difficulty, complex hydrodynamics and char is very, very fine. So, that char cannot be utilized for any better purposes you can restrict itself to only soil amendment.

Rotating cone, advantages are: centrifugal force circulates hot sand and biomass substrate, no carrier gas is required. Difficulty is that: operational processes are (difficult) having disadvantageous position, smaller particle sizes needed - otherwise you cannot circulate them and they will deposit on the bottom, large scale application is difficult.

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Advantages and Disadvantages of Different Pyrolysis Reactors

Reactor	Advantages	Disadvantages
Vacuum	The oil is clean Can process larger particles of 3-5 cm No carrier gas required Lower temperature required Condensation of liquid product is easier	Slow process Solid residence time is too high Require large-scale equipment Poor heat and mass transfer rate Generates more water

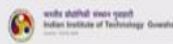


If you talk about vacuum pyrolysis, the advantages are that: the oil that you get from this particular reactor is very clean. Can process larger particles of 3 to 5 centimeter, no carrier gas required, lower temperature required, condensation of liquid product is very easier. The disadvantages are that: it is a slow process, solid residence time is too high, requires large scale equipment, poor heat and mass transfer rate and it generates more water.

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PYROLYSIS (MECHANISM)

- Many dehydration, cracking, isomerization, dehydrogenation, aromatization, coking, and condensation reactions and rearrangements occur during pyrolysis.
- The products are water, carbon oxides, other gases, charcoal, organic compounds (which have lower average molecular weights than their immediate precursors), tars, and polymers.
- When *cellulose* is slowly heated at about 250 to 270 °C a large quantity of gas is produced consisting chiefly of *carbon dioxide and carbon monoxide*.
- Initially, small amounts of hydrogen and hydrocarbon gases and larger amounts of carbon oxides are emitted. The hydrocarbons in the product gas then increase with further temperature increases until hydrogen is the main product. The carbon oxides and most other products owe their formation to secondary and further reactions.

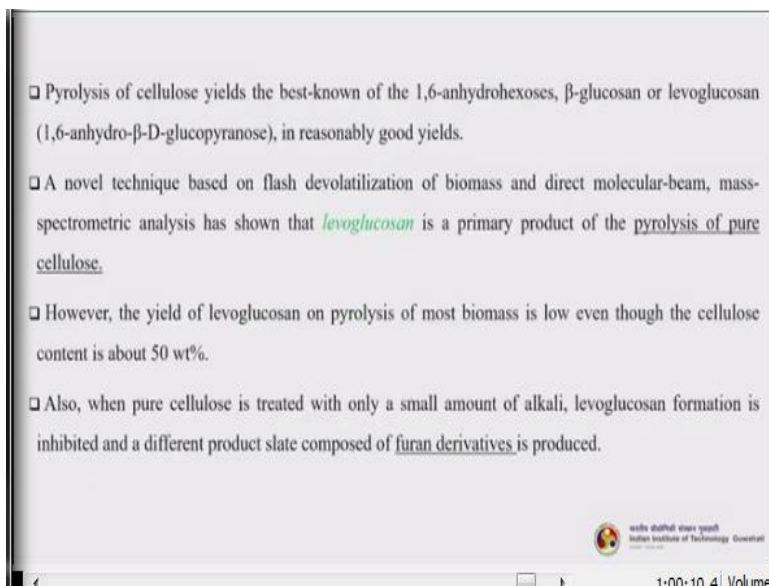


So, we will talk about the pyrolysis mechanisms. Many dehydration, cracking, isomerization, dehydrogenation, aromatization, coking and condensation reactions and rearrangements happen during the pyrolysis reaction. So, the pyrolysis reactions are very complex and predicting them

for a particular biomass is too difficult. The products are water, carbon oxides, other gases, charcoal, organic compounds, tar and polymer.

When cellulose is slowly heated at about 250 to 270 degree centigrade, a large quantity of gas is produced consisting chiefly of carbon dioxide and carbon monoxide. Initially, small amounts of hydrogen and hydro carbon gases and large amount carbon oxides are emitted. The hydrocarbon in the product gas then increase with further temperature increases until hydrogen is the main product. The carbon oxide and most other products owe their formation to the secondary and further reactions.

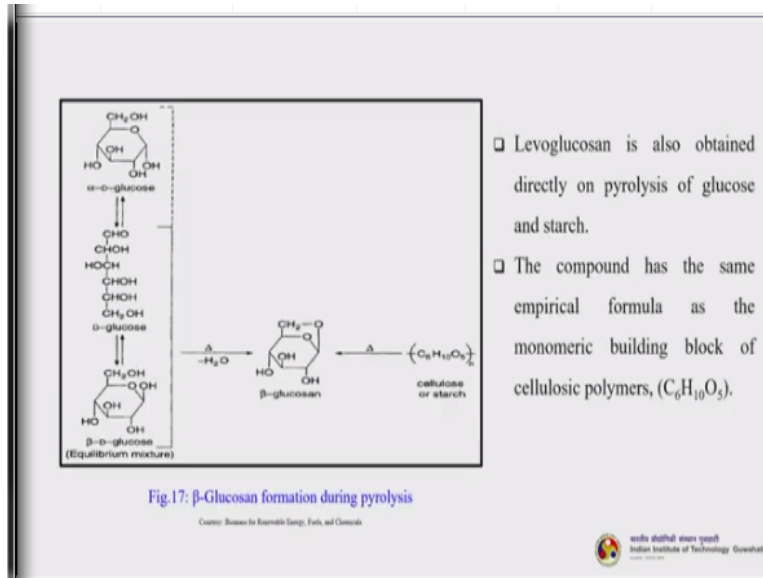
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Pyrolysis of cellulose yields the best known of the 1, 6-anhydrohexoses, β -glucosan or levoglucosan, in reasonably good yields. A novel technique based on flash devolatilization of biomass and direct molecular-beam, mass spectrometric analysis has shown that levoglucosan is a primary product of the pyrolysis of pure cellulose. However, the yield of levoglucosan on pyrolysis of most biomass is low even though the cellulose content is about 50 weight percent.

Also, when pure cellulose is treated with only small amount of alkali, levoglucosan formation is inhibited and a different product slate composed of furan derivatives are produced.

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- Levoglucosan is also obtained directly on pyrolysis of glucose and starch.
- The compound has the same empirical formula as the monomeric building block of cellulosic polymers, $(C_6H_{10}O_5)$.

So, this is the reaction you can see of the β -glucosan formation during pyrolysis. This is from the β -D-glucose, it's a mixture, here it can be from cellulose or starch. So, levoglucosan is also obtained directly on pyrolysis of glucose and starch. The compound has the same empirical formula as the monomeric building block of the cellulosic polymers.

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(Overview of next lecture)

Module	Module name	Lecture	Title of lecture
05	Physical and Thermal Conversion Processes	03	Thermal conversion products, commercial success stories

Thank you

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

So, with this I wind up and thank you very much, so in the next class we will be discussing about the thermal conversion products, what are the different types of products, their composition, their applications and some certain commercial success stories about the gasification and pyrolysis, thank you very much. If you have any query please feel free to register it in the swayam portal or drop a mail to me at kmohanty@iitg.ac.in, thank you.