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Lecture - 20 Utilisation of biomass through bio-chemical and thermo-chemical routes

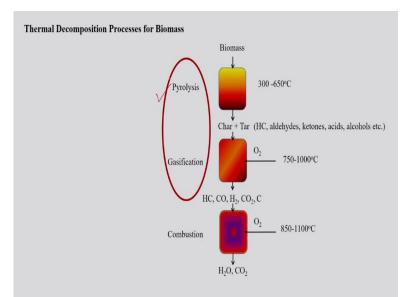
Good morning everyone, welcome to Part 2 of Lecture 1 under Module 7. In the previous lecture, we discuss about the thermochemical conversion processes. In that we discussed about the combustion process, the stages of combustion process as well as the biomass combustion and what is the difference between the partial combustion as well as the complete combustion.

So, in today's lecture, we will continue our discussion again about the thermochemical conversion processes. But in this lecture, will mostly discuss about the pyrolysis and gasification processes.

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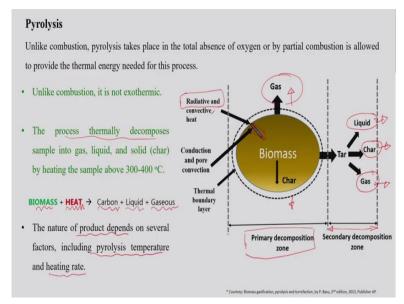
Module	Module name	Lecture	Content
)7	Biomass conversion routes	01 (Part II)	Biomass Residues, Utilisation through Conversion Routes: Bio-Chemical and Thermo Chemical

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Followed by biochemical conversion processes that is fermentation and the anaerobic digestion. So, now, let us start our discussion first about the pyrolysis process.

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So, if you see the pyrolysis process, unlike combustion, pyrolysis is not an exothermic reaction and it takes place in absence of oxygen. So, that is total absence of oxygen. Sometimes, partial combustion is allowed to provide the thermal energy which is required for the process. So, if you try to see the transport of heat in the pyrolyzer it is assumed that heat or the mass transfer is too high to offer any resistance to the overall rate of pyrolysis.

But this is true only in the temperature range say 300 to 400 degree C, but at higher temperature, what happened in that case, the transport of heat and mass is influences by the rate. So, we cannot neglect this particular stage in case of high temperature pyrolysis

reaction. So, during pyrolysis if you see the schematic here, it shows that, so, during the pyrolysis stage, the heat is transported to the particles outer surface.

See here that dotted line which shows the heat which is transported to the outer surface of the particle and that is mostly through radiation and the convection. So, once the heat reaches to this outer surface of the particle, thereafter, it is transported to the interior of the particle. Suppose, if you see here the dotted line shown here. So, this shows here the transfer of heat inside the particle by conduction and by convection inside the pores of this particular particle.

So, if you try to see the mode of heat transfer in the case of sample, there is a heat available outside this particular particle surface. So, mostly it is through the conduction of the heat inside the particle and then convection inside the pores of the particle then followed by the radiation and convection from the particle surfaces. So, this mode of heat transfers are normally occurs when the pyrolysis process is taking place.

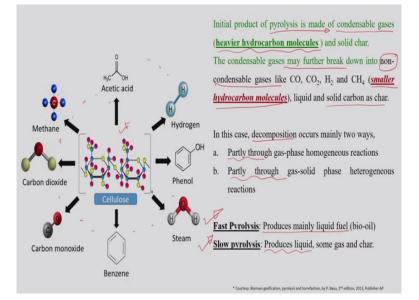
And the sample is heated using a suitable heat source. So, during this particular process, as we mentioned here, it thoroughly decomposes the sample into liquid, gas and char as a product. And the temperature is mostly above say 300 to 400 degree C. And if you see here the reaction that is the biomass will be supplied with the heat. It mostly produce carbon, which is in terms of we say char, the liquid as a product and gas.

So, the first phase here, it represents the primary decomposition zone. In this case once the sample undergoes decomposition, it produces condensable gases and char. Once the produce condensable gases during this pyrolysis stage and the char goes under the secondary decomposition zone. So, it produces liquid as a product, char and non condensable gases. So, if you see here in this case, the first primary zone it mainly produces the condensable gases.

Once it reaches to a secondary decomposition zone, so what happened in that case? The condensable gases along with the char. So, secondary cracking happens in that case and then it mostly yields non condensable gases in the form of CO, CO 2, some traces of hydrogen and methane as well. And then also it yields char and mostly the liquid as a product. So, the nature of product in this particular stage, it depends on several factors.

Mostly the pyrolysis temperature and the heating rate, how the heating rate is being used for the pyrolysis condition.

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So, the initial product which are formed in the pyrolysis are mostly a condensable gases as I have said earlier. And these are nothing but the heavier hydrocarbon molecules. So, these also try to remember this particular point. These are mostly heavy hydrocarbon molecules and the solid char. So, this condensable gases may further break down into non condensable gases.

So, that is what I said in the second zone once it reaches to a second zone, which is also called as a secondary cracking. So, the condensable gases may further break down into non condensable gases, which are like CO, CO 2, hydrogen and the these gases absorbed mostly the hydrogen and methane are in the trace amount here. And these are represented as a smaller hydrocarbon molecules along with liquid and the solid char.

So, this is the difference between the primary zone of the reaction in the pyrolysis and the secondary zone, which we say as a secondary cracking inside the reactor. So, in this decomposition mainly it occurs in the 2 particular ways. That means the first one is it partly happens through the gas phase homogeneous reaction. That means only the gases are reacting with each other.

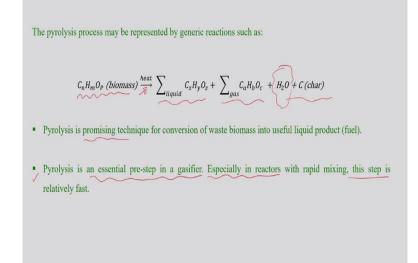
Whereas in the second case, it happened partly through the gas solid phase heterogeneous reaction that means the gases they try to react with the char and then they try to go for the

reduction process there. And because of that, the breakdown of the molecules of higher hydrocarbon molecules to a smaller hydrocarbon molecules happens and then it releases the non condensable gases along with the liquid as a product and the solid carbon as a char.

So, in this case, if the process is carried out under the fast pyrolysis condition, the it mainly produces liquid fuel and that way always term it as a bio oil which is a product of the pyrolysis process. However, if the process is a slow pyrolysis process, so, in that case, it produces liquid, some gases and char also as a product. So, now, if you see here, the small hydrocarbon compounds, which form once it goes under the breakdown in the secondary tracking zone.

So, the small hydrocarbon compound, which form in this particular stage are represented here. And if you see here we are represented the complex molecule in terms of cellulose. The cellulose decomposition in the pyrolysis condition use this kind of small hydrocarbon molecules.

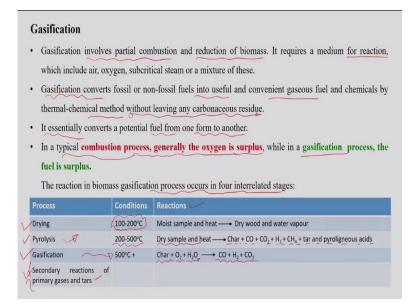
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So, the pyrolysis process may be represented by in a generic reaction. So, this particular form it represents the biomass which is carbon, hydrogen and oxygen. And once the heat is supplied to this biomass so as we discussed earlier, it produces liquid gas and char as a product with some amount of moisture. So, the pyrolysis is a promising technique for conversion of waste biomass into useful liquid product. So, that we also say here is like we are just converting one form of fuel to the another form of fuel just by increasing its energy density. However, in case of pyrolysis product, we need to also go for the further treatment processes to improve the quality of the bio oil as well. And in the second point, if you see here, it is an essential pre step in the gasifier. So, pyrolysis is considered as an essential pre step in the gasifier before it goes under the oxidation and the reduction zone.

Especially in the reactors with rapid mixing this step is relatively fast. So, this is about the pyrolysis process. So, we will also try to discuss in more elaborate way about the pyrolysis and you can say the types of pyrolysis reactor in more elaborate way in the subsequent module as well.

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So, now, the next process in the thermochemical conversion is gasification. So, the gasification and the combustions, these are the 2 closely related thermochemical conversion processes. But there is a important difference between these 2 process which one need to understand. Because what happen in case of the gasification, the energy is packed into chemical bonds in the form of the product whereas in the combustion process what happens is like it breaks down those molecules to release the energy.

So, what happen in case of gasification, it converts or you can say in the gasification, it adds hydrogen to and release or you can say removes the carbon from the feedstock in the form of the produced gas. So, in that case, there is the reason it gives higher hydrogen to carbon ratio. While in the combustion if you see the mainly oxidation of hydrocarbon takes place which releases CO 2 and H 2 O as a product from the combustion process along with the significant amount of heat.

So, this is the difference between the gasification and the combustion process. Because in the gasification, we are adding hydrogen to it, but along with that, we are also trying to remove the carbon from the feedstock so that you can increase the higher hydrogen to carbon ratio of the produced fuel whereas in case of combustion, what happening is like hydrocarbons are getting oxidized and then (()) (11:33) releasing CO 2 and H 2 O as a product along with a significant amount of heat.

But, the gaseous product produced from the combustion process is not a combustible gas whereas, gasification it gives a combustible gas. So, this is the difference between the gasification and the combustion. So, if you see here the gasification it involves the partial combustion as I said and the reduction of the biomass. It requires a medium for the reaction.

So, medium, it can be in the form of air, oxygen, or you can say subcritical steam also or the mixture of these. So, gasification mainly it converts fossil or even the non fossil fuels into useful and convenient gaseous fuel and chemicals by thermochemical method. So, in this case the attempt is like without leaving any carbonaceous residue behind. So, that means the gasification process in the gasification.

We try to convert the entire carbon into the gaseous product so that there should not be any unconverted carbon left in the reactor. It essentially convert a potential fuel from one form to the other. As I mentioned, we are just converting biomass into a gaseous fuel in this case of gasification, whereas, when you talk about the pyrolysis we are producing liquid and solid along with the trace amount of gases as a product.

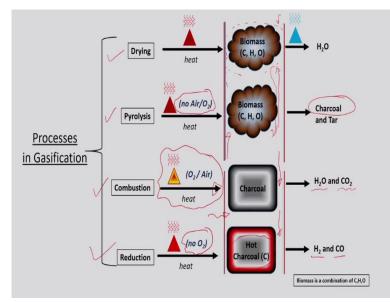
But as we are discussing here about the gasification, so, here the biomass is getting converted into a product gas. In typical combustion process, generally, the oxygen is surplus whereas, if we talk about the gasification process, in this case the fuel is surplus. So, this is the difference between the 2 process. And if you see the typical biomass gasification process, so, the number of steps involved in the gasification processes are these 4.

That is drying you can say pyrolysis, gasification and secondary reaction of primary gases and tar. So, in the drying what happens is like it is carried out in the temperature range of say 100 to 200 degree C. So, in this particular case what happens is mostly it removes the moisture from the incoming biomass or we can say the feedstock which is coming inside the reactor.

So, the second stage is a pyrolysis stage which is carried out say for example, in the temperature range of sometimes 300 or 400 or above that. So, the dry sample and the heat it pyrolyzes the biomass in this particular step. And it produces this kind of product. So, the pyrolyzed product in the form of like condensable gas, char then undergoes the gasification reaction. That is mostly a oxidation and a reduction reaction.

Because, in this particular step, mostly we try to add partial amount of oxygen or air so that the oxidation of the produced product will take place in this particular step where the temperature is 500 plus. And in this case, the char is oxidized and get reduced to produce CO, hydrogen, CO 2 and trace amount of CH4 as well. Further the secondary reactions of this product will take place with the primary gases and tars.

In the particular stage, if you try to provide the more (()) (15:13) time inside the reactor, the reactions will continue further in the this particular step. So, now, if you try to see this table in more elaborate way in the schematic form.



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So, here also this is a representative form of the gasifier. You can see here. And if you see here, these are the 4 stages or you can say the steps in the gasification process. So, in this case, if you just try to see from the beginning, so, the first drying of the sample takes place. So, what happen in this case?

So, the heat of the combustion. Because, as we are injecting partial amount of oxygen in this particular zone which is called as a combustion zone where oxidation of the pyrolyzed product will takes place. So, because of that what happens is like heat is transported from this particular combustion zone in the upward direction in the form of radiation, conduction and a convection.

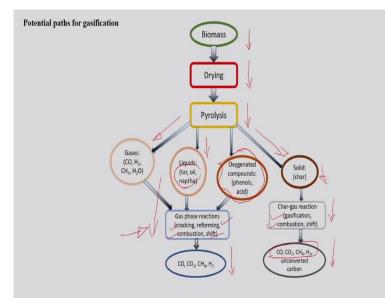
So, the heat which is transported in the upward direction in this case, so, what happened because of that, it provides the heat for the pyrolysis reaction where there is no oxygen involved as well as some amount of heat which is available here, which act as a heat to dry the incoming feedstock inside the gasifier. So, once this particular dried material, it gets pyrolyzed here, it produces mostly as I said the condensable gases and char.

The produced gases in this particular stage along with the char it get oxidized here with the addition of small amount of or you can say partial amount of oxygen. So, because of that, the oxidation will takes place here. And it mostly produces H 2 O, CO 2 and some traces of hydrogen here as well.

And then this particular product of the oxidation stage which undergoes further reduction in this particular zone, where what happened in this case is like the hot charcoal along with the oxidized product, undergo the reduction reaction and then it produces hydrogen, CO and trace amount of CH4 also as a product. So, this is how the gasification reaction it takes place in the gasifier.

So, this is you can say is a representative of the downdraft gasifier as you are seeing the feed is coming from the top and we are just trying to recover the product from the bottom of the gasifier. So, I hope this clarifies your entire concept of the steps of the gasification reaction. So, if you mainly see here, this is the only step where the oxygen or air is supplied to the gasifier so that the oxidation of the incoming product will takes place. So, that it can form mostly H 2 O, CO 2 and some trace amount of hydrogen as well in this case. And other processes are mostly it is represented here that no oxygen or no air is involved in this particular step.

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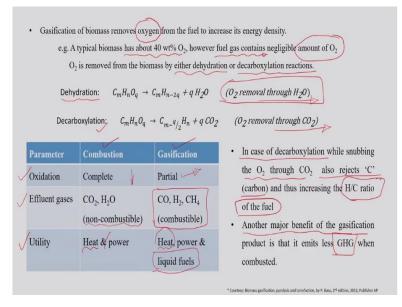
So, this is a potential path for the gasification process. If you see here as we have just discussed in the previous schematic I am just trying to elaborate the discussion what are the basically the gases which forms once you pyrolyze the biomass. So, once the drying process is completed, then the pyrolysis or you can say the pyrolysis of the dried product will carried out in this particular step, which mainly produces gases in the form of the composition which is mentioned here.

Then liquid in the form of this composition, it all depends on the feedstock, which is being used for the pyrolysis process. And then the oxygenated compound, which are nothing but the phenols and the acids. So, if you see in that particular stage, these are the acidic compound and the phenols, which are also getting produced during the pyrolysis stage in the primary zone because of the breakdown of the complex molecule to a smaller hydrocarbon molecule as well.

So, the next is nothing but the solid char which also produced during the pyrolysis process. It undergoes gasification that is we call it as a oxidation reaction. So, in this case, this is mostly a gas phase reaction, because all these are in the gaseous form because the temperature in that cases is relatively high. As a result all these components are in the gaseous form. And as a result, it represents mostly the cracking, reforming, combustion and the shift reaction in this particular zone. So, this is called as a gas phase homogeneous reaction. And once this breakdown of the molecule happens and oxidation and the reduction reaction takes place with these gas molecules along with the char, then it gives this kind of product.

Similarly, the solid char which is there along with this particular gases inside the gasifier, it also undergoes gas solid phase heterogeneous reaction which mostly in the form of gasification and the combustion and the shift reaction and gives this product along with the unconverted carbon. So, this is difference between the gas solid heterogeneous reaction and the gas phase homogeneous reaction in the gasifier.

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So, the gasification of biomass it removes oxygen from the fuel to increase its energy density. Typically, if you see the biomass it has about 40% of oxygen. However, if you just try to see the gas which comes out from the gasifier, it has negligible amount of oxygen. So, O2 is removed in this particular process in 2 different ways, either by dehydration or decarboxylation reaction.

So, in this case the oxygen is removed through H 2 O. Similarly, if you just try to see the decarboxylation reaction, in this case, what happens is like the O2 removal is takes place through CO 2. And hence because of that, as we discussed also earlier, it increases the hydrogen to carbon ratio of the produced gas. So, in case of decarboxylation, as I said earlier, while snubbing the oxygen through CO 2, also rejects the carbon from the feedstock.

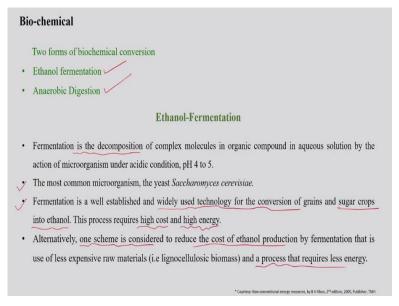
As a result, it increases the hydrogen to carbon ratio of the produced fuel. Apart from that, another major benefit of the gasification process is it emits less greenhouse gas when combusted. So, we just try to see the difference between the combustion process and the gasification process in this tabular form here.

So, the parameter which we have this we are trying to discuss here is oxidation, effluent gases, which are produced from this particular process as well as the utility of the produced gas. So, if you see here the combustion which is terms as a complete combustion process and mostly it produces the effluent gas in the form of CO 2 and the H 2 O. But it is a non combustible.

Whereas, if we see the gasification it is mostly carried out by partial oxidation process and the produced gases in this case are the combustible gases. Similarly, if you just try to see the utility it produces significant amount of heat and the produced heat can be used as a process heat or can be converted into a power as well.

In this case, it is the same that the heat produced by the combusting this particular gases can be used as a process heat as well as can be used to produce power or can be converted into a liquid fuel by subsequent thermochemical conversion processes. So, this is how the difference is between the combustion and gasification process.

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Now, in the biochemical processes, mostly we will be discussing about the ethanol fermentation and the anaerobic digestion. So, fermentation is the decomposition of the

complex molecule in the organic compounds in the aqueous solution by the actions of the microorganism in the acidic condition. So, here mostly the pH varies in the range of say for example, 4 to 5.

The most common microorganism which is used in this case is the yeast Saccharomyces cerevisiae. If you see the fermentation process, it is a well established process, which is used widely for the conversion of grains, sugar crops into ethanol. And this process requires high cost and the high energy.

So, as a alternative in this case, one scheme is considered to reduce the cost of ethanol production by fermentation technique by utilizing a less expensive raw material that is termed as a lignocellulosic biomass and a process that requires less energy. But in case of lignocellulosic biomass, what happens is like if the feedstock is a lignocellulosic biomass, then the biomass need to hydrolyze before it is being used for the fermentation process.

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- Hydrolysis of an abundant carbohydrate polymer (ligno cellulose) yield large number of Glucose units which is being considered for the former.
- Even the large-scale production using less expensive feedstock still faces some challenges to reduce the production costs, and an improvement on technology efficiency for the generation of commercial profit is still necessary
- The sugars may be obtained by the following routes:
- Y. Directly from sugarcane
- 2. From sugar beet, sweet sorghum, grapes, molasses
- 3. From starch crops (i.e. grain and cassava)
- V4. From cellulose (i.e. wood, straw, stems of grasses, bamboo, sugarcane bagasse)

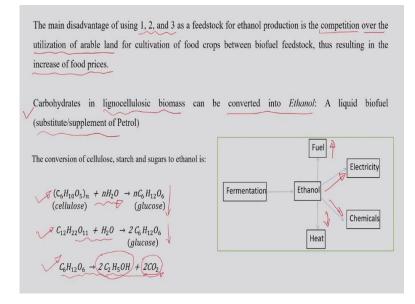
So, the hydrolysis of this particular complex molecule, it yields large number of glucose units, which also termed as a reducing sugars and then the produced reducing sugar can be utilized for the fermentation purpose. So, even the large scale production using such less expensive feedstock still is not feasible here that means still it is facing some challenges to reduce the production cost.

And an improvement on technology efficiency for the generation of commercial profit is still necessary. So, if you see the fermentation process, the mostly the sugar which may be used

for the fermentation process is obtained from the following feedstock. That means we can directly use a sugarcane as a feedstock. Apart from that, sugar beet, sweet sorghum, grapes and the molasses are also act as a feedstock for the fermentation process.

Apart from that, some starch crops like grains and roots cassava can also be used for this particular purpose. And the last point is nothing but the from cellulose as we mentioned, as this is a less expensive material, so it is being used for the production of ethanol now. So, it includes wood, straw, stems of grasses, bamboo, sugarcane bagasse as well.

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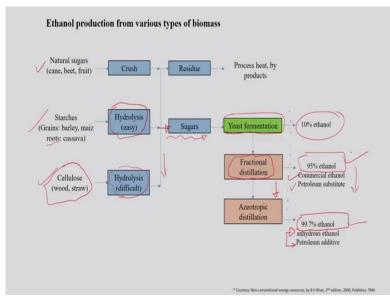


So, if you see in this case, the main disadvantage of using 1, 2 and 3 as a feedstock for the ethanol fermentation is competition over the utilization of arable land for the cultivation of the food crops between the biofuel feedstock, thus resulting in the increase of the food prices. If we just try to use this 1, 2 and 3, as we discussed in the previous slide, as a feedstock, then always there is a criticism about the food versus fuel crisis.

So, as a result, the carbohydrate which are in the form of say lignocellulosic biomass are being used for the ethanol production. And it is also termed as a biofuel that is a bioethanol which act as a supplement to the petroleum fuel. So, if you just try to see the reaction scheme for the cellulose, starch and the simple sugar molecules to produce ethanol, so, which represent here the first reaction represent the cellular molecule suppose.

So, under hydrolysis condition, in this case, it produces glucose units. Similarly, if you talk about the starch, it also undergoes hydrolysis to produce again the glucose molecule which are also termed as a simple sugars. So, the produced ethanol can act as a supplement to the petroleum fuel, also can be used for the heating purposes, electricity generation or it is conventionally being used as a chemical also which is 95% ethanol or 99.7% ethanol.

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So, the ethanol production from these various biomasses if you just try to see this schematic here, just outline here, a schematic which shows the ethanol production from the various biomass feedstock. So, we just try to discuss this particular feedstock one by one. So, first is the natural sugars, the second is starch materials in the form of barley, maize, and the roots that is nothing but the cassava, the cellulose in the form of wood and the straw.

So, if you just try to focus on the first feedstock that is the natural sugars. So, as these are the natural sugars which are nothing but the simple sugars. So, this feedstock can be crushed to release the simple sugar and the produced sugar from this particular feedstock can be fermented using a yeast to produce 10% aqueous ethanol.

Further this 10% aqueous ethanol can be upgraded to 95% ethanol, which is called as a commercial ethanol petroleum substitute by fractional distillation. So, as a result, the fractional distillation of the 10% aqueous ethanol gives around 95% of the ethanol. So, we are just increasing the quality of ethanol in this particular stage.

If you need to further purify this particular ethanol, so, by azeotropic distillation, we can convert it into a more pure form of ethanol which is equivalent to 99.7% ethanol which is called as a anhydrous ethanol and the petroleum additive as well. So, if we just try to see the

second feedstock here which is nothing but the starch material in the form of barley and the maize. So, what happened in this case?

First we need to go for the hydrolysis process, which is not required in the previous feedstock if you see here. Starchy material is being used for the ethanol fermentation. So, the hydrolysis step is relatively easy. So, it releases again the simple sugars in the form of glucose units. So, those sugar molecules can again be passed through a these particular steps to produce the ethanol.

Now, suppose, if the feedstock is a cellulose which is in the form of say wood or the straw. So, in this case also, this particular feedstock has to pass through a hydrolysis process. But in this case, the hydrolysis process is quite difficult. So, relatively harsh conditions are required to hydrolyze this biomass here compared to the starchy material.

So, as a result, apart from that, some intermediate steps are also required to purify this sugar so that you can have monomers or the simple sugar which are in the pure form for the fermentation process. If it is not in pure form, what happen in that case? The traces of some inhibiting component tried to inhibit the this particular fermentation process here. And as a result, the yield of the ethanol goes down.

So, for that case we need to have the pure sugar also from this particular source, which is we say that a cellulose molecule. And then again it pass through a same stages of the conversion to achieve either 99.7% ethanol and a 95% ethanol. So, the next process is the anaerobic digestion. So, when organic matter undergoes fermentation through anaerobic digestion, gas is generated in that particular case.

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Anaerobic Digestion

When organic matter undergoes fermentation through anaerobic digestion, gas is generated. This is known as biogas. Biogas is generated through fermentation or bio-digestion of various wastes by a variety of anaerobic and facultative organisms. The process is favored by wet, warm and dark conditions, residence time, and others.

- It comprises approximately 55-65% of CH₄ and 30-40% CO₂, with small amounts of other gases (H₂, H₂S, N₂) along with a decomposed mass.
- The gases formed are the waste products of the respiration of these decomposer microorganisms and the composition of the gases depends on the substance that is being decomposed.
- If the material consists of mainly carbohydrates, such as glucose and other simple sugars and high-molecular compounds (polymers) such as cellulose and hemicellulose, the methane production is low. However, if the fat content is high, the methane production is likewise high.
- Nutrient such as soluble <u>nitrogen compounds</u> remain available in solution and provide excellent fertilizer and humus.

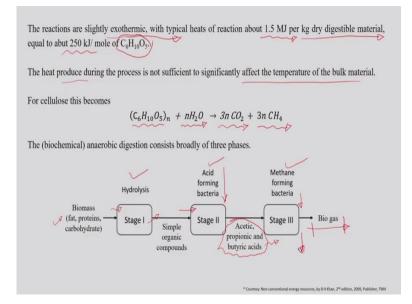
And this is known as the biogas. The biogas which is generated through the fermentation or the bio digestion of various waste by variety of anaerobic and the facultative organisms. The process is favored by wet, warm, dark condition, residence time and some other parameter as well. So, typically, the biogas produced from this particular material, it comprises approximately of 55 to 65% methane and 30 to 40% CO 2 with small traces of other gases in the form of hydrogen, H2S and nitrogen along with a decomposed mass.

The gas form are the waste product of the respiration of this decomposer microorganism and the composition of the gas it depends on the substance that is being decomposed. So, the entire composition of the biogas is solely depends on the substance that is being used for the bio digestion purpose.

If the material mainly consists of carbohydrates such as glucose, other simple sugars and high molecular compound in the form of like cellulose or hemicelluloses, the methane production in those particular feedstock is low. However, if the fat content is high, then the methane production is relatively high. So, this is how we have to understand what kind of substance is being decomposed in the digestion process.

Accordingly, the gas (()) (33:58) will comprise of methane and the CO 2. Along with that, the nutrients such as nitrogen compounds remains available in solution and provide excellent fertilizer and humus.

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The reaction in this case are slightly exothermic reaction. And typically the heat of reaction is about 1.5 megajoule per kg of dry digestible material or we can say equal to about 250 kilojoule per mole of cellulose molecule. And the heat produced during this process is not sufficient to significantly affect the temperature of the bulk material. Now, if you see the reaction here, the decomposition of cellular suppose, in presence of sufficient amount of moisture or you can say water, it releases CO 2 and methane.

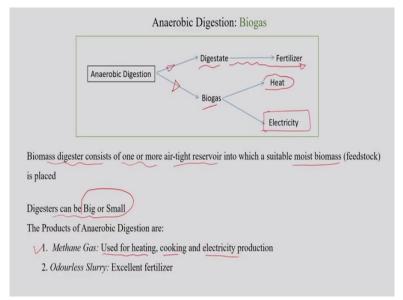
The typical anaerobic digestion process consist of broadly 3 phases. So, the first is nothing but the hydrolysis stage. The second is the acid forming bacteria and third is the methane forming bacteria where the methane production will takes place. So, in the first case, if you see here, the complex carbohydrate molecules along with the fats and proteins, we will get hydrolyzed in the stage one with the influence of water.

And it forms water soluble compound. So, after this Stage 1, the product of the Stage 1 undergo the formation of acetic acid, propionic acid and butyric acid mostly by the acid former bacterias. So, once this particular product is available inside the digester, what happen is like in that case, in the Stage 3, now, the anaerobic bacteria mostly the methane forming bacterias try to decompose this particular material and produce biogas in the form of methane and a CO 2.

So, in this case also the temperature is mostly in the range of say for example, 25 to 33 or 34 degree C. And the product obtained in this particular last stage is nothing but the methane and

the CO 2. But in Stage 3, mostly, the methane forming anaerobic bacteria will take part into the decomposition reaction to yield the methane.

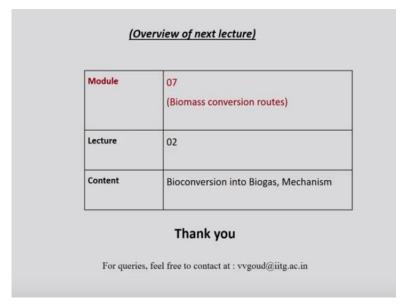
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Anaerobic digestion use 2 different product mostly in the form of biogas and the digestate. The digestate can act as a fertilizer and a humus. Similarly, the biogas which is produced during the anaerobic digestion process is used as a heat source along with that it can be also used to produce the electricity. So, the biomass digester mainly consists of one or more air tight reservoir into which a suitable moist biomass is placed.

So, the digester can be small or big in size, but the product of the anaerobic digestions are mostly methane gas, which is used for heating, cooking and the electricity production and odourless slurry, which is act as an excellent fertilizer. So, this is what is about the anaerobic digestion of the biomass.

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So, today, we will stop here. In the next lecture, we will discuss about the bioconversion into biogas and its mechanism in more detail. If you have any query or doubt regarding this particular lecture, feel free to contact me at vvgoud@iitg.ac.in. Thank you.