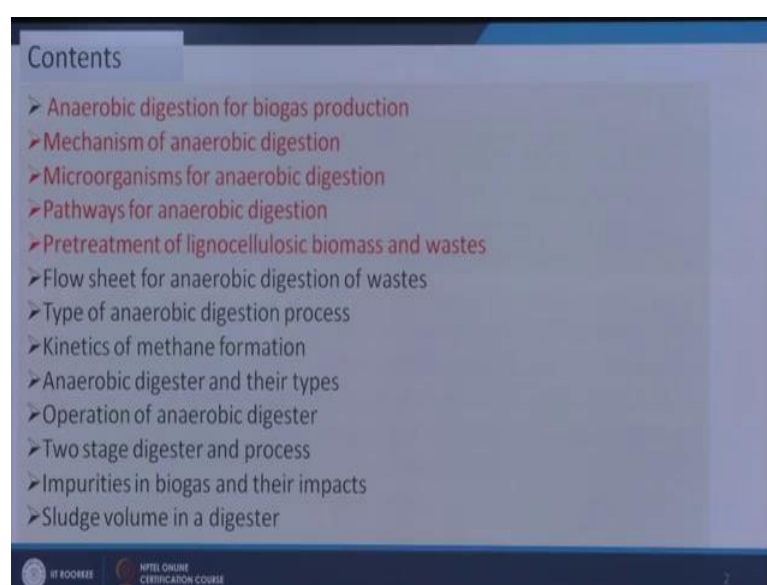


**Waste to energy conversion**  
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**Department of Chemical Engineering**  
**Indian Institute of Technology, Roorkee**

**Lecture – 26**  
**Energy production from Organic Wastes Through Anaerobic Digestion-1**

Good morning. Now we will start discussion on a new module energy production from organic waste through anaerobic digestion.

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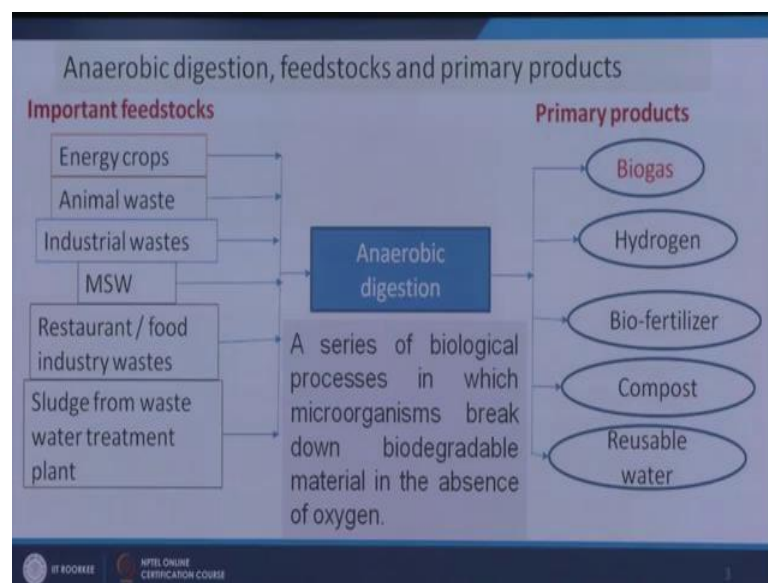
In the previous modules we have discussed on different thermal routes for the conversion of waste to energy. And in this module we will start discussion on the biological route for the conversion of waste to energy. Among different biological routes for the waste to energy conversion anaerobic digestion is one important route. And we will start with this first. So, in anaerobic digestion organic compounds are digested in absence of oxygen in the presence of microorganisms and produces different products, out of which the biogas is the most important product.

So, depending upon the nature of the organic compounds, the complexity of the process will increase, and the flow sheets will also be changed to some extent. And in this process number of steps are involved, and number of microorganisms are responsible for those different types of reactions, different pathways are applicable to get the output of this process. And there are many factors which influence the performance of this

anaerobic digestion process. Type of reactors also influences it. So, all those things we will cover here in this module. And we will discuss on the anaerobic digestion of biogas production, mechanism of anaerobic digestion, microorganisms for anaerobic digestion, then pathways for anaerobic digestion then pretreatment of lingo cellulosic biomass and wastes. So, lingo cellulosic biomass and waste are a special type of wastes which is getting more interest nowadays, but having some difficulty for processing through this anaerobic digestion. So, pretreatment is required and we will discuss on this thing.

Next the flow sheet of anaerobic digestion of wastes, type of anaerobic digestion process kinetics of methane formation then, anaerobic digestion digester and the types operation of anaerobic digester, 2 stage digester and processes and then impurities in biogas and their impacts and finally, we will also discuss on sludge volume in a digester.

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Now, let us see the first the anaerobic digestions and biogas production. So, what is anaerobic digestion? It is a series of biological processes in which microorganisms breakdown biodegradable material in the absence of oxygen. So, in anaerobic conditions microorganisms we will react on organic substrate and the organic substrate will be converted to biogas this is the ultimate process, but this is not so simple and not a single step process, it is a multi steps and a complex process; it involves number of microorganisms, number of mechanisms or pathway is etcetera.

Now, we will see what are the feed stocks that can be used in anaerobic digestion. So, anaerobic digestion can use energy crops. It can use animal waste, it can use industrial wastes it can use MSW municipal solid waste, it can use restaurant food industry wastes, it can use sludge from waste treatment plant. So, there are the possible imported feed stocks, and what we can get from this? We can get biogas, we can get hydrogen, we can get bio fertilizer, we can get compost and we can get reusable water. So, out of this feed stocks the animal waste particularly cow dung to biogas that is gobar gas, this is a very known technology, but use of energy crops industrial shares and other these things through this route is not very well developed. Particularly the energy crops and MSW some part is having ligno cellulosic biomass. So, this ligno or waste, so ligno cellulosic wastes and ligno cellulosic biomass have good potentials and in terms of availability, good potential, and if we can improve this anaerobic digestion. So, those can also be process through this route.

Now if you think about the primary products the biogas, basically it contains methane. So, this is will be having some heating value and as on today in basically the gobar gas, this is used for domestic application the domestic cooking. Or not in very big scale plant we are having, but small scale plant we are having. So, apart from this we can get hydrogen through this route also, but this technology this is not very matured one and people are working, how to get more hydrogen through this different routes of microbiology and then bio fertilizer.

So, when the anaerobic digestion reaction is going on number of reactions are taking place, and some products are formed which are nitrogenous in nature. And which are having good fertilizer, fertilizer values and the residual part after biogas production that can be used for composting. So, compost can be formed and in this process if we compare the thermo chemical or thermal route with this biological route, the basic difference is that in this route we use huge amount of very large amount of water. So, solid content in this anaerobic digestion unit for a typically for a conventional anaerobic digestion it is around 8 percent. So, it is around 8 percent only.

So, remaining 92 percent is liquid, but if we use thermal plant as a thermal route, then the moisture content should be very less. So, most of the say around 80 percent should be say solid content. So, in this case we get large amount of slurry. So, that is slurry contents significant amount of water that water has to be removed are has to be reused.

Otherwise this process will not be acceptable on environmental point of view. That is why people are trying to improve this process in terms of low requirement of water. So, 8 percent slurry which is conventionally used here for anaerobic digestion in wet anaerobic digestion, that is going to be upgraded to dry anaerobic digestions using up to 20 percent of slurry 20 percent of solid in the slurry.

So, these are the feed stocks and these are the primary products which one which we can get through anaerobic digestion route.

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**WHAT IS BIOGAS ?**

Biogas is a combustible mixture of gases. It consists mainly of methane( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ) and is formed from the anaerobic bacterial decomposition of organic compounds, i.e. in absence of oxygen.

Major components of biogas

Gas	%
Methane	50-75%
Carbon dioxide	25-50%
Nitrogen	0-10%
Hydrogen	0-1%
Hydrogen sulphide	0-3%
Oxygen	0-1%

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Now, we will see what is the biogas. So, biogas is produced through the anaerobic digestion, from the organic materials. And this biogas contains significant amount of the methane that is 50 to 75 percent methane and waste is carbon dioxide 25 to 50 percent apart from these 2 major components it may also contain nitrogen 0 to 10 percent it may also content hydrogen 0 to 1 percent, and it may also content H to s hydrogen sulphide that is 0 to 3 percent and in some cases oxygen 0 to 1 percent.

So, these are the typical composition of the biogas and here we see H to s are to be separated. So, this separation we have discussed nitrogen separation we have discussed in the earlier modules. So, this is the biogas. So, as methane is higher it can be used as a source of energy.

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Specific biogas production potential & methane content for several wastes			
Wastes	Average Dry Matter(DM) content (wt%)	Biogas Potential l/ kg Substrate	Methane Content %
Wheat straws	86.5	367	78.5
Barley straws	84	380	77
Lucene	22.5	445	77.7
Grass	16	557	84
Corn silage	34	108	52
Corn stalks	86	309	-
Dried leaves	12.5	260	58

Now, we will see different types of feed stocks or wastes which are available with us and what are the potential of this waste in terms of solid content in terms of bio gas potential in terms of methane content in the biogas. So, this table shows us that with a variation of these feed stocks these values also very significantly.

So, in this 16 12.5 percent solid to 86.5 percent solid we are getting in this case dry matter, but in spite of having this very high dry matter in case of wheat straw it is giving 367 liters per kg substrate potential of biogas production whereas, you see grass it is an only 16, but it is giving us 557 liters per kg of substrate that production. So, this indicates that although waste here dry matter content is required, but it is dependent on the type of matters which is present in it compounds present in the dry matter. So, if it is a lingo cellulosic biomass. So, lingo cellulosic biomass is having good amount of lignin. So, if say 20 to 30 percent or 25 percent of lignin is present. So, that is not useful and it also requires some pretreatment, if due to the presence of cellulose semi cellulose so that process become slower.

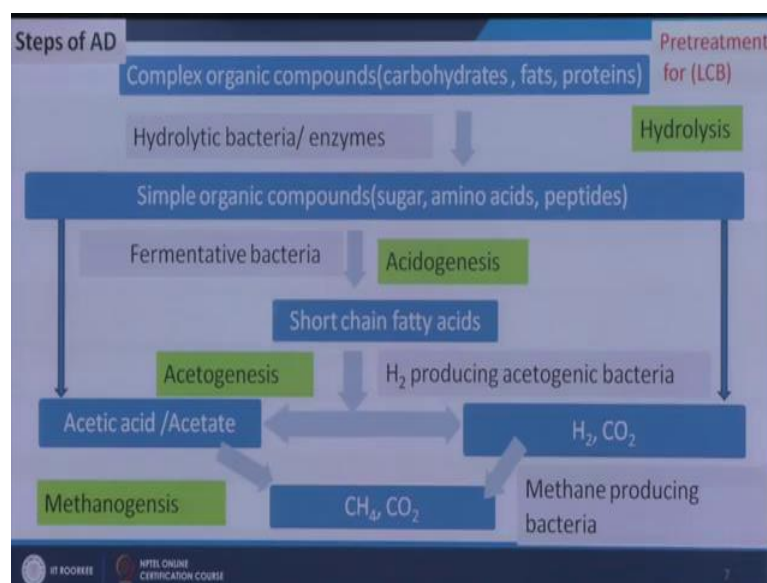
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Specific biogas production potential & methane content for several wastes			
Wastes	Average Dry Matter(DM) content (wt %)	Biogas Potential l/ kg Substrate	Methane Content %
Beet leaves	13.5	501	84.8
Poultry wastes	27.5	520	68
Cattle manure	14	260-280	50-60
Horse dung	27.5	200-300	66
Sheep dung	25	320	65
Pig manure	13.5	480	60

So, and also that is why may be the reason that it is giving the lower biogas potential than this we will see some other examples here. That is beet leaves poultry wastes cattle manure horse dung sheep dung and pig manure. So, these are different ways which are having different dry matter content and also different biogas potential and also the different methane content in the biogas. So, if we see the cattle manure, this is one typical applicable for gobar gas plant, so here cattle manure cow dung around 14 percent solid that is dry matter is present in it gives 262 to 280 liter per kg substrate and 50 to 60 percent of methane. In the first slide we have given that the biogas contains around 50 to 75 percent of methane, but here we are getting say 50 to 60 percent and somewhere even more than 70 75 percent like say 84 like this somewhere 84 like this.

So, these are not used in commercial scale, but efforts are going on to develop some technology for the applications of these feed stocks in commercial scale also just the improvement of this anaerobic digestion process.

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Now, we will see the different steps which are responsible for the whole process of anaerobic digestion. So, if you think about the organic compounds present in it, those are complex in nature. If we exclude the lignocellulosic biomass, then other type of organics basically those are either carbohydrates fats or protein types. So, carbohydrates fats or proteins those are complex molecules. So, those molecules need to be broken down to their monomers or the smaller molecules and that is done by the hydrolysis.

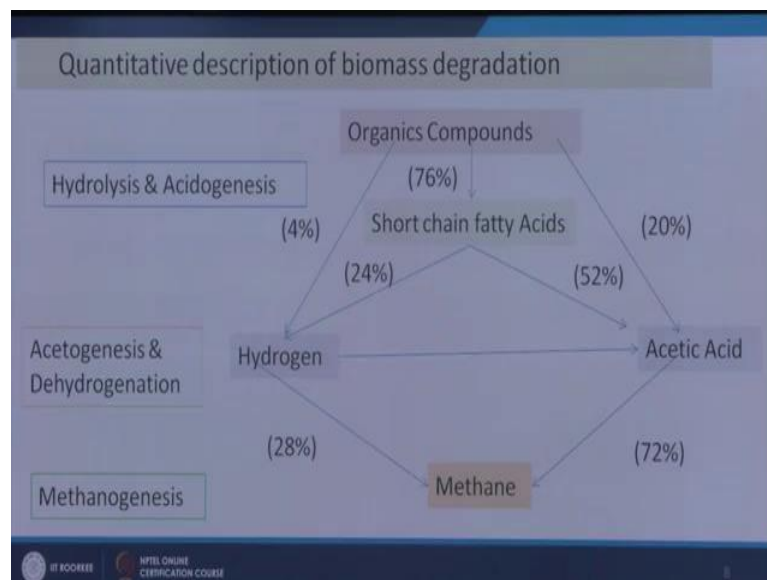
So, hydrolysis is the first step for the anaerobic digestion through which those complex organic compounds are converted to simple organic compounds like sugar amino acids peptides etcetera. So, then simple organic compounds in next step through acidogenesis it is converted to short chain fatty acids. So, this acidogenesis step also this short chain fatty acids also include some acetic acid, and that is a fermentation process. The whole process is basically based on fermentation process. So, carbon dioxide is also produced. So, carbon dioxide hydrogen acetic acid and short chain fatty acids apart from acetic acid are produced through this acetogenesis step. So, after acetogenesis step, this short chain fatty acids can be converted to acetic acid through acetogenesis or can be converted to H<sub>2</sub> and CO<sub>2</sub> through hydrogen producing acidogenesis bacteria.

So, this short chain fatty acids can be converted to acetic acid acidogenesis or can be H<sub>2</sub> and CO<sub>2</sub> through hydrogen producing acetogenesis bacteria. So, this is both these are under acidogenesis step and this H<sub>2</sub> and CO<sub>2</sub> further reactor and forms acetic acid.

So, this is another type of microorganism responsible for this reactions hydrogen and CO<sub>2</sub> will react and give us acetic acid or acetate. Then once the acid acetic and acetate is formed then the next step starts to work that is methanogenesis. So, in this methanogenesis acetic acid or acetate is converted to methane, or this some micros have are also available which directly converts hydrogen and CO<sub>2</sub> to methane.

So, these are the different types of reactions which takes place during the total anaerobic digestion process. This is for organic compounds not lingo cellulosic biomass, or if lingo cellulosic biomass and lingo cellulosic wastes are there. So, the process is more complex and we need some pretreatment step before this. So, carbohydrates fats and proteins this materials can be produced from basically the cellulose hemi cellulose etcetera can be produced from this pretreatments process. So, this is additional step required for handling lingo cellulosic biomass through this anaerobic digestion route. Now we will see what are the contribution of different processes or different steps that is typically how much contributions of different steps are there on the overall ad process or anaerobic digestion process.

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So, here we are considering organic compounds. So, organic compounds are present not lingo cellulosic biomass. So, organic compound is present here. So, that will be converted to hydrogen acetic acid and short chain fatty acid through acidogenesis and fermentative route. So, 76 percent of the organic compounds is converted to short chain



fatty acids, 4 percent is directly to hydrogen, and 20 percent is to acetic acid. So, this is the fermentative route. So, these are the contribution 76 percent 4 percent and 20 percent.

So, if we have total hundred percent here. So, 76 percent we are getting short chain fatty acids out of this 76 percent of short chain fatty acid 24 percent short chain fatty acid is converted to hydrogen and 52 percent short chain fatty acid is converted to acetic acid. And there is some interchange the hydrogen plus CO<sub>2</sub> react to form the acetic acid and then these acetic acid gives methane around 75 percent of methane produced is through the acetic acid and around 28 percent is produced from the hydrogen.

So, this is 28 or round figure 30 and this is say 70. So, 70 and 30 this is the ratio of the methane produce through this 2 routes acetic acid to methane and hydrogen to methane. So, hydrolysis and acidogenesis this is the step next is acetogenesis and dehydration this type, is this is the hydrolysis and acidogenesis and this is the methanogenesis step. So, these are the steps and these are the relative contribution on the overall process. So, this is the typical values it may differ from case to case.

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Elementary description of AD Source- <http://www.fao.org/>

• In case the chemical composition of the organic matter is known, the stoichiometric equation according to McCarty (Pavlostathis et al., 1991):

$$C_nH_aO_bN_c + (2n + c - b - 9sd/20 - ed/4) H_2O \longrightarrow de/8 CH_4 + (n - c sd/5 - de/8) CO_2$$

$$+ sd/20 C_5H_7O_2N + (c - sd/20) NH_4^+ + (c - sd/20) HCO_3^-$$

where:  $d = 4n + a - 2b - 3c$ ,

$s$  = fraction of waste converted into cells,

$e$  = fraction of waste converted into methane for energy ( $s + e = 1$ ),

$C_nH_aO_bN_c$  = empirical formula of waste being digested

$C_5H_7O_2N$  = empirical formula of bacterial dry mass (VSS)

Now, elementary description of anaerobic digestion. So, we have discussed in the previous modules also that to understand a process and to predict the products distribution, we need to express the mechanism with the phenomena in terms of some equations. So, there is stoichiometric equation is required, but in this case anaerobic

digestion the substrates are different may be different and microorganisms may vary reactors may different.

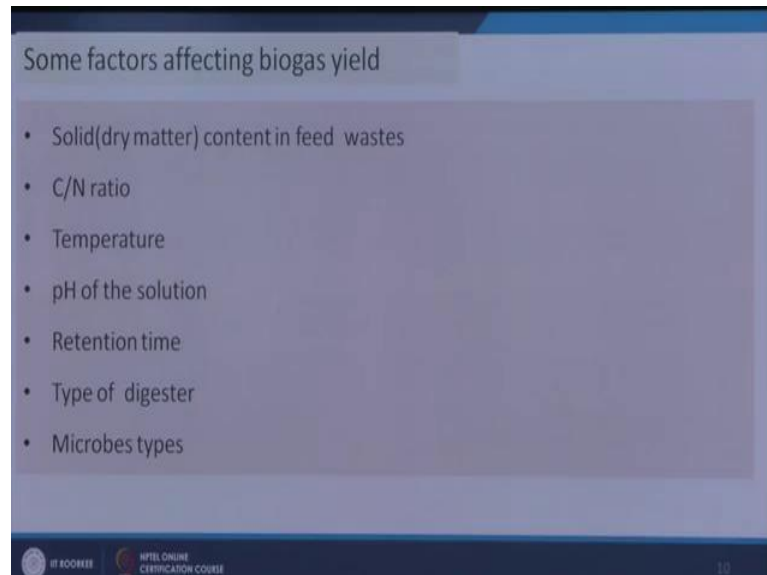
So, it is very complex systems and this complex system it is very difficult to exactly express the stoichiometric equation. So, people tried to express it on the basis of experimental data and some empirical correlations was developed and proposed in 1991 and that has been provided here that is the biogas production that is  $\text{CH}_4$  and  $\text{CO}_2$  production takes place from organic substrate say organic substrate having a  $\text{CH}_n\text{O}_m\text{N}_p$  analysis or elemental analysis. So,  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$ . So, this is the molecular representation of the formula of the organic waste or the organic material which we are using. So, that will be available in water. So, that what will be say in higher content say this this concentration is only say 8 percent or say 10 percent and this say around 92 or 90 percent.

So, this percent is  $\text{H}_2$  and this is our organic materials. So, people tried and shown that this relationship  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  plus  $2\text{N}$  plus  $\text{C}$  minus  $b$  minus  $9s$  divided by  $20$  minus  $e$  divided by  $4\text{H}_2\text{O}$  in presents of microorganisms here microorganisms will give some  $d$   $e$  by  $8\text{CH}_4$  plus  $\text{N}$  minus,  $\text{C}$   $s$  divided by  $5$  minus  $d$   $e$  by,  $8\text{CO}_2$  plus  $s$  divided by  $20\text{C}_5\text{H}_7\text{O}_2\text{N}$ . So, this is nothing, but the empirical formula bacterial dry mass. So, bacterial dry mass will be produced in the media in the system plus  $\text{C}$  minus  $s$  divided by  $20\text{N}_4$  plus. So,  $\text{N}_4\text{H}_4$  will also be available in the in the slurry plus  $\text{C}$  minus  $s$  divided by  $20$  into  $\text{HCO}_3$  minus.

So, this is the formula empirical formula proposed by this researches now it is interesting to see here that the whole equation includes  $a\text{N}_c\text{b}$   $s$   $d$  in the coefficients of this. So, what is that  $\text{N}_c\text{b}$  are here we are getting from  $\text{CH}_n\text{O}_m\text{N}_p$  Analysis  $\text{N}_a\text{b}_c$  we can get, but 2 important things that is  $s$  and  $e$   $s$  and  $e$  has also be incorporated in the expression. So, what is that  $s$  that is the fraction of waste converted into cells, the waste or organic material which is used as a feedstock part of it is converted to bacterial biomass and part of it is converted to energy. So, that  $s$  is the fraction of waste converted to cells and  $e$  is the fraction of waste converted to methane for energy. So, if we take  $s$  plus  $e$  that will be one. So,  $s$  plus  $e$  is equal to 1. So, this is the empirical formula and here we are getting one  $\text{C}_5\text{H}_7\text{O}_2\text{N}$  that is the empirical formula of the bacterial dry mass and  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  and  $\text{N}_c$  is the empirical formula of the waste being digested.

So, this is the empirical relationship or the stoichiometric expressions people have proposed for the anaerobic digestions.

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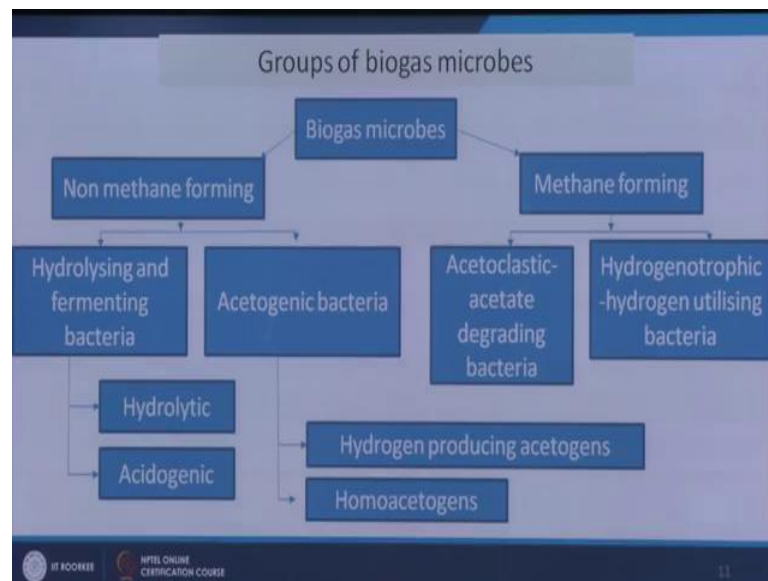


Now, we will see some factors which influence the anaerobic digestion process. Some important parameters like say solid content feed wastes, that we have just discussed that typically 8 percent is maintained in conventional anaerobic digestion methods, but efforts are on to increase this to around 20 percent for dry anaerobic digestion. C by N ratio carbon and hydro nitrogen ratio is also important because nitrogen is required for the growth of the microorganism. So, C N C N ratio also influence the rate of reactions and the gas productions temperature is important because the microbes are sensitive to temperature different types of microbes are able to grow in different temperature range.

So, different types of microbes will be used different temperature range you will be used we will discuss in later on and pH of the solution that is also important because that we will influence the growth of the microorganisms. Microorganisms can one sustain all pH. So, pH has to be selected on the basis of the suitability of the microorganisms and retention time because you know this is the biological methods. So, microorganisms degrade or reacts on the substrate. So, this is very slow process. So, retention time is very high in this in this system and retention time play significant role if we cannot choose a retention time in a proper way. So, we may not get the efficient use of the system and type of digesters there may be some other types maybe one step 2 step.

We will discuss later on. So, types of digesters also influence the performance of the process and microbes types what type of microbes you are using just to have seen in different types of steps are there. So, different microbes are responsible if we do not use one particular type of microbes so; obviously, that phase will be stopped or will be less. So, our overall eff efficiency of the process will be affected.

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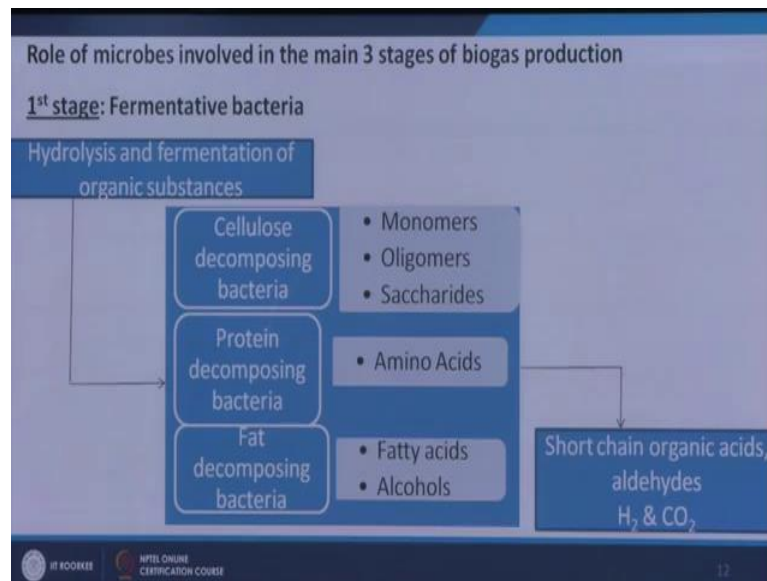
Now, we will see the groups of biomass biogas microbes. So, what are the groups our objective to get methane. So, one will be methanogenic or methane farming microorganisms and another is that is non methane forming microorganisms. So, the initial steps are not methane farming. So, the initial steps will be responsible for the non methane forming microorganisms and the different steps are hydrolyzing and fermenting bacteria and then acetogenic bacteria.

So, hydrolyzing and fermenting bacteria and acidogenic bacteria are under non methane forming and these bacteria hydrolyzing and fermenting; obviously, acetogenic and hydrolytic. So, hydrolytic this microorganism will help to hydrolysis and acidogenic will help to convert the sugars to acids. And then acetogenic bacteria will be long chain small chain acids will be converted to our acetic acid and acetates and hydrogen. So, these are 2 hydrogen producing acetogens means acetic acid plus hydrogen will be formed and in another case hydrogen plus CO<sub>2</sub> will be converted to acetic acid that homo acetogens and methane forming that is acetoclastic acetate degrading bacteria acetoclastic means

acetate will be degraded to form  $\text{CH}_4$  and another is hydro genotrophic hydrogen utilizing bacteria hydrogen or tropic.

So, hydrogen plus  $\text{CO}_2$  will be reacting and give us  $\text{CH}_4$ . So, these are the different types of microbes which are used in case of a d anaerobic digestion process.

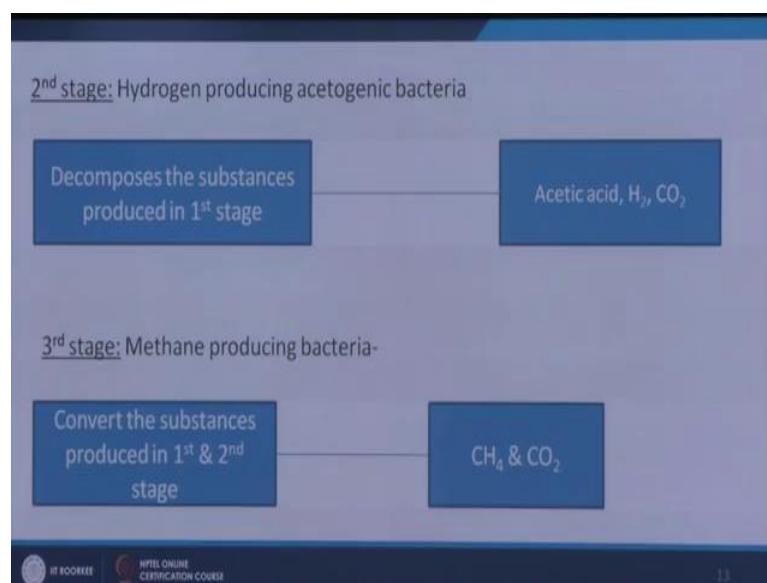
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So, what the microbes work what type of work they do on this. So, first step that fermentative bacteria those work on cellulose to decompose bacteria. There is a cellulose decomposing bacteria, then maybe protein decomposing bacteria may be fact decomposing bacteria, and they decompose the cellulose forms monomers oligomers and saccharides, the protein decomposing bacteria forms amino acids and fat decomposing bacteria fatty acids an alcohol and all those compounds in the later stage is converted to shot chain organic acids aldehydes hydrogen and  $\text{CO}_2$ .

So, this is fermentative including acidogenic bacteria. So, these are the activities of this bacteria role of this bacteria.

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And the second step that is acetogenic bacteria, the first the acids which is formed that is converted to acetic acid and H<sub>2</sub> CO<sub>2</sub> and the third is methane that comes methane CH<sub>4</sub> and CO<sub>2</sub>.

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The slide is titled 'Hydrolysing and fermenting bacteria'. It contains three bullet points: 1. 'The first step in the fermentation of complex substrates is the hydrolysis of polysaccharides to oligosaccharides and monosaccharides, of proteins to peptides and amino acids, of triglycerides to fatty acids and glycerol, and of nucleic acids to heterocyclic nitrogen compounds, ribose, and inorganic phosphate'. 2. 'Relative anaerobes of genera like Streptococcus and Enterobacterium, Bacillus, Cellulomonas, Mycobacterium are some important hydrolytic bacteria.' 3. 'Hydrolytic enzymes like cellulases, hemicellulases, amylases, lipases and proteases from these bacteria depolymerize carbohydrates, lipids, and proteins to soluble molecule.' The slide includes a footer with 'IIT ROORKEE' and 'NPTEL ONLINE CERTIFICATION COURSE' logos, and the slide number '14'.

So, now we will see what are the fermenting and hydrolyzing bacteria. So, as we discuss that this hydrolyzing bacteria at first reaction the complex organic compounds and different organic compounds are there. So, those, complex compounds will be converted to relatively smaller molecular rate compounds, and oligosaccharides the

polysaccharides to oligosaccharides and monosaccharides and proteins to peptides and amino acids triglyceride to fatty acids and glycerol and nucleic acid to heterocyclic nitrogen compounds ribose and inorganic phosphate.

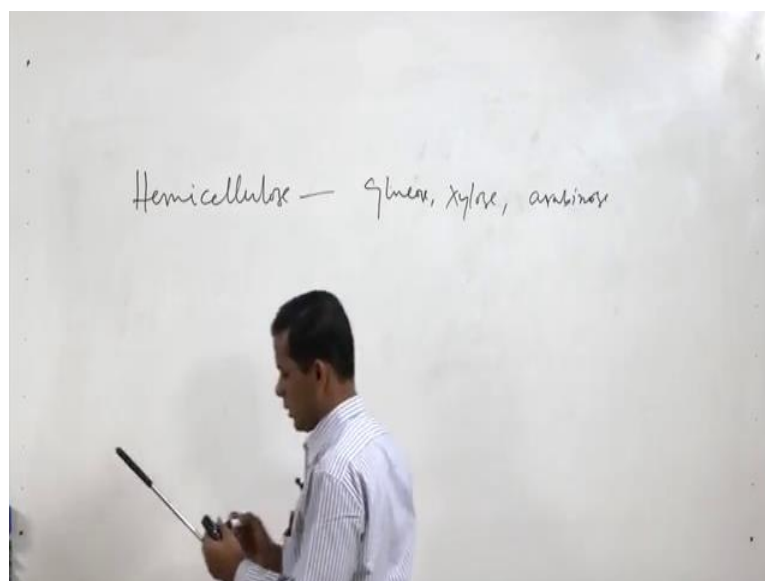
So, these are the conversion the first step, and we will see the relative anaerobes of general like streptococcus and enter bacterium, that is bacillus cellulomonas and mycobacterium are some important hydrolytic bacteria. So, these are some important hydrolytic bacteria which can hydrolyze the organic complex organic compounds. Now we can use the enzymes extracted from this microorganism in place of the whole microorganism cells. So, those enzymes are cellulases hemi cellulases amylases lipases proteases and from this bacterium we can get and they deep polymerize the carbohydrates lipids and proteins to solve will molecule.

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Hydrolysing and fermenting bacteria	
Complex compounds in feedstocks	Typical Hydrolysis products
Carbohydrates	Sugars, alcohols
Cellulose	Glucose, cellobiose
Proteins	Amino acids
Peptides	Fats, Fatty acids, glycerol
Lignin	Degraded very slowly

And these are the different complex compounds and these are the converted forms through the acidogenic bacteria, carbohydrates to sugars and alcohols cellulose to glucose and cellubiose it may be say hemi cellulose.

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So, it is hemi cellulose to say glucose xylose and arabinose. So, those will be the product if feed stocks are hemi cellulose. Now proteins amino acids peptides to fatty acids and lignin is not degraded by the microorganisms.

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Hydrolysing and fermenting bacteria	
<ul style="list-style-type: none"><li>• Obligate anaerobes including <i>Bacteroides</i>, <i>Bifidobacterium</i>, <i>Butyrovibrio</i>, <i>Eubacterium</i>, and <i>Lactobacillus</i> act as acidogenic bacteria.</li><li>• Many enteric coliform bacteria, classically represented by the pathogen <i>Escherichia coli</i> in the genus <i>Escherichia</i> and pathogens in the genera <i>Salmonella</i> and <i>Shigella</i>, are also some common fermentative(acidogenic) bacteria.</li></ul>	
Hydrolysis product	Conversion during acidogenesis
Sugar	Fatty Acids (succinate, acetate, propionate, lactate, formate), carbon dioxide, hydrogen
Alcohols	Fatty acids, CO <sub>2</sub>
Amino acids	Fatty acids
ammonia, sulphides, CO <sub>2</sub> , H <sub>2</sub>	
Glycerol	Acetate, CO <sub>2</sub>

And hydrolyzing after then we are coming to acidogenic bacteria. So, some examples of this acidogenic bacteria are like this, though bacteroides bifid bacterium butyrovibrio eubacterium and lactobacillus. Those microorganisms act as acidogenic bacteria. Apart from this some bacteria like coliform bacteria like say escherichia coli salmonella and



shigella. So, these microorganisms also react as acidogenic bacteria, but these bacteria these microorganisms can produce formic acid and you see the sugar can be converted to fatty acids alcohol to fatty acids amino acids fatty acids glycerol acetate and CO<sub>2</sub>.

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Acetogenic bacteria

- **Hydrogen producing acetogens**

Clostridia and Acetivibrio are some example of acetogenic bacteria

  - Propionate  

$$\text{CH}_3\text{CH}_2\text{COOH} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{CO}_2 + 3\text{H}_2$$
  - Propanol  

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{CO}_2 + 5\text{H}_2$$
  - Butyrate  

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + 4\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2\text{CO}_2 + 6\text{H}_2$$
- **Homoacetogens**  

$$4\text{H}_2 + 2\text{CO}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$$

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So, these are the converted product by this microorganisms, now we will see acetogenic bacteria acetogenic bacteria. We have seen 2 types of that is your hydrogen producing acetogens and another were homo acetogens H<sub>2</sub> plus CO<sub>2</sub> is converted to CH<sub>3</sub>COH by this microorganisms clostridia and acetivibrio are some examples of this acetogenic bacteria, and propionic acids propanols butyric acids are converted to acetic acid by this microorganisms by the in this case hydrogen is formed and in the second case is hydrogen and CO<sub>2</sub> reacts to give us CH<sub>3</sub>COH.

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**Methanogenic bacteria**

- **Acetoclastic methanogens**  
$$\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$$
  - ~70 % of methane is produced by this route
  - These are highly sensitive and having slowest growth rate
- **Hydrogenotrophic methanogens**  
$$4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$$
  - ~30 % of methane is produced by this route
  - These are less sensitive and having higher growth rate
- Formic acid and methanol can also be converted to methane by bacteria  
$$4\text{HCOOH} \rightarrow \text{CH}_4 + 3\text{CO}_2 + 2\text{H}_2\text{O}$$
$$4\text{CH}_3\text{OH} \rightarrow 3\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O}$$

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Now, we are coming to methanogenic bacteria. So, methanogenic bacteria we have seen that acetic acid to methane and this CO<sub>2</sub> plus H<sub>2</sub> to methane. So, this is called acetoclastic methanogens and another is hydrogenotrophic methanogens. So, these are the reactions here. So, this is a 70 percent and this is a 30 percent, but these microorganisms these are highly sensitive and having slowest growth rate and these microorganisms are less sensitive and having higher growth rate. So, apart from this there the methane can also be formed from formic acid and methanol they can give the CH<sub>4</sub> also. So, some microbes will be responsible for this.

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**Methanogenic bacteria**

Methanogenic bacteria are unicellular, Gram-variable, strict anaerobes that do not form endospores. Their morphology, structure, and biochemical makeup are quite diverse. More than ten different genera have been described.

The methanogens have been divided into three groups based on the fingerprinting of their 16S ribosomal RNA (rRNA) and the substrates used for growth and methanogenesis

Group I contains the genera *Methanobacterium* and *Methanobrevibacter*;  
Group II contains the genus *Methanococcus*; and  
Group III contains several genera, including *Methanomicrobium*, *Methanogenium*, *Methanospirillum*, and *Methanosarcina*

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On the basis of this the methanogenic bacteria are classified into 3 categories, depending on their 16S ribosomal RNA or RNA and their substrates used and growth and methanogenesis.

So, they are group just we have discussed the 3 groups 1 2 3. So, the 3 types of microorganisms are available the first groups. So, methanobacterium and methanobrevibacter and the second is methanococcus and the third group generally includes methanomicrobium, and methanogenium and methanospirillum and methanosarcina. So, these are the different types of microorganisms which are you are responsible for the methanogenic phase.

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**Pathways for fermentation**

*Embden-Meyerhof-Parnas (EMP pathway) is responsible for the production of pyruvate from sugar as an intermediate product, which is further converted to acetate, fatty acids, carbon dioxide, and hydrogen*

- At low partial pressures of hydrogen, acetate is favoured.
- At higher partial pressures, propionate, butyrate, ethanol, and lactate are favoured, generally in that order (McInerney and Bryant, 1981)

There is also a special mode of cleavage of intermediate pyruvic acid to formic acid by enteric bacteria that is not found in other bacterial fermentations

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And this is the path way through which the acids are formed. So, EMP path way that is Embden, Meyerhof and Parnas math pathway this pathway explains the production of intermediate product pyruvate from the sugar. Then pyruvate it is further converted to different acids. And depending upon the partial pressure of hydrogen in the system's acetate and other higher acids are formed.

So, if the hydrogen procedure is lower acetate is favoured, if higher hydrogen is there. So, partial pressure of the higher is higher than propionate butyrate ethanol and lactate are formed. So, and we have already that there is also special mode of cleavage of intermediate pyruvic acid to formic acid in presents of equali bacteria or enteric bacteria.

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Pretreatment for lignocellulosic biomass and wastes			
Pretreatment method	Processes	Possible changes in biomass	Notable remarks
Physical pretreatments	Milling(ball milling, hammer milling)	-Increase in accessible surface	-Most of the methods are highly energy demanding
	Irradiation(gamma-ray irradiation, microwave irradiation)	-Decrease in cellulose	-Most of them cannot remove lignin
	Other methods (Hydrothermal, pyrolysis)	-Decrease in degrees of polymerization	-Preferable not to use for industrial applications

And this is the pretreatment for lingo cellulosic, biomass and waste as we have discussed that non lingo cellulosic biomass and waste as we have discussed that non lingo cellulosic biomass and waste can be converted through the routes which you have discussed just now, but if we have lingo cellulosic biomass we need one pretreatment step, we have to convert cellulose and hemi cellulose we have to remove the lignin part from it and cellulose and hemi cellulose has to be converted into mono sugar.

So, that for that purpose physical pretreatment chemical pretreatment or chemico physical pretreatment and biological pretreatment methods has been applied and this physical pretreatment method include some milling some irradiation and some other methods there is hydrothermal and pyrolysis method. So, these are the 3 major important methods which have been used under pretreated method under physical pretreatments, and these are the possible changes in the biomass. This decrease in cellulose decrease in degree of polymerization increase in accessible sugar, and these are the notable demarks most of the methods are highly energy demanding and most of them cannot remove lignin.

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Pretreatment method	Processes	Possible changes in biomass	Notable remarks
Chemical & physico-chemical pretreatments	Explosion( $\text{CO}_2$ , $\text{SO}_2$ explosion)	-Increase in accessible surface area	-These methods are among the most effective & include the most promising processes for industrial applications -Usually rapid treatment rate -Typically need harsh conditions -There are chemical requirements
	Alkali(sodium hydroxide, ammonia)	-Partially or nearly complete delignification	
	Acid(sulphuric acid, hydrochloric acid)	-Decrease in cellulose crystallinity -Decrease in degrees of polymerization	
	Gas( $\text{NO}_2$ , $\text{SO}_2$ )	-Partial or complete hydrolysis of hemicelluloses.	
	Oxidizing agents( $\text{H}_2\text{O}_2$ , $\text{O}_3$ )		

So, this is not suitable one for the lignin cellulosic biomass signal, but this is more suitable one further lingo cellulosic bios, but this is more suitable one chemical it can remove the legnins and this can be done by alkali treatment by acid treatment by gas treatment or reaction with some oxidizing agent. And it decreases the cellulose crystallinity decrease the degree of polymerizations, and these methods are among the most effective and include the most promising process for industrial applications for the pretreatment of the lingo cellulosic biomass.

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Pretreatment for lignocellulogic biomass and wastes			
Pretreatment method	Processes	Possible changes in biomass	Notable remarks
Biological pretreatments	Fungi & actinomycetes	-Delignification -Reduction in degree of polymerization of cellulose -Partial hydrolysis of hemicelluloses	-Low energy requirement -No chemical requirement -Mild environmental conditions -Very low treatment rate -Did not consider for commercial applications

Another is biological pretreatment methods, there is some fungi and actinomycetes have been used, but this method is very slow method and delignification can take place, but due to the slow rate of reactions, these are not getting that much of interest. So, up to this in this module and we will discuss the rest part in the next module.

Thank you very much.