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Lecture - 36 Energy from Biomass and Wastes 1 (Biological Route)

Hi friends, now we will discuss on the topic energy production from biomass and waste. Already we have seen that biomass is one of the most important resource for renewable energy production and this biomass can be used as a fresh biomass or the waste biomass like say agricultural residues, forest residues, etc and this biomass and waste can be processed in different routes like say thermal route, chemical route, and biological route.

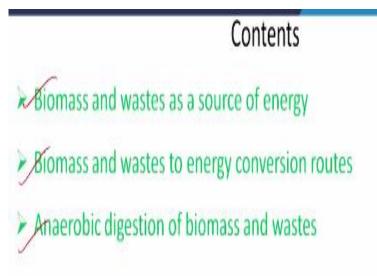
Physical routes can also be used for the preparation or pretreatment or to make the biomass suitable for use in a particular type of reactor. Now all of us we know that the coal is produced from biomass, plant biomass basically. Should the technologies or the processes which we have discussed for the conversion of coal to energy those can also be applicable in case of biomass, but in this case as you know the volatile matter is higher in case of biomass, so the requirement of reaction conditions will be milder than that of the coal conversion.

Now if we see that biomass is having more volatiles, so apart from thermal combustion route, thermal processes like combustion, gasification, pyrolysis, etc, we can use biological routes also for the conversion of energy from it, particularly when we will consider the waste biomass and organic part of the municipal solid waste, so municipal solid waste contains good amount of organic part that contains high amount of carbon as well as moisture content is also high so that part can be converted to bio-gasification routes.

Some of the waste contains lipid containing materials, high amount of lipid is available in it, for example say oils seeds to oil, so vegetable oil and edible oils and non-edible oils both can be converted to biodiesel through the chemical route or say waste cooking oil that can also be converted to biodiesel through chemical route. As you know, the biomass is highly reactive than coal and its density is less, so to use this biomass in a particular reactor to give the sufficient strength and to maintain the particle size, the densification of the biomass and waste is required.

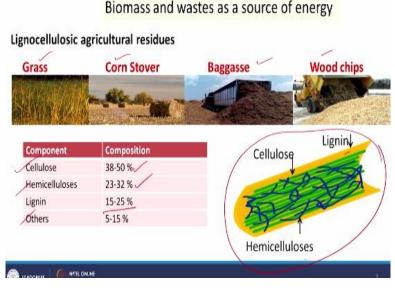
So we will discuss all those things, but we will not cover the thermal conversion routes because we have already discussed these things in these processes in case of coal conversion, so similar concept will be applicable for biomass also for its conversion to electricity or other fuels.

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For this class, the contents are biomass and waste as a source of energy, then biomass and wastes energy conversion routes, and then anaerobic digestion of biomass and wastes.

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We see here this slide shows us some biomass residues, grass, corn stover, baggasse and wood chips. So these are the agricultural wastes and you see in the agricultural waste, this contents cellulose, hemicellulose, lignin and others. So good amount of cellulose and hemicellulose is available, lignin also we have significant amount. So this is the structure of a

lignocellulosic biomass, so you have lignin outer part, then we had cellulose mostly in structure and then hemicellulose not that structure one. So these 3 components are available in biomass and biomass residues or waste biomass, so this can be a source of energy.

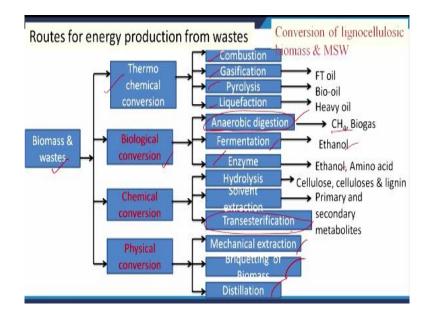
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Biomass and wastes as a source of energy					
Moisture content and heating value of Municipal refuse components					
Components	Moisture (%)	Heating value (MJ/Kg)			
aper, cardboard, bags	5 🗸	17.82			
Nood crates, boxes, scrapes	7	18.20 .			
Bush, branches	17	16.61			
eaves	30	11.40			
Grass	50	8.89			
Şarbage 🏒	75 🗸	4.23			
Green stuff	50	8.07			
Greens	50	9.47			
Rags, cotton, linen	10	14.98			

If we see the municipal solid waste, so different part of the municipal solid waste or components of the MSW are provided here, so paper, cardboard, bags, wood crates, boxes, scrapes, bush, branches, leaves, grass, garbage, green stuff, greens, rags, etc. So you see here out of these components, somewhere we have moisture 5, somewhere we have moisture 75%. So as we had discussed that low moisture content will be processed through thermal route and high moisture content will process through biological route.

These biological routes we will be discussing now and we see here all the cases we get some heating value. So it is very clear from this that we can recover this heat which is available in the waste and biomass for energy production. Now we will see the different routes which can be used for the production of energy from the biomass and waste.

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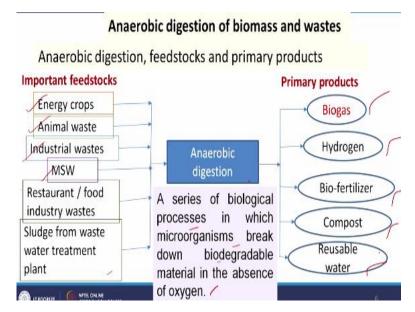


So if we have biomass and waste, we can use it through thermochemical conversion and like say combustion, gasification, pyrolysis, and liquefaction, the similar to coal, so we are not covering this part. Then biological conversion we can use for the use of this biomass and waste and its conversion to energy. So the important biological routes are anaerobic digestion which gives us methane that is biogas, then fermentation can give us ethanol or higher alcohol, and some enzymatic routes again the ethanol and amino acid they can give.

We will be concentrating in this class on anaerobic digestion, so this is a commercial process and the fermentation is under development particularly for the waste materials. Then chemical conversion another method we have that is hydrolysis, solvent extraction, and transesterification, we will be giving more focus on transesterification in the next class. Then physical conversion is also required as I have mentioned that to make the feedstock suitable for its use in a reactor system, so then these are these are say densification or briquetting.

Then other physical methods, mechanical extractions and distillation we will discuss these 3 routes consecutively. Now we will see the anaerobic digestion of biomass and waste. So all types of waste and biomass may not be suitably converted through anaerobic processes, but certain waste and biomass can be processed easily and most economically also you can say can be converted.

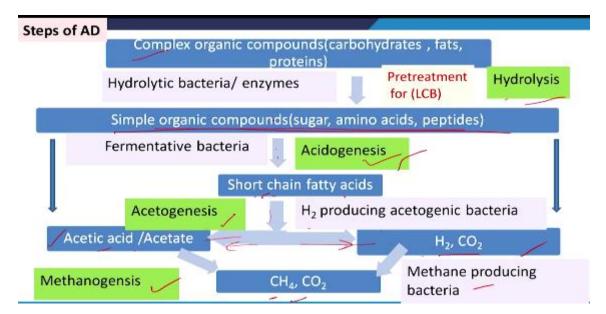
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So some examples of those food feedstocks here are energy crops, animal waste, industrial waste, MSW, some part of it, then restaurant and food industry waste, and sludge from wastewater treatment plant. So all those things are the feedstocks for the anaerobic digestion process. This anaerobic digestion process is a complex process a series of biological processes in which microorganisms break down biodegradable material in the absence of oxygen.

So anaerobic condition is required for this process and then it gives us biogas, it can give us hydrogen, it can give us bio-fertilizer, compost, and we can also get some water from the slurry after proper treatment. Now we will see the mechanism or different types of phenomena which takes place during the production of biogas or methane in the anaerobic digester.

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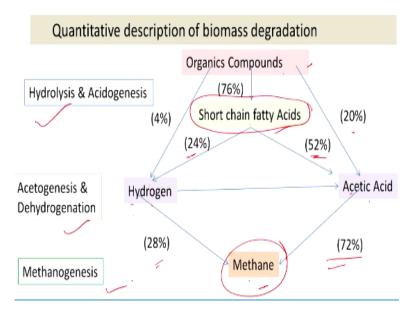
So we have complex organic compounds, carbohydrates, fats and proteins available in our feedstocks. Then the first step is the hydrolysis, so after hydrolysis, we will get simple organic compounds that is sugar, amino acids, and peptides. So those are our preliminary feedstocks for biological reactions. So far we have hydrolysis and then it will be having some fermentation also.

Then these sugars can be converted to short chain fatty acids through the acidogenesis route and some microbes are available to convert it to hydrogen, some microbes also convert it to acetic acid. These acidogenic microorganism, so this simple sugar will be converted to short chain fatty acids. Then short chain fatty acids will be converted to acetic acid through acetogenesis. So this is acidogenesis, that is simple organic compounds to short chain fatty acids, and this is acetogenesis that is short chain fatty acids to acetic acid or acetate.

So this can be either this way or some microbes also produce hydrogen, then that hydrogen and CO_2 that also be converted to this, so both type of a complex biological reactions are going on in AD or anaerobic digester. Then the acetic acid which is formed that is further converted to methane through methanogenesis, some microbes are responsible for this conversation, and this H₂ and CO₂ which is available in the media those can also be converted to CH₄ and CO₂ can also be produced and this is called methane producing bacteria

So this is the overall reactions, reaction scheme which takes place in an anaerobic digester. Now we will see the relative contribution of different type of processes.

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So if we have organic compounds here, then short chain fatty acids we can get around 76% of that and then short chain fatty acids directly acetic acid we can get 20%, directly hydrogen we can get 4%. The major process is through the short chain fatty acid production, the first step, major step is a conversion of organic compounds to short chain fatty acids through hydrolysis and then acidogenesis.

Then, these fatty acids will be converted to acetate mostly and some part is hydrogen around 52% and 24% and this is the relative abundance of different type of processes. Then acetic acid to methane and then hydrogen to this, so out of total methane, so 72% is coming through this route and around 28% is coming through this route. So this is the major reactions hydrolysis and acidogenesis, then acetogenesis and dehydrogenation, and then methanogenesis. So these are the basic reactions which take place in anaerobic digester.

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Elementary description of AD	Source- http://www.fao.org/
•In case the chemical composition of the organ stoichiometric equation according to McCarty (Pavlosta	
$C_{p}H_{a}O_{b}N_{c} + (2n + c - b - 9sd/20 - ed/4) H_{2}0 \rightarrow de/8$	CH ₄ + (n - c sd/5 - de/8) <u>CO</u> 2
+ sd/20 C ₅ H ₇ O ₂ N + (c - s	d/20) NH4 ⁺ + (c - sd/20) HCO3 ⁻
where: d = 4n + a - 2b - 3c,	
s = fraction of waste converted into cells,	
e = fraction of waste converted into methane fo	r energy (s + e = 1),
$C_n H_a O_b N_c$ = empirical formula of waste being dig	gested
$C_5H_7O_2N$ = empirical formula of bacterial dry ma	ass (VSS)

Now how we can represent this formula. This is a complex process, unlike say coal combustion or gasification, we cannot represent very simple formula here. So this a complex one, and then people try to represent in terms of chemical expressions and empirical relationship have been proposed. One example as available in this and proposed by this researcher you see CnHaObNc reacts with this amount of oxygen, this many moles of H_2O and gives this one.

Actually, there are some microbes, so microbes are there, they take in water and then react on these and then gives the product CH_4 , CO_2 , HCO_3 , NH_4 and this is and these organic compounds since taken up by the microorganisms and their biomass growths, so this is the biomass $C_5H_7O_2N$, the cell biomass growth. So this is the empirical relationship. Now we can get the value of n, a, b and c on the basis of elemental composition of the feedstock and then we have to know s and e, then all the coefficients we can know.

So what is s and e, we see here, s is the fraction of waste converted into cells. So how much waste we are taking here that will be if we take the mass balance, then it will be partially converted to the cell biomass and remaining part will be converted to the energy. So that is why s is equal to fraction of waste converted into cells, then e is equal to fraction of waste converted into cells, then e is equal to fraction of waste converted into cells.

So now by mass balance, we can get the value of s and e and we can put this expression, we can we can predict what can be the biogas formation in this particular feedstock and in this process. This $C_5H_7O_2N$ is the empirical formula for bacterial biomass and CnN is the

empirical formula of the waste being digested.

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Hydrolysing and fermenting bacteria

• Obligate anaerobes including Bacteroides, Bifidobacterium, Butyrovibrio, Eubacterium, and Lactobacillus act as acidogenic bacteria.

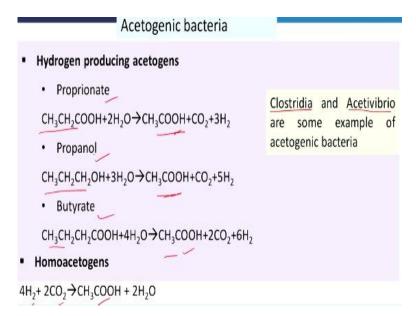
 Many enteric coliform bacteria, classically represented by the pathogen Escherichia coli in the genus Escherichia and pathogens in the genera Salmonella and Shigella, are also some common fermentative(acidogenic) bacteria.

Hydrolysis product	Conversion during acidogenesis Fatty Acids (succinate, acetate, proprionate, lactate, formate), carbon dioxide, hydrogen	
Sugar 🖊		
Alcohols	Fatty acids, CO ₂	
Amino acids ammonia, sulphides, CO ₂ , H ₂	Fatty acids	
Glycerol /	Acetate, CO ₂	

Now we will see different type of bacteria which are responsible for this anaerobic digestion processes. So hydrolysis or hydrolyzing and fermenting bacteria, so hydrolysis takes place and then fermentation also takes place. So here what we get, hydrolysis product sugar, then alcohols, then amino acids, and glycerol, so they will be further converted to different compounds in the acidogenesis stage. So acidogenesis stage sugar is converted to fatty acids, then alcohols to fatty acids and CO₂, ammonia is also fatty acids, and glycerol acetate.

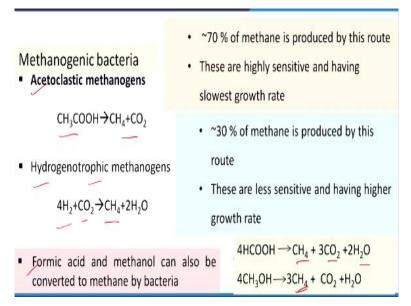
So these are the different products which are produced through this acidogenesis step. Some example of this bacteria are also given here that is Bacteroides, Bidifobacterium, Butyrovibrio, Eubacterium and Lactobacillus those act as acidogenic bacteria. E. coli is also helps in this process.

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Now we will see the acetogenic bacteria. So acetogenic bacteria that is Clostridia and Acetivibrio are some example of acetogenic bacteria. So these bacteria convert the fatty acids to acetic acid conversion, so acetogenic bacteria. Then these are the presentation of propionate to acetate, propanol to acetate, butyrate to acetate. Then homoacetogens are also available, those convert $H_2 + CO_2$ to acetic acid just we have if you see this one, this conversions from acetogens and hydrogen producing acetogens are also these reactions.

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Now methanogenic bacteria, so some bacteria are there which helps the methane formation reactions and these are basically 2 types, one is acetoclastic methanogens. So acetoclastic methanogens means acetic acid will be converted to methane by these microorganisms and another is your hydrogenotrophic methanogens. Hydrogenotrophic methanogens means hydrogen plus carbon dioxide will be converted to methane plus $2H_2O$.

So if we see out of these 2 routes, that means here this say two, this route and this route, the contribution here is around 70% and here it is around 30%. So now, the formic acid and methanol present in the in the media, then those can also be converted to methane as per the formula HCOOH to $CH_4 + 3CO_2 + 2H_2O$ and this is methanol to methane conversion.

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Methanogenic bacteria

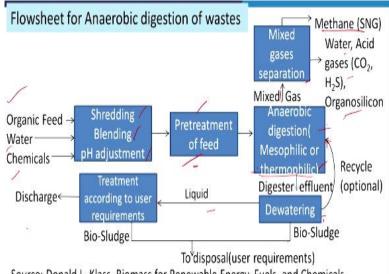
Methanogenic bacteria are <u>unicellular</u>, <u>Gram-variable</u>, strict anaerobes that do not form endospores. Their morphology, structure, and biochemical makeup are quite diverse. More than ten different genera have been described.

The methanogens have been divided into three groups based on the fingerprinting of their <u>16S</u> 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

These methanogenic bacteria have been classified into different groups depending upon their 16S ribosomal RNA fingerprinting and group I, group II, and group III are some examples are given here. These bacteria are unicellular, these are gram-variable, strict anaerobes and do not form endospores. So these are some basics of the microorganisms which have been used for the anaerobic digestion process.

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Source: Donald L. Klass, Biomass for Renewable Energy, Fuels, and Chemicals

Now, we will see how we can perform the anaerobic digestion reactions or how we can process the feedstocks, that is the waste and biomass, to produce biogas. So obviously, the reactor or microorganisms which react on certain types of molecules, so initially what feedstocks we are having in terms of waste that has to be converted to the initial compound which will be degraded by the microorganism, so some pretreatment is required and also we have to get the size reduction, etc, from the original feedstock.

So if we have organic feed, then water and chemicals then there were some shredding, blending, and pH adjustment which is the pre-requirement for the growth of bacteria and the conversions of the molecules from the higher molecular rate to the lower molecular rate and finally to methane. Then we need the pretreatment of feed, this is basically very useful when we will consider for lignocellulosic biomass because lignin is not biodegradable, so you have to separate the lignin part from the biomass and then the non-lignin part will be used for further processing.

So this pretreatment is required, then after pretreatment by removing the undesirable materials in this and making the feedstock more suitable for biological conversion, it is going for anaerobic digestion. So this in anaerobic digestion, we maintain mesophilic or thermophilic condition. So this temperature around say 35-40 degree centigrade temperature, the biogas is formed and then this biogas goes up from the digester and this biogas can have some impurities, so you need to remove the impurities and we need mixed gas separation.

Then water, acid, gases and organosilicon mostly available, so we need to purify this gas and we can get the methane or that is called synthetic natural gas or biogas. Then the slurry part which we are getting here so that will go for dewatering step, and dewatering step will give us some sludge and some liquid, so liquid will be treated further for the production of water and sludge we are getting that sludge will be used for other purposes, may be say composting or as a fertilizer, etc.

This part of this sludge recycling is required to maintain the microbial biomass in the anaerobic digester. So this is the overall flow sheet of the anaerobic digestion process.

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Type of anaerobic digestion			
Processing mode	Dry	Wet	
Total solids content	High 25-45 %	Low 2-15 %	
Reactor volume	Minimized /	Increased Expensive Less improved Less improved	
Solid liquid separation	Simple /		
Energy Balance	More Improved		
Economic performance	More improved		
Retention time	Shorter	Bigger	
Type of feedstock accepted	Greater flexibility	Lesser flexibility	

Now we will see the type of anaerobic digestion process. So initially, anaerobic digestion process was the used with a substrate concentration of around 8 to 10% and that is the wet state of anaerobic digestion, now gradually people developed some improved version of these and that is called dry anaerobic digestion, and we see the difference between these two wet and dry anaerobic digestion processes in this table.

So we have some processing mode and then we will compare those, that is total solids content and then we see dry as you have mentioned that is 20-25 to 45% solid may be available whereas this is 8-10% and here it is mentioned that 2-15% for wet process. So once the moisture is more, water is more, so obviously the reactor volume will be higher in case of wet process and dry pusses the volume will be less. Solid liquid separation, again dry will be simple and this will be expensive because more liquid is available here.

Energy balance, this is more improved for dry and less improved for the wet process. Economic performance, more improved for dry than the wet process. Retention time, also here shorter than the wet process. Type of feedstock accepted that is greater flexibility we have for dry process, but wet process we have lesser flexibility. So this is the development of the wet process in last few years.

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KINETICS OF METHANE PRODUCTION

• One of the steps might be rate-limiting among hydrolysis, acidogenesis, acetogenesis and methanogenesis for high rate digestion.

· Normally the methanogenesis is the rate limiting step.

· If cellulose content is higher in feedstock, hydrolysis may be rate limiting step

Presence of lignin decreases the rate of hydrolysis.

•Transfer of the gaseous products to the gas phase may also be the rate-limiting step for some cases.

We will see now the kinetics of the methane productions. So we have seen that there are number of steps, so as the overall kinetics of the biogas production, obviously any one step which one will be the lowest step that will control the overall kinetics. So basically normal cases, the methane production step is very slowest step and then that controls the overall kinetics of the AD process, but depending upon the feedstocks, the other steps may also be responsible to govern the overall kinetics of this.

Like say if lignin is very high, then obviously the biological conversions will be less and the hydrolysis will also be slow and that will be the rate limiting step. If cellulose content is high in feedstock, then hydrolysis may be rate limiting step. Somewhere gas transfer can also be limiting the process.

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Theoretical substrate conversion rates per unit reactor volume can be estimated

as:

where R is the substrate converted per liquid volume at hydraulic retention time θ ,

 $R = S_{o} (\mu_{max}\theta - 1) - K_{s}$ $\theta(\mu_{max}\theta - 1)$

S_o is the substrate concentration in the feed,

 μ_{max} is maximum specific growth rate

and K_s is saturation constant or substrate concentration at which the specific growth rate is $\%\,\mu_{max}$

At $30 - 37^{\circ}$ C, optimum conversion of glucose can be achieved at θ 's of 4 h and 4 days in the acid- and methane-phase reactors respectively.

Now overall rate kinetics if we want to represent, so $R = S_0 x \mu max$ theta-1-Ks/theta x μmax theta-1. S_0 here S_0 is the substrate concentration in the feed, μmax is the maximum specific growth rate and theta is the retention time. So Ks is the saturation constant or substrate concentration at which the specific growth rate is 1/2 of μmax . So that way, we can get the value of R that is the substrate converted per liquid volume at hydraulic retention time of theta.

So this theta value, hydraulic retention time, that will be dependent upon the nature of materials we are using. So you see here at 30 to 37 °C, optimum conversion of glucose can be achieved at theta of 4 hour for acidogenic phase and 4 days in methane phase reactors.

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For cellulosics, the corresponding θ 's are much higher, about 1 to 2 days for acidphase digestion and 5 to 8 days for methane-phase digestion

Kinetic	Acidogenesis of		Methanogenesis of acetate
constant	Glucose	Cellulose	1
µ _{max,} day ^{,1} 🧹	7.2	1.7	0.49
K _s , g/L	0.4	36.8	4.2

Kinetic constants are: μ_{max} , maximum specific growth rate; and K_s, saturation constant or substrate concentration at which the specific growth rate is ½ μ_{max} .

Source: Donald L. Klass, Biomass for Renewable Energy, Fuels, and Chemicals

But if we use others say cellulose, then this theta value will be increased, so that was 4 hour in this for glucose, but now here we are 1 to 2 days for acidogenic phase and which was 4 days and then it is 5 to 8 days for methanogenic phase. This table shows us some μ max and Ks value for different types of compounds, the glucose, cellulose for acidogenic phase and also for methanogenesis phase.

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Some important facts

• Methane fermentation at thermophilic temperatures increases the methane production rate because of higher reaction rates.

Reduced pressure also provides little or no benefit (Hashimoto, 1982).

• Low pH and short retention time precludes growth of methanogenic bacteria and thus reduces methane production.

•Rapid, continuous agitation of anaerobic digesters is not necessary, and in some cases is even harmful (Stafford, 1982).

Specific methane yield is directly proportional to biodegradable COD or VS loading in the digester.

Now there are some important facts regarding the anaerobic digestion of biomass and waste. In the digester if we maintain high temperature, we will get more production of biogas, lower the temperature, lesser the biogas production. So in a country where the temperature is very less at the time some heating arrangement is made making some jacketed vessels like this or some heat or steam or some other fluid is sent through it, hot fluid is sent through it to maintain the temperature and pressure has not much significant affect on it.

Reduced pressure also provides little or no benefit. Then low pH and short retention time precludes growth of methanogenic bacteria, if pH is very low, then methanogenic bacteria will not grow and retention time is also less, so complete conversion will not be possible. Here we do not need a very vigorous stirring, we need rapid continuous agitation of anaerobic digester is not necessary, and in some cases it is even harmful.

Specific methane yield, so how much methane will be produced per unit mass of substrate that will depend upon the volatile metal content in it, that is how much biodegradable COD or VS loading in this. So these are the some important facts related to anaerobic digestion reactions.

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Types of anaerobic digesters

- Low rate (Conventional digesters)
- Intermittent mixing, sludge feeding and sludge withdrawal
- Detention time = 30-60 days
- Feeding rate 0.5 to 1.5 kgVS/m³.day

High rate digesters

- Continuous mixing (homogenous)
- Continuous or intermittent sludge feeding and sludge withdrawal
- Detention time = < 15 days
- Feeding rate 1.6 to 6.4 kgVS/m³.day

Most digesters are heated and operated in the mesophilic range and usually made of concrete or steel

Now we will see types of anaerobic digesters. There are 2 types of digesters, one is low rate and another is high rate. So low rate means retention time will be higher and high rate means retention time will be lower. So here for low rate, retention time is 30-60 days whereas for high rate retention time is less than 15 days. So feed rate will also be lower in case of low rate and higher in case of high rate, here you see 0.5 to 1.5 kg volatile solid per meter cube per day and then we are getting 1.6 to 6.8 kg volatile solid per meter cube per day.

So this is the difference between these 2 types of anaerobic digesters. Most digesters are heated and operated in the mesophilic range and usually made of concrete and steel as a material of construction.

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Digester operation

- Most digesters operate in the temperature range of 30-38° C to optimize time.
- The digester gas produced from the process may be used for the heating purposes.
- •Optimum pH range is 7.0 7.2.
- ✓ Maintained by properly seeding fresh added sludge and not excessively
 - withdrawing sludge (should not exceed 3-5 % of dry solids weight in digester).
- ✓ Temporary solution for acidification: lime addition.
- · Heavy metals may inhibit digestion process. Must be eliminated at the source.
- The supernatant liquor is the water released during digestion.
- ✓ May have BOD as high as 2000 mg/l and SS concentration as high as 1000 mg/l.
- ✓ Fed back to the influent to primary clarifiers.

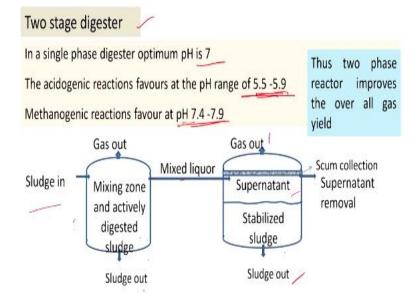
Then what would be the digester operation, obviously it handles the microorganism, so

certain pH should be maintained. So pH, microbial growth is very specific to pH, so optimum pH is 7.2-7.0. Most digester operates in the temperature of 30-38 degree centigrade. What you see pH, how can we maintain the pH, we can add some alkali if needed or by maintained by properly seeding fresh added sludge and not excessively withdrawing sludge.

If we do not withdraw excess sludge and we do not add very high amount of fresh sludge, if you can maintain certain ratio, then the pH can be adjusted because pH changes can take place during the reaction. Then heavy metals may inhibit digestion process and must be eliminated at the source. The pretreatment and heavy metal removal will be done at the earlier stage.

The supernatant liquid which is generated here that also contains some amount of organic that can be biodegradable organics so those can be treated and clean water can be produced.

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Now we will see the development in the anaerobic digestion processes and the anaerobic digester we will see. So we have come to know that anaerobic digestion process takes through 2 important routes, one is acidogenic and another is your methanogenic routes. So acidogenesis takes place at lower pH and methanogenesis takes place at higher pH. The pH range is given here say 5.5-5.9 for acidogenesis and then for methanogenesis 7.4-7.9.

We are maintaining our pH around 7, so both microorganisms are not able to give us their maximum performance. So if we can use 2 reactors in place of one, one is at this acidic range and another is at basic pH as mentioned here, so the microorganisms can give us their best

performance and our overall efficiency can be improved. So that is the concept for use of two-stage digester and which has sludge in we are using here for the feedstock here, then we have mixing zone and actively digested sludge, then gas out, then it is sludge out the first step.

Then it is a mixed liquor is coming out from the acidic zone, acidic pH is this one, then this is coming here and is coming to after pH adjustment say we are going through methanogenesis steps, then we are getting gas, and we are and getting supernatant the liquid part and then the sludge. So that way we can use two step AD process in place of one, so we will get better performance of the process. So up to this in this class. Thank you very much for your patience.