

Municipal Solid Waste Management
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Lecture - 31

Pretreatment and Co-digestion for Enhancement of Biogas Production

So hello students. So, we are continuing the lecture on anaerobic digestion. And today in this lecture we will talk about pretreatment and co-digestion see in the previous lecture I shared about there are 4 stages major stages of the anaerobic digestion process, starting from hydrolysis, acidogenesis, acetogenesis and finally, methanogenesis. So, here in this one and if you see that the major stage is a hydrolysis process, that is the important one and without this hydrolysis very difficult to go for acid phases or methane phases.

So, here in this lecture, we will talk about the hydrolysis process which is a great limiting stage if it enters if you, do not have a proper hydrolysis stage, it will take a longer period for the entire anaerobic digestion process means, the hydraulic residence time or HRT will be very high if you do not have proper hydrolysis process. Normally, with this hydrolysis we can talk we can also say that pretreatment, so, pretreatment is nothing but there is a hydrolysis process. And along with that, I am also going to talk about the co-digestion process.

Now, I think in the last lecture also I was talking about different substrates that could be possible to use for the anaerobic digestion process, but I did not talk about how 2 substrates are 3 substrates together for the digestion period and what will the benefits of the biogas production by having the co-digestion process that we will discuss today. So, first, we will start with the pretreatment techniques, what are the benefits of the pretreatment order especially the hydrolysis process, which is the rate-limiting stage.

And also talk about different ways we can have the hydrolysis process of pretreatment process could be possible before starting the acid phases and methane phases in the anaerobic digestion process.

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WHAT IS PRETREATMENT ?

- Pretreatment is a **process of initiating or improving the efficiency of microbial attack** on a substrate (biomass).
- During the pretreatment process, the **compact structure of biomass is disrupted** and exposed to microbial attack.
- Pretreatment processes can be-
 - ✓ Physical (communion, irradiation etc.)
 - ✓ Chemical (alkali, acids, wet oxidation etc.)
 - ✓ Biological (fungi or enzymes)

Can also be combination of these processes

- The pretreatment technology ensures **biomass disintegration** and **improved solubilization** in order to overcome the biological limitations of anaerobic digestion.
- Through pretreatment of any substrate, not only **biogas yield can be increased** but also **higher calorific value of the gas can be obtained** leading to **less effort in purification for bio-methane** production.

So, what is pretreatment, this is improving the efficiency of microbial attack on the substrate. So, because, see, I already shared in one of the lectures that for composting normally you will be the required size of 1 centimeter to 2 centimeters, but for anaerobic digestion, you will be required very small size of the substrate could be 2 mm to 4 mm likewise size if there. So, these anaerobic bacteria will easily get degradation they can start very easily the degradation process.

So, this pretreatment is the initial processor for improving the efficiency of microbial degradation and during the pretreatment process, the compact structure of biomass is easily exposed to the microbial attack. So, that is what see if the substrate is not properly pretreated. So, it is very difficult for them and the anaerobic bacteria to directly go through the degradation process.

So, after some particular time, I think they can start the degradation of such kind of waste also, but it will take more time and especially for some of the organic matter like lignin is very difficult to get degrade very easily by this pretreatment process, this lignin kind of organic matter will be easily converted into the sugar, so, that easily can be attacked by the microbes. So, this pretreatment process can be physical can be chemical can be biological.

Or otherwise, we can combine the physical process followed by a chemical process or physical process followed by a biological process. Likewise, we can make some combinations also. So, these pretreatment technologies ensure biomass disintegration and improve the solubilization to

overcome the biological limitations of the anaerobic digestion process. So, the idea is that if the entire organic material is solubilized very easily solubilize one so that it will be easy going for the anaerobic digestion process.

Though pretreatment of any substrate not only biogas yield can be increased, the also higher calorific value of gas can be obtained, leading to less effort in the purification of bio-methane production. See, this is another very important benefit of the pretreatment process not only it will increase the biogas yield, it will reduce the degradation period miss here HRT will be lower down by having the proper pretreatment process and also the highly calorific value of the gas. What do you mean by the calorific value means, more amount of methane could be possible?

So, normally suppose, if you do not have a proper pretreatment process, your methane concentration will go maybe 50 55% or 60%, but having the proper pretreatment process could be possible to have more amount of methane could save up to 70%. So, obviously, it will have more calorific value and also it will have less effort to the purification of the bio-methane production. So, obviously, more amount of methane and less amount of carbon dioxide will be available. So, obviously, the effort for the purification also will be less now, if you have the proper pretreatment process.

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NEED FOR PRETREATMENT

- Pretreatments are necessary when-
 - ✓ Readily biodegradable and soluble organic matter is unavailable leading to lower digestion rate.
 - ✓ Rate of hydrolysis through conventional anaerobic digestion is lower resulting in higher HRT of digester and larger digester capacity or volume.
 - ✓ Lower biogas yield.

EFFECT OF PRETREATMENT ON DIFFERENT TYPES OF SUBSTRATES

- There can be various types of substrates from which biogas can be produced. Some of them are-
 1. Lignocellulosic substrate
 - ✓ Crop biomass

Maize Wheat Barley

And this pretreatment is necessary when the readily biodegradable and soluble organic matter is unavailable leading to a slower digestion rate. So, suppose, why to think the organic matter if it

is not easily biodegradable and if it is not soluble very easily or soluble organic matter. So, obviously, it would not be simply available for microbial degradation in the anaerobic digestion process. So, in that case, you will be required pretreatment process also rate of hydrolysis.

The conventional anaerobic digestion is lower result in the higher HRT of the digester and larger digester capacity or volume. See, this is also very important. The HRT hydraulic retention period or hydraulic retention time is very important because of that only you will design the volume of the reactor and if suppose HRT is high, so, obviously, you will be required the larger volume of the digester and if HRT is lowered down obviously.

In the small reactor itself or small digester volume, you will be able to feed more amount of substrate as well as more amount of methane could be possible to produce from such kind of reactor or lower biogas yield if suppose, any organic matter is producing lower biogas. So, by having or by including the pretreatment process or hydrolysis process, we can increase the bio gassy. Now the effect of pretreatment on different types of substrate.

So, there are various types of substrate for which biogas can be produced and some of them are the lignocellulose substrate like crop biomass. So, there are different types of organic matter apart from MSW organic MSW possible to produce biogas out of different substrates, including lignocellulose substrate, what do you mean by these lignocellulose means, the organic matter which is having more amount of lignin and cellulose or hemicellulose one see I think before starting that.

Just remember that if I am saying organic matter, it will have 4 kinds of different organic components. The first will be the sugar, which is very easily degradable from whether it is aerobic bacteria or anaerobic bacteria and if there is sugar after that cellulose, cellulose also could be possible by the bacteria but not that very easily. So, you need to convert again that cellulose to sugar for easy degradation by the bacteria. Now third is the hemicellulose.

And last is the lignin. Now, both these hemicellulose and lignin are very difficult to get degraded by whether it is aerobic bacteria or anaerobic bacteria. Now, I think in the composting process

we already know that these kinds of lignin or hemicellulose will be degraded by fungus by fungi different in the maturation phase or the end of the thermophilic phase, but in the anaerobic digestion process now is very difficult to degrade in one single digester.

So, these kinds of ways, which is having more amount of hemicellulose more amount of cellulose, or more amount of lignin are very difficult to produce the biogas, but it is organic in nature. So, obviously, could be possible very poor is possible, but only you will be required very special kind of treatment process. So, that this lignin or cellulose or hemicellulose could be easily converted into the easily available organic phase like sugar for microbial degradation.

So, the first is the lignocellulose substrate like the crop biomass is like maize, wheat and there is a huge amount of crop biomass is producing and you know that in Delhi when everyone is talking about air pollution by firing of agriculture subtract in Haryana and other nearby states of Delhi, they are talking about the firing of these kinds of agriculture biomass. So, this agricultural biomass can be useful for the production of biogas.

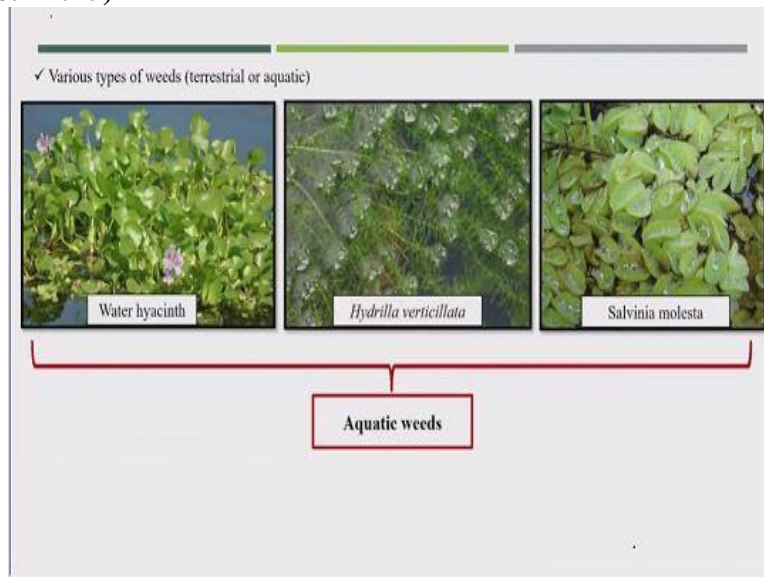
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Now, next is crop residues. So, like rice straw, banana stem this is also could be possible this is what the huge amount of agriculture waste is producing in India or most of the developing countries. Now, next is the energy crops like sunflower crop like oilseed crop, this is also so, once the product will come out from here remaining will be the biomass this biomass could be

possible to use for the anaerobic digestion process but the problem is that is a high concentration of lignocellulose concentrations.

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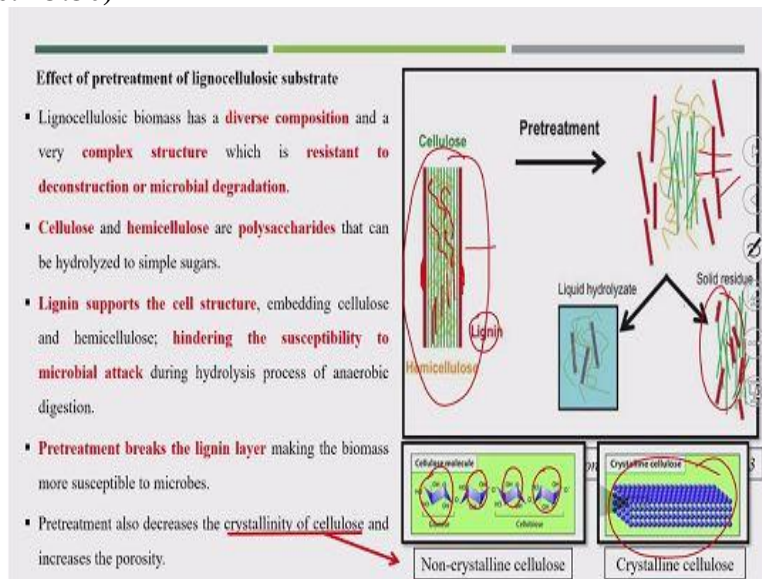
Various types of weeds like water hyacinth *hydrilla Salvinia*, this is all aquatic weeds, this is also lignocellulose biomass could be useful for the biogas production.

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These are some terrestrial weed or soil weeds like this is the well known one pathogens well-known weed is available I think most of the states in India under the organic waste such as food waste, this is what now, this is all MSW organic, MSW municipal solid waste, where a huge amount of food waste is getting produced or getting generated. So, this is also possible to produce biogas possible to use for biogas production.

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Now, what is the effect of pretreatment on lignocellulose of substrate you see here, now, I put it here, this is the entire structure of organic matter. So, you see here, the cellulose hemicellulose then lignin, lignin will be in the outside area will be the lignin. And these lines you are seeing these are the hemicellulose and this you are seeing this is cellulose. So, now, when some mores any bacteria will target to degrade this one. Now, this lignin is not easily degradable.

So very difficult to reach to the cellulose also, if suppose cellulose also will get degraded. So, the, if you do the pretreatment, it will be now the cellulose hemicellulose lignin, everything is available for the microbial degradation. And now, this is another way like liquid hydrolysis. By that also we can produce some solid residues which will be easily available for microbial degradation. Now, this lignocellulose biomass has a diverse composition and very complex structure.

Which is resistant to microbial degradation and cellulose hemicellulose and polysaccharides. That can be hydrolyzed to simple sugar. And lignin supports the cell structure, embedded cellulose, and hemicellulose hindering the susceptibility to microbial attack during the hydrolysis process of anaerobic digestion. So, that is what I was talking about here. And pretreatment breaks the lignin layer and making the biomass to available to the microbes and also the pretreatment also decreases the crystallinity of cellulose and increases the porosity you see here.

Now, this is the crystalline structure of cellulose. Now, here attack from the bacteria is very difficult in this kind of structure, crystalline structure, but now, because of pretreatment, this entire crystalline structure will convert into a non-crystalline structure now, here is a separated organic part that can be easily targeted by the pore microbial degradation process. So, this is another benefit of the pretreatment process and food waste can be easily degraded, but resulting in low bio gassing due to the presence of inhibitory inhibitors and the required pretreatment process.

Now, especially the food waste, if you talk about these fruit waste, or even vegetable waste, which we are normally disposing of, which is not easily degradable or easily not edible for the humans, which were disposing of, that is consist of the huge amount of hemicellulose or lignin, for that, you will be required pretreatment to get available to the microbial degradation.

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Now another substrate is a sludge biomass. So, there could be different industrial sludge can be a municipal wastewater treatment sludge and there is a huge amount of sludge getting produced by aerobic wastewater treatment facility or aerobic sewage treatment facilities. So, is a huge amount of sludge is getting generated. So, that also could be possible to use for the anaerobic digestion process.

Also animal dungs the different dung like cow dung and any cattle dung could be useful for the biogas production and also the sludge from the various types of processing industries, different

industries, different processing industries, but I think the sludge should be organic in nature that is possible to utilize further anaerobic digestion process.

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Effect of pretreatment of sludge biomass

- Sludge biomass from wastewater treatment have **high organic content**.
- Secondary wastewater sludge **consists of numerous microbial cells** and the walls of these cells act as **barriers against exo-enzyme degradation**.
- In activated sludge floc structure, extracellular polymeric substances (**EPS**) comprise a major organic fraction and binding mechanisms of EPS to cations happens to be a significant factor determining the digestibility of activated sludge.
- Therefore, **hydrolysis step becomes rate limiting** and **degree of degradation is limited** (30-35% COD reduction in conventional anaerobic sludge treatment).

Source: Tamilarasan Karupiah and Vimala Ebenezer Azariah (January 18th 2019). Biomass Pretreatment for Enhancement of Biogas Production, Anaerobic Digestion, J. Rajesh Bann, IntechOpen, DOI: 10.5772/intechopen.82088.

Now, what will happen with what is the effect of pretreatment of the sludge these kinds of sludge biomass is? Now, normally these sludge biomass is will have extracellular polymer substrate. So, like sludge biomass from wastewater treatment on high organic content, but are consist of numerous microbial cells and all of these cells act as a barrier against the enzyme degradation or microbial degradation.

Also, these sludge will have extracellular polymer substrate like EPS comprise a major organic fraction and binding mechanism of EPS to the cations happening to be a significant factor determined that degradability of activated sludge. So, what is the benefit of that by pretreatment process or hydrolysis process? See you here this is the entire structure of the polymer substances. Now, after the pretreatment process, the substrate will be easily available finally, for the microbial degradation process.

So, therefore, in this case, hydrolyzes step becomes rate limiting and degree of degradation limited 30 to 35% COD reduction in conventional biogas anaerobic sludge treatment.

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Effect of pretreatment of sludge biomass

- Sludge biomass from wastewater treatment have **high organic content**.
- Secondary wastewater sludge **consists of numerous microbial cells** and the **walls of these cells act as barriers against exo-enzyme degradation**.
- In activated sludge floc structure, **extracellular polymeric substances (EPS)** comprise a major organic fraction and binding mechanisms of EPS to cations happens to be a significant factor determining the digestibility of activated sludge.
- Therefore, **hydrolysis step becomes rate limiting** and **degree of degradation is limited** (30-35% COD reduction in conventional anaerobic sludge treatment).

Pretreatment of sludge ruptures the cell wall of sludge floc structure and facilitates release of intracellular matter into aqueous phase, improving biodegradability with lower retention time and higher biogas yield.

Now pretreatment of sludge ruptures the cell wall of sludge floc structure and facilitates the release of intracellular matter into the aquatic phase improving biodegradability with lower retention time and higher biogas yield this is what we are looking for. Improve the biodegradability and lower retention time, low HRT, and high biomass yield that is what the benefit of pretreatment of such kind of sludge biomass is.

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3. Non-conventional biomass


Crude glycerol

- Crude glycerine is a by-product of biodiesel produced from esterification of vegetable oil with the help of an alcohol such as methanol and a catalyst such as potassium hydroxide.
- Crude glycerin is a suitable carbon source for anaerobic digestion.
- Digestion of crude glycerin as a mono-substrate is not possible due to absence of nitrogen (required for formation of bacterial mass).
- Crude glycerin as a carbon source when co-digested with substrates with sufficient nitrogen content and low carbon content yields sufficient biogas.

Now, another is non-conventional biomass like crude glycerol could be one of the substrates for the anaerobic digestion process, which is producing from the different, different processes.

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3. Non-conventional biomass



Microalgae

- Algae are capable of using sunlight and carbon dioxide and produce protein, carbohydrate, and lipid through photosynthesis.
- Microalgae biomass supports higher photosynthetic efficiency, higher biomass yield, and higher CO₂ fixation than higher plants.
- Biogas production has been considered the simplest bioconversion process to obtain energy from microalgae biomass.

Now, this is another one the microalgae, this is also a huge amount of production. So, algae are capable of using sunlight and carbon dioxide and produce protein, carbohydrates, and liquid through the photosynthesis process. Microalgae biomass supports higher photosynthesis efficiency, higher biomass yield, and higher CO₂ fixation than higher plant compared to the plant, and biogas production has been considered the simplest bioconversion process to obtain energy from the microalgae biomass.

Now, normally these microalgae are used for the carbon dioxide fixation process. So, this is a well-known technique for the fixation of carbon dioxide. Normally we use the microalgae, but once it is having more amount of carbon dioxide and now it has to be disposed of. So, rather than disposing into the landfill area, we can use and this is one of the simplest processes for the getting benefit of the disposal of these kinds of microalgae.

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Effect of pretreatment of macroalgal biomass

- The macroalgal cell envelope is made of **thick and hard layer composed of complex proteins and carbohydrates** with more **mechanical power and high chemical resistance** restricting the attack of the biopolymers by methanogenic bacteria during AD.
- Pretreatment **improves the liquefaction process by biopolymer release enhancement** and leads to **solubilization of the organic fraction**.
- Pretreatment methods increase the biogas yield.
- Pretreatments **should be carried out at mild conditions** to prevent excessive sugar degradation.

Source: Tamilarasan Karuppiah and Vimala Ebenezer Azariah (January 18th 2019). Biomass Pretreatment for Enhancement of Biogas Production, Anaerobic Digestion, J. Rajesh Banu, IntechOpen.

Now, these microalgae also will have these kinds of structure is very this is also not so easy for the microbial attack. So, by having the proper pretreatment process, you see here already has been cell wall is already ruptured by having the pretreatment process which will be easily available for the microbial degradation process. So, the microbial cell envelope is made of a thick and hard layer composed of complex protein and carbohydrates this is what and pretreatment improves the liquefaction process by biopolymer release enhancement.

And lead to solubilization of organic fraction and pretreatment method increased the biogas yield and should be carried out in mild condition to prevent excessive sugar degradation.

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DIFFERENT TYPES OF PRETREATMENT

Mechanical pretreatment

- Reduce particle size and break down the crystalline structure (Recommended particle size 1 to 2 mm for effective hydrolysis of lignocellulose).
- Increase specific surface area.
- Enhance enzyme degradation rate for hydrolysis.
- Some mechanical pretreatment types:
 - ✓ Knife mills and shredders
 - ✓ Hammer mills
 - ✓ Ultrasonic treatment

Knife milling slices the fibres and typically produces small pieces (similar to chopping with a knife)

Hammer milling grinds the fibres and typically produces long thin fibres (similar to a mortar and pestle)

Difference between knife and hammer milling

Source: Pretreatment of feedstock for enhanced biogas production Technical Brochure written by: Lucy F. R. MONTGOMERY and Günther BOCHMANN

Now, there are different types of pretreatment processes. So, we saw that the different kind of biomass is or different kind of software could be possible to use for biogas production, but all these kind of biomass is which, in the last few slides, I had shown that he has the more amount of hemicellulose more amount of cellos or more amount of lignin, so, it is very difficult to get attacked by the microbial degradation.

So, if you have the proper pretreatment facility can easily available for microbial degradation and also could be possible to improve the biomass yield from the degradation process. So now, we will see the different types of the pretreatment process. So, first is the mechanical pretreatment it will reduce the particle size break down the crystalline structure. So, it is recommended 1 to 2 mm size for the effective hydrolyzes of lignocellulose.

I think this is what I think some can consider that, you will be required energy again to produce the biogas increases the specific surface area by having the mechanical pretreatment mechanical, pretreatment is nothing but a shedding, shedding you can say off converting the entire material in a smaller size like 1 to 2 mm size, increase the enzyme degradation rate for hydrolysis. So, there are different mechanical pretreatment types that could be possible by knife mill by different shredder hammer mill or even ultrasonic pretreatment also is possible.

So, now you see them by using the knife or hammer we can reduce the size and this knife milling slices the fibers and typically produce small pieces and also these a hammer milling grind the fibers and typically produce the long thin fiber is easily both these are easily available for the microbial degradation.

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DIFFERENT TYPES OF PRETREATMENT

Mechanical pretreatment

- Reduce particle size and break down the crystalline structure (Recommended particle size 4 to 2 mm for effective hydrolysis of lignocellulose).
- Increase specific surface area.
- Enhance enzyme degradation rate
- Some mechanical pretreatment techniques
 - ✓ Knife mills and shredders
 - ✓ Hammer mills
 - ✓ Ultrasonic treatment

- ✓ Ultrasound treatment can be used as pretreatment for sludge or to treat the liquid effluent from anaerobic digesters (e.g., solid-liquid separation).
- ✓ Ultrasound frequencies (over 20 kHz) cause cavities to form and implode, producing shockwaves in a process called cavitation.
- ✓ These forces cause the disruption of microbial cell walls in the liquid setting hydrolytic enzymes free, increasing the hydrolysis rate of a biomass.

And ultrasonic techniques can be used for pretreatment for the sludge or to trade the liquid effluent from the anaerobic digestion process and ultrasonic frequency like over 20 kilohertz cause cavities to form and can easily available for those micros for the degradation process.

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An industrial shredder in Austria
Source: Pretreatment of feedstock for enhanced biogas production. Technical Brochure written by: Lucy F. R. MONTGOMERY and Günther BOCHMANN




A cross-flow shredder (mechanical pretreatment unit)
Source: Pretreatment of feedstock for enhanced biogas production. Technical Brochure written by: Lucy F. R. MONTGOMERY and Günther BOCHMANN

So, this is the industrial shredder for the mechanical pretreatment process, this is a simple cross-flow shredder. This is also a mechanical pretreatment process.


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Thermal pretreatment


- Substrate is heated (typically 125 to 190 °C) and held at that temperature for a particular duration (hours).
- In the laboratories, this can be carried out with autoclaves, hot air ovens, water baths or microwave heaters. Dry substrates need additional water before thermal treatment.




Autoclave ✓



Hot air oven ✓



Microwave oven ✓



Hot water bath ✓

- In lignocellulosic substrate, the presence of heat and water disrupts the hydrogen bonds that hold together crystalline cellulose and the lignocellulose complexes, causing the biomass to swell (Garrote et al., 1999).

*Source: Garrote G, Dominguez H and Parajo JC (1999) 'Hydrothermal processing of lignocellulosic materials', *European Journal of Wood and Wood Products*, 57, 3, 191-194.

Now, next is thermal pretreatment. So, substrate is heated around the typically 125 to 190 degrees centigrade and held at the temperature for a particular duration or particular time. So, by heating that particular substrate, it a higher temperature that is the thermal pretreatment process. So, in the laboratory, these can be carried out with the autoclave. So, this is also a temperature in the autoclave that can go up to 120 to 150 degrees centigrade hot air oven.

So, where the temperature goes to 100 degrees or 120 degrees microwave oven temperature can go 300 degrees centigrade hot water bath. So, why these different techniques, we can increase the temperature of a particular substrate, and in the lignocellulose substrate, the presence of heat and water disturb the hydrogen bonds that hold together as crystalline cellulose and the lignocellulose complex causing the biomass to swell. So, once it will be swelled by having the mold temperature, the high temperature it will be available for the microbial degradation process.

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Thermal pretreatment (Cont.)

- Thermal pretreatment is only **effective up to a certain temperature** due to **formation of inhibitory compounds** at temperatures beyond **decreasing the biogas yield**. (e.g., during pretreatment of lignocellulosic compounds at very high temperatures, certain dark-coloured xylose and lignin breakdown products are formed which include heterocyclic and phenolic compounds (such as furfural) which are toxic in nature).
- **Temperatures above 200°C** have been found responsible for the **production of recalcitrant soluble organics** or **toxic/inhibitory intermediates** during the pretreatment process.
- **Optimum temperature conditions** that break down the substrate **should be evaluated** which varies from substrate to substrate. [e.g., 175°C for waste activated sludge (⁴Distefano and Ambulkar, 2006) and 190°C for crops (⁸Dinglreiter, 2007)]



Industrial scale thermal pretreatment in Germany

⁴ Source- Distefano, Thomas & Ambulkar, A. (2006). *Methane production and solids destruction in an anaerobic solid waste*
⁸ Source- Dinglreiter U (2007) *How can be biomass best get small? Processes and materials for energy technology: Volume 3. Sulzbach-Rosenberg: Verlag Föyster Druck und Service.*

So, they say industrial-scale thermal pretreatment, one of the industry so, thermal pretreatment is only effective up to a certain temperature due to the formation of inhibitory compounds at a temperature beyond decreasing the biomass yield. So, now, here the important is that is not that if you have the more temperature below mold degradation, and because of that more biogas yield it is not like that, so, is there this temperature will be only beneficial for one particular temperature.

And beyond that temperature, there could be a possibility of the formation of inhibitory compounds, and because of inhibitory compounds, your biomass field also will be reduced. So, temperatures about 200 degrees centigrade have been found responsible for the production of the recalcitrant soluble organics or toxic or inhibitory compounds during the pretreatment process and for different biomasses, different temperatures will be required.


I think initially we had to do some laboratory studies where on a particular substrate will require how much temperature and how much duration this is also important fact factor like some substrate will be required 30 minutes only some substrate will be required 2 hours this particular temperature under depending upon the temperature change like in the microwave oven, the time requirement will be maybe only 5 minutes or in the 10 minutes itself could be possible to finish the pretreatment process.

So, the optimum condition that breaks down the substrate will be evaluated which varies from the substrate to substrate. So, like 175 degrees centigrade for waste activated sludge and crop 190 degrees centigrade.

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Thermal pretreatment (Cont.)

- Thermal pretreatment is only **effective up to a certain temperature due to formation of inhibitory compounds** at temperatures beyond **decreasing the biogas yield**. (e.g., during pretreatment of lignocellulosic compounds at very high temperatures, certain dark-coloured xylose and lignin breakdown products are formed which include heterocyclic and phenolic compounds (such as furfural) which are toxic in nature).
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Industrial scale thermal pretreatment in Germany

Disadvantage- Energy requirement is huge so potential benefits should surpass the energy investment.

So, what is the disadvantage of these thermal pretreatment processes the energy requirement is huge. So, potential benefits should surpass the energy investment. So, this is one of the disadvantages because to get the temperature up to 150 degrees centigrade and they are also you will be required good amount of energy.

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Chemical pretreatment

- Chemical pretreatment uses a range of different chemicals, **mainly acids and bases of different strengths under different conditions**.
- Some types of chemical pretreatments are-
 - **Alkali pretreatment-**
 - ✓ Carried out with different alkalis. [e.g., lime, sodium hydroxide (NaOH), calcium hydroxide (CaOH₂)]
 - ✓ Alkali addition causes swelling of lignocelluloses and disruption of lignin with partial solubilization.
 - **Acid pretreatment-**
 - ✓ In lignocellulosic substrates, acid pretreatment does not disrupt lignin (as in the case of alkali pretreatment) but breaks hemicellulose and disrupts ether bonds between lignin and hemicellulose.
 - **Oxidative pretreatment-**
 - ✓ Uses hydrogen peroxide (H₂O₂) or ozone (O₃).
 - ✓ Disadvantage- Too much oxygen into the system increases the proportion of CO₂ in the biogas so dosage has to be optimized for each substrate.

Next is the chemical pretreatment. So, chemical pretreatment uses a range of different chemicals mainly acid and base of different states and different conditions. Some types of chemical

pretreatments are alkali pretreatment. So, where we can use lime NaOH calcium hydroxide by addition of these chemicals, we can have the pretreatment process, acid pretreatment.

So, in acid treatment, we can use acids, different acids we can use for the degradation process and some oxidative pretreatments also could possible by adding hydrogen peroxide even ozone, but what is the disadvantage of this process too much amount of oxygen into the system by the addition of these because oxygen is adding here. So, that is not that advantage.

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Biological pretreatment

- Biological pretreatment involves using microbial agents (bacteria, fungi, enzymes) for biogas enhancement from substrates.
- Complex biopolymers such as protein and carbohydrate can be transformed into simpler end products due to the action of various enzymes produced by the bacteria which in turn solubilizes the organic compounds present in the biomass with minimum energy, with no major changes in substrate environment.
- Biological pretreatment with microbial agents lead to an increase of 29.54 % in biogas yield as compared to non-biological processes (Yan et al., 2009) but these processes are much slower than non-biological processes.
- Biological pretreatment is applied by using direct microorganisms as well as enzymes extracted from microbes as catalysts to modify and to degrade the complex biomass polymers.
- These are less energy-intensive pretreatments with high selectivity, no inhibitory by-products, and mild operational conditions (pH and temperature).
- **Disadvantage**- The cost and the complexity of formulating the optimum biological agent mixture.

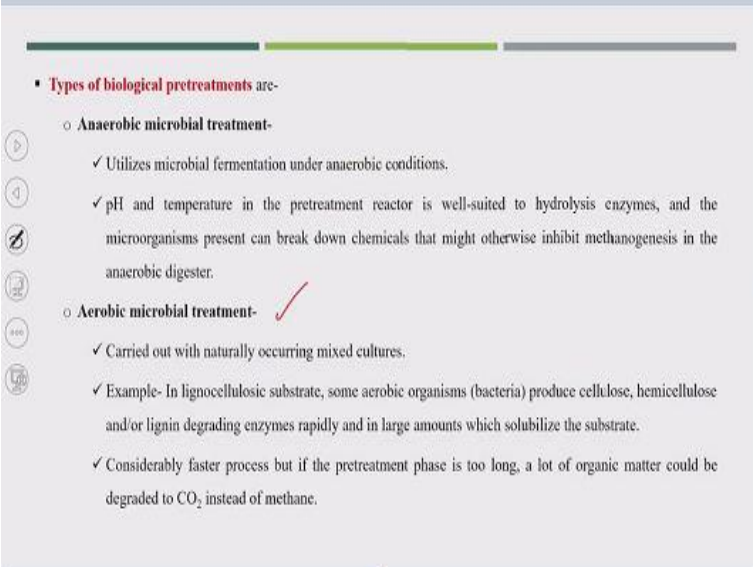
Now, next is the biological pretreatment process biological pretreatment involves using microbial agents like bacteria, fungi, or even direct enzymes addition for the degradation process could be possible. So, complex biopolymers such as protein carbohydrates can be transformed into simple and products due to the action of various enzymes produced by the bacteria means, which will increase the solubility of organic matter.

And biological treatment with microbial agents leads to increase to around 30% biogas yield can be increased by having some research the this is more beneficial and biological patronage applied by using direct micro ism as well as the enzyme extracted from the microbes as catalysts to modify to degrade the complex biomass polymer. So, we can use direct micro ism a particular bacteria or fungus we can take and can add for the degradation process or we can extract the enzyme from the microbes, and these enzymes we can add for the degradation process.

So, these are less energy-intensive pretreatment with high sensitive no inhibitory byproducts and mild operation conditions. So, this is one of the very beneficial processes, but the disadvantage the cost and complexity for formulating the optimum biological agent mixture. So, this cost is only of micro ism cost and enzyme cost you will be required and also because these all degradation will be an optimum operating condition especially this pH and temperature because the growth of these kinds of bacteria and these kinds of enzymes are dependent upon the local conditions.

So, these local conditions have to be obtained for the degradation process and if you do not have those optimum conditions maybe that added microbes or added enzyme would not work for the proper pretreatment process.

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▪ **Types of biological pretreatments are-**

- **Anaerobic microbial treatment-**
 - ✓ Utilizes microbial fermentation under anaerobic conditions.
 - ✓ pH and temperature in the pretreatment reactor is well-suited to hydrolysis enzymes, and the microorganisms present can break down chemicals that might otherwise inhibit methanogenesis in the anaerobic digester.
- **Aerobic microbial treatment-** ✓
 - ✓ Carried out with naturally occurring mixed cultures.
 - ✓ Example- In lignocellulosic substrate, some aerobic organisms (bacteria) produce cellulose, hemicellulose and/or lignin degrading enzymes rapidly and in large amounts which solubilize the substrate.
 - ✓ Considerably faster process but if the pretreatment phase is too long, a lot of organic matter could be degraded to CO₂ instead of methane.

Now, what are the types of biological pretreatments are could be anaerobic microbial pretreatment that utilizes microbial fermentation on the anaerobic condition and could be aerobic microbial treatment process could be both can be useful, because see hydrolysis process is the first phase of the anaerobic digestion process. So, these could be aerobic also is not only for anaerobic, so, it is possible that we have 2 units and the first unit the hydrolysis is possible and second unit the anaerobic degradation will be there for biogas production.

So, these hydrolysis process could be aerobic and obviously, these are aerobic microbial treatment is more beneficial than the anaerobic microbial treatment, because these aerobic

bacteria are faster growth could be possible and their degradation rate also will be far better than the anaerobic one.

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o **Fungal treatment-**

- ✓ Fungi (such as white-rot fungi) are known for their ability to remove environmental pollutants from solid and liquid waste by delignifying the substrates.
- ✓ In the process they increase the solubilization and biogas yield.
- ✓ Pretreatment of lignocellulosic substrate (straws) with white-rot fungi that degrade lignin have been investigated by various researchers.

o **Enzyme addition-**

- ✓ To enhance biomass breakdown, a mixture of enzymes can be added which may include cellulose-, hemicellulose-, pectin- and starch-degrading enzymes.
- ✓ Enzyme additives can be applied in three different ways:
 - By direct addition to a single-stage anaerobic digester
 - By addition to the hydrolysis and acidification vessel (first stage) of a two-stage system
 - By addition to a dedicated enzymatic pretreatment vessel

Disadvantages-

- Some enzymes are very costly.
- In some substrates, enzyme dosage requirement is very high making it uneconomical inspite of getting increased methane yield.

White-rot fungi

And also the fungal treatment could be possible like such as white-rot fungi is a well-known fungus-like, here also we can see in our kitchen. Also, we saw after 6 days, 7 days, if suppose that some food is getting degraded, we will see these kinds of fungi. So, in this process, this fungus will increase the salivation increase the biological lead. So, this was again the enzyme addition also is beneficial, I think I believe that rather than adding directly the microbes if you are adding the enzymes that are more beneficial for the anaerobic digestion process.

So, what are the disadvantage, this one again for especially for the enzyme addition, because it is very costly because that extraction will be required and in some substrate, the enzyme dosage requirement is very, very high making it uneconomical despite getting an increase in methane yield. So, you will be required a large amount of these enzymes for the degradation process. So, obviously, the cost will be more. Now, the pretreatment we finish so, and if you ask me sir, which will be the best method for the pretreatment process in the field.

So, I believe that the chemical pretreatment, I would not accept much, because the handling of those chemicals like whether is an alkali or acid sandling that is why I did not talk much about the chemical pretreatment process, now for biological pretreatment process is possible to use, but only the requirement of the production of more amount of bacteria or enzymes or fungi. Now, if

you are able to produce more also, you have to maintain also those and will require the proper optimum conditions for that.

And in the field, if you talk about that, the quantity requirement is more under if you talk about the size of 200 tons per day capacity or 5000 tons per capacity biogas reactor you will be required huge amount of microbes that is also very difficult in the field one, but it is possible in developed countries there are many countries are utilizing such kind of techniques, but in India or developing countries I believe that the mechanical pretreatment is or physical pretreatment under the mechanical pretreatment is more beneficial.

And they are also the shredding or grinding, if you do that itself is highly beneficial for anaerobic digestion process. So, I believe that whenever you install any reactor, you have 1 grinder or shredding process. So, under what should be the target of this grinding process, the target is to convert the entire material in the size of 2 mm or less than that or 4 mm less than that, that should be the target. So, that this entire material size will be lowered down and can easily go to the anaerobic digestion process that is easy to work in the field.

And even the large quantity of waste also can be handled by mechanical pretreatment process now for co-digestion process.

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WHAT IS ANAEROBIC CO-DIGESTION (AnCoD) ?

- ❖ AnCoD is the **simultaneous anaerobic digestion of a homogenous mixture of two or more substrates** to overcome the disadvantages of mono-digestion and improve the economic viability of anaerobic digesters.
- ❖ Use of co-substrates **improves biogas production and methane yield** due to:
 - ✓ Establishment of positive synergisms in the digestion medium.
 - ✓ Optimal attainment of lacking nutrients from the co-substrates.
- ❖ Substrates having **high C/N ratio, mono-digestion has poor process stability.**
- ❖ **Addition of nitrogen rich co-substrates** at optimum ratio enhances biomass degradation.
- ❖ Co-digestion of different feedstocks with animal manure can increase biogas production from 25 % to 400 % compared to the mono-digestion of the same substrates. E.g., in co-digestion of pig manure with glycerol at a pig manure/glycerol mixing ratio of 24/1 under mesophilic conditions, almost a 400% increase in biogas was observed in comparison with the conventional mono-digestion of pig manure alone.

So, what is anaerobic co-digestion? So, anaerobic co-digestion is a simultaneous anaerobic digestion of homogeneous mixture of 2 or more substrates to overcome the disadvantage of mono digestion and improve the economical viability of anaerobic digester. So, this is another idea about the hydrolysis process. See, now, the one issue I talked about these, hydrolysis or pretreatment could be by different physical-chemical biological process.

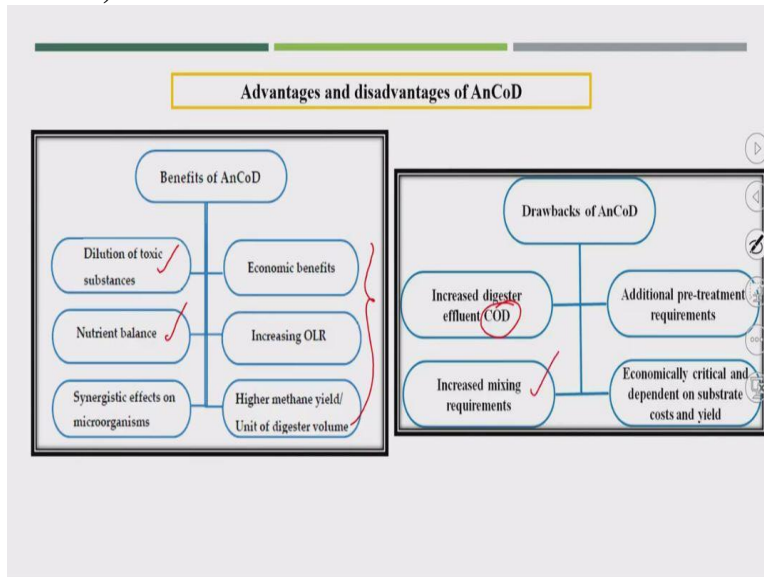
They this is another idea, if you add 2 different kinds of substrate, so, we can easily maintain the carbon to nitrogen ratio, suppose the food waste which is lower in carbon to nitrogen ratio and the agriculture waste which is having the more lignocellulose concentration also have more carbon to nitrogen ratio. So, by mixing up these 2 different substrates, we can optimize the carbon to nitrogen ratio that is, will be more beneficial for biogas production.

So, under the mono digestion especially the mono digestion are the specially these lignocellulose biomass alone for biogas production is required very proper pretreatment process and if you do not want to use for pretreatment process go for co-digestion process by addition of different easily degradable organic matter. So, use of co-substrate improves the biogas production in methane yield due to establishment of positive synergism in the digestion medium and optimum attainment of lacking nutrients from the co-substrate.

The substrate having high carbon to nitrogen ratio mono dilution has poor process stability. So, the substrate is having high carbon to nitrogen ratio having the mono digestion is a poor process stability and the addition of nitrogen-rich co-substrate is optimum ratio enhanced biomass degradation. So, co-digestion of different feedstock with animal manure can increase biogas production from 20 to 400%.

Compared to the mono-digestion of the same substrate, so, especially had talked about animal manure suppose that is why I think in India when anyone is running the biogas reactor, they are talking always talking about the addition of some cattle manure spatially cow dung and because cow dung is a high nitrogen-rich organic matter easily and also having the huge amount of microbial consortia. So, if you add such kind of animal manure or animal waste or could be used for the biogas production co-digestion of the lignocellulose material.

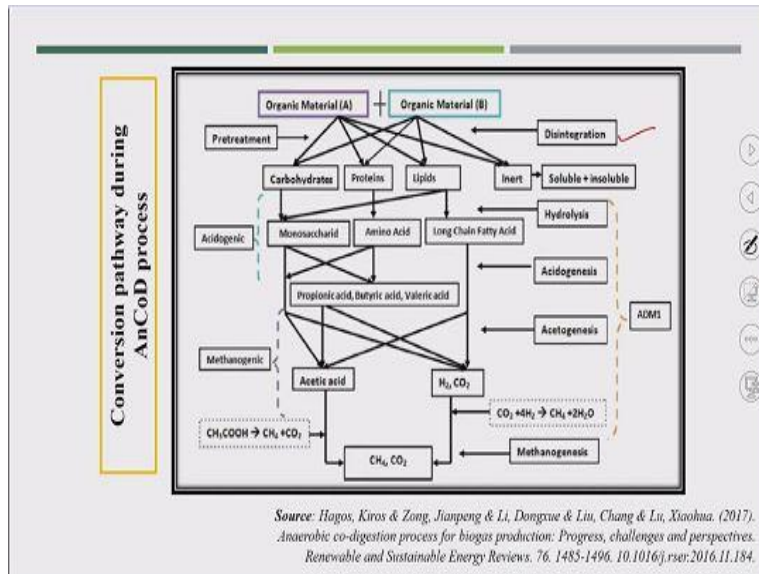
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So, what is the advantage and disadvantage, so, the advantages or benefits of the anaerobic co-digestion process like dilution of toxic substances nutrient balance that is carbon to nitrogen ratio and also the synergetic effect of microorganism. So, these are the benefits from the addition of other nitrogen-rich materials. So, what are the drawbacks? Drawbacks could be increased digester efficient COD.

So, because when you are adding even cow dung also into the reactor or any other nitrogen-rich organic matter is not only your nitrogen you are adding, but also the carbon you also you are adding into the particular material particular mass. So, obviously, our total chemical oxygen demand will also increase and also the increased mixing requirement, because both have to be mixed properly. So, there also will be required energy.

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Now, I think we saw this as the one particular flow of biogas production. So, starting from pretreatment acidogenic methanogenic, so, by adding of another organic matter, this integration with could be possible and also parallelly the hydrolysis acidogenic this method will follow and obviously, it will be beneficial for an increase of more biogas.

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FACTORS AFFECTING AnCoD PROCESS

a) Carbohydrate-rich organic materials

1. Chemical compositions of the substrates
 - Characterization of chemical compositions of different substrates is helpful to identify the appropriate substrates for AnCoD.
 - Classifying the substrates according to their biochemical compositions can be useful to evaluate the bioaccessibility, biodegradability, and bioavailability of substrates.
 - There are different factors that affect the degradation of organic substrates, such as bioavailability, bioaccessibility, temperature, pH, moisture, nutrient concentrations.

- Carbohydrates are present in all substrates in different proportions.
- Food waste (sugar industry, fruit and vegetable processing) is enriched with simple sugars and disaccharides, easily decomposable with the formation of VFAs.
- Problem:**
 - High levels of simple sugars result in rapid VFA accumulation, decreased pH, and suppression of methanogenesis.
- Solution:**
 - For balanced operation of anaerobic reactors, mixing the feedstock containing high amounts of simple carbohydrates with waste with a lower content of easily degradable organic components is recommended.

Now, what are the factors affecting anaerobic digestion process like first is the chemical composition of the substrate. So, the characterization of chemical composition of different substances helpful to identify the appropriate substrate and classifying the substrate according to their biochemical compositions can be useful to evaluate the biodegradability and bioavailability of the substrate there are different factors. So, different factors could be bioavailability temperature pH moisture.

So, the first is the carbohydrate-rich organic material. So, like carbohydrates are present in all substrates in different proportions like food waste is enriched with complex sugar and disaccharides easily decomposed with the formation of volatile fatty acids. So, what could be the problem of the addition of these kinds of organic matter for the co-digestion process like higher level of simple sugar result in rapid volatile fatty acids accumulation? So, because of that, it will decrease the pH and because of that, your methane production will be reduced.

So, what is the solution that for balance operation of anaerobic reactor mixing the feedstock containing high amount of simple carbohydrates with waste with a lower content of easily degradable organic components is recommended. So, here what is the idea, to balance both so, by adding the high amount of simple carbohydrates with waste with a lower content of easily degradable organic compounds, if you mix both kinds of material, you would not find the problem of rapid VFA accumulation.

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The slide is titled "Chemical compositions of the substrates (Cont.)" and is divided into sections. The current section is "b) Protein-rich organic materials". It contains two main bullet points: "Problem:" and "Solution:". Under "Problem:", there are three sub-bullets: "During digestion, proteins convert to amino acids which have an amine group (-NH₂).", "Microbial degradation of proteins results in the release of ammonium ions, which are strong inhibitors of methanogenic bacteria.", and "At high concentrations, ammonia (not ammonium) inhibits microorganisms and when its concentration increases, it leads to process instability and system failure." The word "ammonia" is circled in red, and the phrase "process instability and system failure" is underlined in red. Under "Solution:", there is one sub-bullet: "Suitable co-substrates and adjustment of C/N ratio to its optimum value or culture enrichment in the system can minimize this problem."

Now next is the protein-rich organic material what could be the problem the during digestion protein converts to amino acids which amino groups and could produce ammonia which will innovate the microbial degradation process that will be also a major problem. So, what is the solution of that suitable co-substrate with adjustment of carbon to nitrogen ratio you maintain should be optimum to minimize this kind of problem.

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Chemical compositions of the substrates (Cont.)

c) Fat-rich organic materials

• Problems:

- Substrates with high concentrations of fats/lipids cause blocking, adsorption to biomass (causing mass transfer problems) and microbial inhibition in anaerobic digesters.
- The degradation of triglycerides produces long chain fatty acids (LCFAs) (over 12-C) and glycerol; and glycerol is rapidly converted to biogas, while decomposition of LCFAs is complex.
- High concentration of LCFAs inhibit the activity of anaerobic microorganisms, cause foaming (especially at elevated temperature) and produce toxic elements.

• Solution:

- Mixing carbohydrate-rich materials with the fat-rich materials (slowly degradable and fast degradable) are advantageous in nutrition balance, microorganism enrichment, reducing the accumulation of inhibitors, increasing reactor stability, improved methane yield.

So, another addition by fat-rich organic materials, there could be also possible high concentration of fats lipid causes blocking the absorption of biomass as and microbial innovation could be possible. So, for that solution also the mixing carbohydrate-rich material with a fat-rich material, slowly degradable and fast degradable are advantages in nutrient balance. So, see here carbohydrate-rich material with a fat-rich material may slowly degradable to the fast degradable or advantages in nutrient balance that will improve the methane yield in the biogas reactor.

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2. Temperature

- Microorganisms grow best at temperature ranges of mesophilic and thermophilic.
- An increased temperature increases the metabolic rate of microorganisms and accelerates the digestion processes, but thermophilic process is harder to control and needs more energy to maintain the constant temperature of the reactor.
- **Co-digestion process with a high concentration of ammonia is unstable in the thermophilic temperature range.**

3. pH

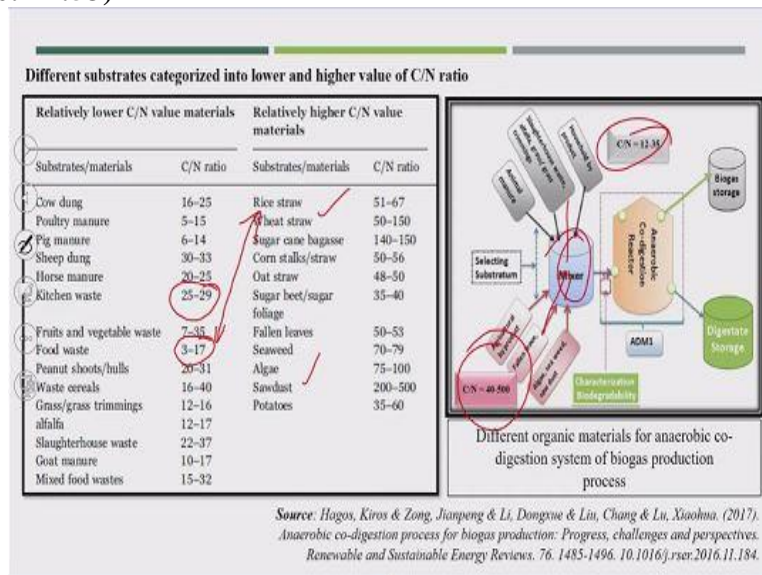
- The most **favorable range of pH** to obtain maximal biogas production in anaerobic digestion is **6.8-7.2**
- The **co-digestion can enable stable pH** value by **avoiding the extreme acidification condition.**
- The **change in pH** of the mixed raw materials in **co-digestion is more stable** and easier to maintain in optimum pH range during the digestion process compared to the single substrate digestion.

Now, the next factor is temperature. So, micro ism grows best at temperature ranges of mesophilic and thermophilic. And co-digestion process with a high concentration of ammonia is unstable in the thermophilic temperature range. Now, the next factor for temperature. So, these

biogas reactors could be possible to run it mesophilic temperature also it thermophilic temporary also which we talked about in the previous lecture.

So, here is the only problem in the co-digestion process with a high concentration of because it a thermophilic temperature that could be possibilities of higher concentration of ammonia and you know that this ammonia is inhibitory for methane yield. Next is the pH. So, the optimum pH is 6.8 to 7.2 for co-digestion to process. So, the co-digestion can enable stable pH value by avoiding the extreme acidification condition the change in pH of mixed raw material in co-digestion is more stable easier to maintain the optimum pH range for the degradation process.

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Next is the carbon to nitrogen ratio. This is important for the degradation process. So, mixing of the carbon-rich substrate with a nitrogen-rich substrate like animal manure and kitchen waste. So, that will be more beneficial to maintain the proper carbon to nitrogen ratio. And normally the optimum range of carbon to nitrogen ratio is 20 to 30 is good for methane production. And if the carbon to nitrogen ratio is high, there could be a possibility of producing a large amount of volatile fatty acids, which is inhibitory for biogas production.

And if C/N ratio is low, there could be possible of more ammonia production. So, that is also inhibitory for biogas production. Now, if you see that there are different substrates are having different carbon to nitrogen ratios as you see here, kitchen waste is 25 to 29. And suppose, you

take here sawdust or even other kinds of agriculture ratio below more carbon to nitrogen ratio, if you mix like here you take food waste, 3 to 70 so, this is not optimum.

So, by mixing these to these a particular concentration could attain proper carbon to nitrogen ratio. So, by CN ratio high CN ratio, and lower CN ratio if you mix into the same reactor, it proper concentration we can get proper the biogas production also and good quality of digested also could be possible. So, now, in this lecture, I talked about there are 2 ways we can have the hydrolysis process one for the pretreatment process and the other for the co-digestion process.

Now, if you compare both techniques is again depends upon the local conditions. So, suppose in the local conditions you are finding there are a large variety of organic matters are available. So, obviously, I think I believe that the co-digestion will be more beneficial, and in some of the locations where only one particular kind of waste is available that you are going for an anaerobic digestion process. So, in that case, plan for some mechanical pretreatment process.

So, based on the local conditions, local waste availability we can go for either mono digestion with the mechanical predetermine process or co-digestion with available different organic matters in the local area. Also, it can mix both by having the different substrate mix and we can go for a mechanical pretreatment process that is also more beneficial. So, the target is that your HRT should be lower down that is the first point, the second point there should not be the production of innovative compounds like VFA or ammonia.

And these are the important and the maximum methane production these are the 3 major factors you consider and go for either pretreatment process or co-digestion process. So, thank you.