Biofuels

Lec 3-Biogas: part 3

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The need of pretreatment

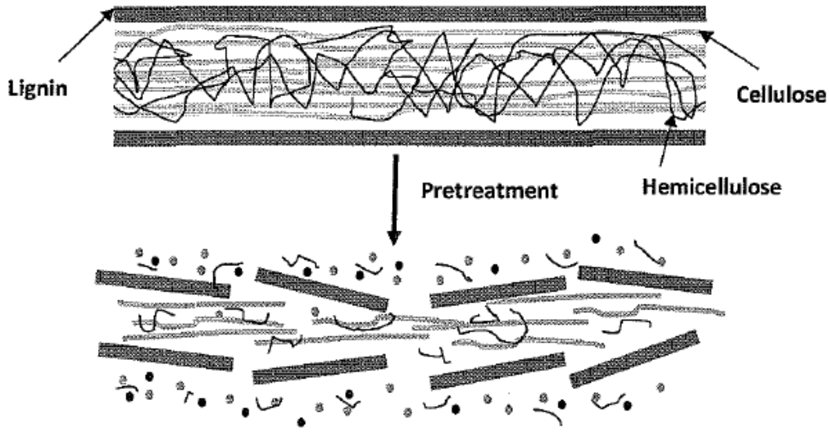
- Lignocellulosic biomass exists as the most abundant raw materials such as hardwood, softwood, grasses, as well as household, industrial and agricultural residues.
- However, their low digestibility is one of the major problems when considering utilizing these materials for renewable fuel production.
- Pretreatment is therefore an important step prior to the bioconversion of lignocellulosic biomass into value added products.
- These materials contain mainly cellulose, hemicelluloses and lignin making up a compact structure, where lignin physically shields the utilizable cellulose and hemicelluloses part from the degrading enzymes.
- Thus, it is crucial to change this compact structure in order to make cellulose and hemicelluloses more accessible to the enzymes breakdown and to convert them into fermentable sugars

Structure of energy crops

- The structure of energy crops or agriculture residues mainly consists of cellulose, hemicellulose and lignin.
- In addition to these compounds, crop biomass can contain e.g. nonstructural carbohydrates such as glucose, fructose, sucrose and fructans, proteins, lipids, extractives and pectin.
- Lignin is not degraded in anaerobic conditions, and the rate and extent of lignocellulose utilization is severely limited due to the intense cross-linking of cellulose with hemicellulose and lignin.
- Moreover, the crystalline structure of cellulose prevents penetration by micro-organisms or extracellular enzymes.

Structure of energy crops

- As the rate-limiting step in anaerobic digestion of solid materials such as energy crops and crop residues is hydrolysis of complex polymeric,
- One way of substances improving the methane production from anaerobic digestion of lignocellulosics is to pre-treat the substrate in order to break the polymer chains to more easily accessible soluble compounds.



Pre-treatment of the substrate

- An ideal pre-treatment would increase surface area and reduce lignin content and crystallinity of Cellulose.
- Pre-treatments can be carried out either physically, chemically or biologically, or as combinations of these.

Size reduction:

- Biogas yield can be improved by reducing the particle size of the crop biomass because size reduction can increase the available surface area and release the intracellular components
- biogas yields increased with decrease in particle size, but the difference between the smallest particle sizes is small

Mechanical pretreatment: Size reduction

Pretreatment methods	Crops	Particle side (mm)	CH4 potential (m3 CH4/kg VS added)
Mechanical size reduction (mm)	Wheat straw	150	0.13
	"	6	0.20
	"	1	0.24
	"	0.4	0.23
	"	0.088	0.23
	"	20	0.26
	"	0.5	0.33
	Rice straw	150	0.24
	"	6	0.35
	"	1	0.36
	"	0.4	0.37
	"	0.088	0.37
	Mirabilis leaves	80*50	0.29
	"	6	0.33
	"	1	0.33
	"	0.4	0.34
	"	0.088	0.34

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Size reduction

Pretreatment methods	Crops	Particle side (mm)	CH4 potential (m3 CH4/kg VS added)
	Dhup grass	30	0.14
	"	6	0.21
	"	1	0.21
	"	0.4	0.23
	"	0.088	0.23
	Oats	20	0.25
	"	10	0.25
	"	5	0.26
	Grass hay	20	0.27
	"	10	0.35
	"	5	0.32
	Clover	20	0.21
	"	10	0.14
	"	5	0.2

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Steam pretreatment/steam explosion

- It is one of the pretreatment in thermal pretreatment category.
- During steam pretreatment the biomass is put in a large vessel and stearm with high temperature (up to 240°C) and corresponding pressure, is applied for few minutes.
- After a set time, the stearm and pressure is released and biomass is quickly cooled down.
- The objective of the steam pretreatment/steam explosion is to solubilize the hemicellulose to make the cellulose better accessible for enzymatic hydrolysis and to avoid the formation of inhibitors

Steam pretreatment/steam explosion

- Steam pretreatment of wheat straw under the condition of 170°C and 10 minutes can increased the biogas yield by 31 % compared to untreated straw
- Steam explosion pretreatment of municipal solid waste under the condition of 240°C and 5 minutes biogas yield increased 40%.
- However, steam pretreatment includes a risk on production of compounds like furfural, HMF, and soluble phenolic compounds.
  - These compounds are inhibitory to the methane production.
  - The biogas producing bacteria are however capable of adapting, at least to a certain concentration, to such compounds
- Moreover, steam pretreatment includes a risk on condensation and precipitation of soluble lignin components, making the biomass less digestible, and therefore reducing the biogas production.

Acid pretreatment

- The pretreatment can be done with dilute or strong acids.
- The main reaction that occurs during acid pretreatment is the hydrolysis of hemicellulose, especially xylan as glucomannan is relatively acid stable.
- Solubilized hemicelluloses (oligomers) can be subjected to hydrolytic reactions producing monomers, furfural and other (volatile) products in acidic environments
- During acid pretreatment solubilized lignin will quickly condensate and precipitate in the acidic environments
- The solublization of hemicellulose and precipitation of solubilized lignin are more pronounced during strong acid pretreatment compared to dilute acid pretreatment

Acid pretreatment

- For methane production, acid pretreatment of lignocelluloses material is one of the attractive methods because methanogens can handle compounds like furfural to a certain concentration
- The biogas yield from treated newsprint bioconversion with acetic acid concentration of 35%, 2% nitric acid and boiling for 30 min increased nearly three times over that of untreated newsprint.
- The major drawback of this pretreatment method, particularly at low pH, is the formation of different types of inhibitors such as carboxylic acids, furans and phenolic compounds.
- If the concentration of these compounds is high they usually inhibit the microbial growth and fermentation, and this will result in lower productivity of biogas,
- Therefore, the pretreatments at low pH should be selected properly in order to avoid or at least reduce the formation of these inhibitors

Alkaline pretreatment

- During alkaline pretreatment the first reactions taking place are solvation and saphonication.
- This causes a swollen state of the biomass and makes it more accessible for bacteria.
- Application of alkaline solutions such as NaOH, $Ca(OH)_2$ (lime) or ammonia to remove lignin and a part of the hemicellulose, and efficiently increase the accessibility of enzyme to the cellulose. The alkaline pretreatment can result in a sharp increase in saccharification with various yields.
- Treatment of waste-activated sludge with 0.3 g NaOH/g volatile solids (VS) at l30^{o}C for 5 min resulted in 40-50% solubilization of VS and more than 200% improvement in methane production compared to the control experiment.
- Pretreatment mixture of sugar beet tops grass hay straw at condition: 2% NaOH 24 hours and 72 hours, the biogas production was increased 9 and 17% respectively,

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Alkaline pretreatment

Pretreatment methods	Crops	Pretreatment condition	CH4 potential (m3 CH4/kg VS added) Before pretreatment	After pretreatmen	% CH4 increase
Chemical pretreatment	Sugarbeet tops Grass hay Straw	Alkalis	0.23	0.25	9
	"	2% NaOH 24h	0.23	0.25	9
	"	2% NaOH 72h	0.23	0.27	17
	"	3% Ca(OH) 2+4% Na2 CO3 72h	0.23	0.27	17
	"	xylanases, cellulases	0.23	0.27	17
	Summer switchgrass	7 g/L NaOH 3h	n.r.	0.38	0-+32
	Winter switchgrass	7 g/L NaOH 3h	n.r.	0.13	

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Wet-oxidation pretreatment

- In this process, the biomasses are treated with water and oxygen or oxidation agent such as hydrogen peroxide (H_2O_2) at high temperature above 120°C and for 5min
- Wet oxidation has been applied as pretreatment for both ethanol and biogas production.
- The most important parameters in wet oxidation are amount of reaction time, oxidation agent (Oxygen), pressure and temperature.
- The objective of the pretreatment is to breakdown the hemicellululose and lignin structures to increase the accessibility of the cellulose.
- During the wet oxidation pretreatment several reactions can take place such as electrophilic substitution, displacement of side chains, cleavage of alkyl aryl ether linkage or the oxidative cleavage of aromatic nuclei.
- The wet oxidation process can increase biogas yields by approximately 35-70% from raw and digested lignocelluosic bio-wastes.

Wet-explosion pretreatment

- The principle of the treatment is to heat the biomass with water on a high temperature of at least 170°C, and provide an oxidation reaction under high pressure by addition of an oxidizing agent (H_2O_2).
- In subsequent step, the material undergoes a sudden pressure release (steam explosion).
- The method is a combination of steam explosion, and wet oxidation and it enables operating with high biomass concentrations and handling of big particle sizes, thereby, avoiding initial energy intensive mechanical milling.
- Moreover it is an easy controllable process with low total energy consumption.
- The most important parameter of evaluation the wet explosion process is to exam the amount of soluble sugar released from lignocellulosic biomass
- The characterization results of soluble sugar concentration were significantly high after wet explosion pretreatment compared to raw biomass.

Wet-explosion pretreatment

	g of soluble sugar released/100g (TS)				
Energy crops and Crop residues	Retention time (min) 2/5/8	TS concentration (%) 10/15/20	H_2O_2 concentration (% of TS) 3/6/8	Temperature (^oC)150/180/195	Pressure (bar) 5/10/14
	12.07±0.2	19.53±0.20	13.13±0.20	13.13±0.30	13.13±0.30
	15.83±0.53	15.83±0.53	15.83±0.53	15.83±0.53	15.83±0.53
Wheat straw	13.86±0.45	15.40±0.22	15.22±0.60	0.92±0.60	0.92±0.60
	29.84±1.34	28.54±1.55	33.66±1.15	30.29±1.83	30.29±1.83
	29.89±1.45	29.89±1.38	29.89±1.23	29.89±1.10	29.89±1.10
Corn stalker	31.92±1.35	46.62±1.33	18.28±1.27	11.71±1.37	11.71±1.37
	6.51±0.54	9.08±0.33	7.01±0.33	1.35±0.25	1.35±0.25
	12.23±1.02	12.23±1.02	12.23±1.02	12.23±1.02	12.23±1.02
Willow	9.57±0.45	9.21±0.55	9.06±0.55	4.87±0.38	4.87±0.38
	7.56±0.52	25.09±1.15	9.00±0.66	5.15±1.23	5.15±1.23
	13.51±.98	13.51±0.98	13.51±0.98	13.51±0.98	13.51±0.98
Miscanthus	18.26±1.35	14.56±0.85	16.20±0.35	15.13±0.93	15.13±0.93

Silage pretreatment

- Ensiling is a biological process that has been used to preserve forages for animal feed for centuries.
- Ensilage is also a convenient process for protecting the moisture of crops for biogas production because drying is not a favorable method when crops are used for biogas production.
- Instead, methods based on ensiling are often preferred.
- In the ensiling process, the soluble carbohydrates contained in biomass undergo lactic acid fermentation.
- This reaction will lead to a drop in pH and to inhibition of the growing detrimental microorganisms.
- At the same time, the acidification produces intermediates for methanogenic fermentation.

Silage pretreatment

- In this way the ensiling process can be considered as a pretreatment which simultaneously has potential to promote methane production from plant matter
- Ensiling of maize for 7 weeks influenced the methane production per VS in subsequent anaerobic digestion by up to 22.5%.
- The methane potential of silage rye (3 months), barley, milky (3 months) and maize (4 months), increase more than 20% compared to that fresh crops

Co-digestion

- The concept of anaerobic co-digestion is a cost effective waste treatment method, in which two different types of organic wastes are mixed and treated tighter in single facility.
- By doing so, one takes advantage of the abundance of special compound in one waste type to compensate for its shortage in other waste type, and consequently increase biodegradability and biogas production .
- Using such approach, satisfactory results were obtained with several combinations of agriculture waste, e.g. swine and poultry waste or energy crops and cow wastes.
- Co-digestion not only facilitated biodegradation of the organic compounds but also enhanced biogas production

Feedstock	Temperutur e (oC)	Manure: crop (VS ratio)	Feed TS (%)	HRT. Hydrolic retention time (d)	ml CH_4 per g-VS added
Swine manure, corn stalker	39	75:25	8	16	210
Swine manure	35		n.r.*	39	140
Swine manure, potato waste	35	85:15	n.r.	26	220
ʼʼ	35	80:20	n.r.	39	315
ʼʼ	35	80:20	n.r.	25	290
Swine manure	35		n.r.	15	320
Swine manure, wheat straw	35	75:25	n.r.	15	240
ʼʼ	35	50:50	n.r.	15	220
Cow manure	35		7.3	15	350
Cow manure, wheat straw	35	50:50	7.8	15	100
ʼʼ	35	25:75	7.6	15	70
ʼʼ	35	10:90	7.9	15	30
Cow manure	n.r.		10	40	107
Cow manure, wheat straw	n.r.	80:20	10	40	109
ʼʼ	n.r.	60:40	10	40	113
ʼʼ	n.r.	40:60	10	40	103
ʼʼ	n.r.	20:80	10	40	97