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Increasing biogas production from maize silage by ultrasonic treatment

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Maize silage is one of the most commonly used substrates in biogas plants all over Europe today. However, a considerable part of it is not biologically converted into biogas during anaerobic digestion process (AD). This is caused by content of materials unsuitable for AD (e.g. lignin) and substances requiring very long residence time to be decomposed under anaerobic conditions (which would be ineffective from economical point of view). In case of such complex phytomass, the rate-limiting step of AD is hydrolysis of biomacromolecules (mainly polysaccharides). Cavitation induced by ultrasonic treatment of substrate causes increase of particles' specific area, cell lysis and sonochemical reactions, resulting in splitting of complex organic compounds due to formation of radicals. As a consequence, faster and more efficient conversion of substrate into methane is achieved. To evaluate effect of sonication on biogas production, parallel batch experiments in CSTR bioreactors were carried out. Assessment of substrate disintegration caused by sonication was based on measurements of Chemical oxygen demand (COD) in liquid phase of substrate samples. The biogas and methane CH_4 yields were determined by continuous measurement of biogas flow rate and composition. The resulting biogas production enhancement was 13 - 29.5%, methane yield was increased by 16.9 – 29.5 %. The key evaluation of ultrasonic treatment process is the energy balance. Its results proved its suitability from the environmental point of view.

1. Introduction

The main disadvantage of AD may be found in relatively slow bio-degradation of the substrate. Depending on the digester type, process temperature and other factors, the residence time is usualy 3 weeks and more, resulting in necessity of large fermentors. In biotechnological processes generally three ways to increase the degradation rates are followed i) modification of the process parameters (pH, temperature) ii) modification of biological factor (different microorganism' strains, GMO) and iii) modification of substrate (different substrate or its pre-treatment).

First two ways provide good results but there are limitations - pH and temepreature optimum of methanogenous bacteria are relatively narrow, utilization of GMO is

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impossible due to legislation etc. Therefore, the only way how to improve significantly the biological activity is addition of enzymes into the fermentor to stimulate faster degradation.

The most promising way of increasing the AD biodegradation rate seems to be the pre-treatment of substrate. Biochemical conversion of organic material into biogas is a multi-step process of consecutive and parallel reactions. In such cases, the limiting factor is always the slowest reaction. According to microbiologists' research (Boone et al., 1993), the "bottleneck" of AD of complex substrates is hydrolysis, first step of the biological transformation, during which organic macromolecules (fats, proteins and polysaccharides) are split into simpler ones by extracellular bacterial enzymes. Following phases (acidogenesis, acetogenesis and methanogenesis) are faster.

One of the possible pre-treatment methods is ultrasonic disintegration of biomass. Cavitation induced by sonication causes increase of local temperature (up to 5000 K) and pressure (up to 1000 atm) and formation of jet streams (Suslick et al., 1999). Resulting enormous shear stresses lead to cell lysis (destruction of cell walls and release of cell's content into the solution), sonochemical conversion of complex organic compounds into simpler ones due to formation of $OH^{\bullet}$ and $H^{\bullet}$ radicals (Parsons et al., 2004) and increase of specific area of substrate particles (Straka et al., 2006). The hydrolysis phase is significantly accelerated and the biodegradation of substrate is faster and more effective. However, additional energy is required - the positive energy balance is the key condition of the treatment feasibility.

Ultrasonic treatment of input raw material for AD was tested various times before (Braguglia et al., 2008; Tiehm et al., 2001) but only with activated sludge from WWTP - sonication of maize silage has not been documented yet.

2. Experimental Materials and Methods

2.1 Inoculum and substrate

Inoculum was taken from waste water treatment facility (Česká Lípa) in form of digested sludge from the anaerobic stabilization tank. To eliminate the influence of endogenous (residual) production of biogas, the inoculum was stored for 48 - 72 hours at temperature of 40°C under anaerobic conditions.

As a substrate maize silage samples were used. Their elementary analysis were carried out to determine important technological parameters: C/N ratio, degree of reducibility γ, COD and mainly theoretical methane yield Y_{CH4_th} [Nm^3 $kg^{-1}{}_{VS}$]., which could be determined from stoichiometric relation of AD.

2.2 Experimental design – sonication

According to (Tiehm et al., 2001), disintegration by ultrasound (US) is most significant at low frequencies, because the bubble radius is inversely proportional to the frequency and large bubbles mean strong shear forces. Therefore, the ultrasound with frequency of 20 kHz was used. Other observed parameters of ultrasonic treatment were intensity I [$W \cdot m^{-2}$], treatment time t [s], power P [W] and specific US power in ultrasonic chamber P_V [$W \cdot m^{-3}$]. The cavitation threshold intensity I for water is approximately 40-50 $W \cdot cm^{-2}$ (Tiehm et al., 2001), similar values were recorded during our experiments. Ultrasonic generator SONOPULS 3400 (Bandelin GmbH, Germany) with maximal power input of 400 W was used.

Ultrasonic treatment was carried out in glass beakers of different volumes – this was necessary mainly during experiments aimed at determination of suitable P_V value in the ultrasonic chamber. Acoustic cavitation takes place only in liquid phase and acts on particles only at their surface. Maize silage is material with total solids (TS) of approximately 33 %. Therefore, water was added to samples to reach 8 % of TS in the mixture. Samples were usually mechanically pre-treated by kitchen mixer BOSCH MMR0801 with power input of 400 W in order to inrease the particles` specific area and improve effect of ultrasonic treatment.

The quantitative evaluation of disintegration efficiency is based on the idea that there is a direct relationship between disintegration of cells and tissues and their content released into the solution. The increase of the amount of dissolved organic matter in liquid phase by disintegration process characterizes the disintegration efficiency and may be quantified by *COD* measurements. Degree of disintegration *DD* [%] is then defined as the ratio of COD **-** increase in liquid phase caused by disintegration to COD in the solid phase of substrate. Following relation holds (Straka et al., 2006):

$$DD = \frac{COD_{dis\ (liq)} - COD_{0\ (liq)}}{COD_{0\ (\mathrm{hom})} - COD_{0\ (liq)}} \tag{1}$$

To determine the COD in the liquid phase, the samples were centrifuged at 7000 r/min for 5 min at centrifuge Hettich Zentrifugen UNIVERSAL 320R.

Evaluation of disintegration would be incomplete without consideration of its energy demand. Therefore, specific disintegration energy e_{dis} (energy for disintegration per increase of DD by 1% and per kg of solids in the material) was defined as follows:

$$e_{dis} = \frac{E}{DD \cdot m_{sol}} \tag{2}$$

2.3 Experimental design – fermentation

In order to minimize the differences not-caused by ultrasonic treatment the fermentation was carried out in two experimental units in parallel. The *Bioengineering 75 L* (working volume 50 L) CSTR bioreactors were utilized. Both fermentors were equipped with precise gas flow meters Ritter TG01, composition of biogas was measured with analyzer Aseko AIR LF. Main process parameters were temperature of 40 °C, initial pH of 8, pH lower limit (contolled by addition of NaOH 30 % w/w solution) and load of the ferrmentor 1.2 kg/kg (volatile solids in substrate/volatile solids in inoculum).

Total biogas and methane volumetric yield was calculated from measured biogas composition and flowrate. Then, by comparison of measured and theoretical values it was possible to calculate biological efficiency η. This is the ratio of experimental methane yield to theoretical one (Sobotka et al., 1983):

$$\eta = \frac{Y_{CH4\,\mathrm{exp}}}{Y_{CH4theor}} \tag{3}$$

3. Results

3.1 Disintegration Experiments

Disintegration process characteristics (mainly e_{dis}) are useful for estimation of suitable disintegration process parameters. However, it is not possible to determine the overall biogas production increase from their results. Experiments were aimed mainly at determination of optimal specific power in the ultrasonic chamber P_V. First set of experiments was done with whole pieces of maize silage diluted with water to TS of 8 %. The results showed very little effect of ultrasonic treatment on the disintegration of maize silage. Even with high intensity of ultrasound I over 55 W/cm^2 and P_V over 1000 kW/m^3 the feasible value of *DD* was in average only 3.1 %. The explanation is to be found in the principle of cavitation: this phenomenon occurs only in liquid phase and because the pieces of maize silage are relatively big (and thus have small specific area where the liquid phase is in contact with the solid one) the sonication is less efficient.

Therefore, it was decided to introduce mechanical pre-disintegration step. For another set of experiments the substrate had been pre-disintegrated by a kitchen mixer with nominal power of 400 W and consequently sonicated. The feasible *DD* was approximately 8 %. From the dependence of e_{dis} and *DD* on P_V it was derived that increase of specific power over 250 kW/m^3 does not further induce significant improvement of disintegration effect. Therefore, for other experiemnts the P_V value of approximately 250 kW/m^3 was set. It is necessary to emphasize that this value could be recommended only for our system of substrate and ultrasonic device.

3.2 Fermentation experiments and energy balance

Results of fermentation experiments proved significant acceleration of the AD process. Time course of methane yield Y_{CH4} is presented in Fig. 1. For batch with US treatment, the production ceases after approximately 300 hours and further, the biogas gain is negligible – organic substrate was already biodegraded. In the untreated batch a slight increase is still visible even at the end of the fermentation

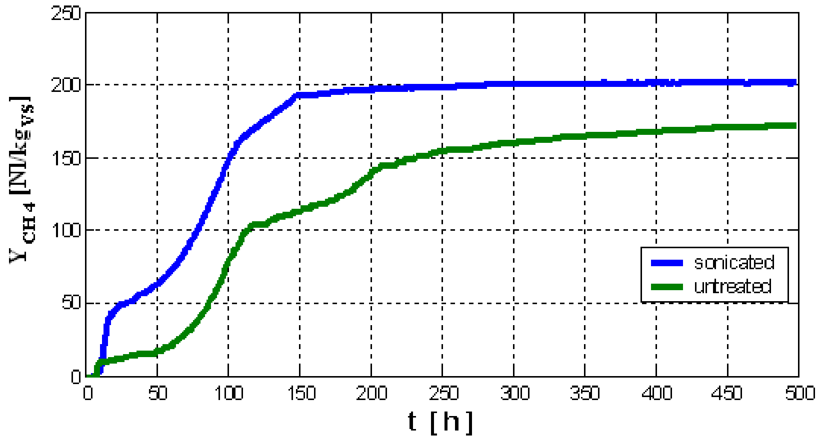

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Figure 1: Methane yield

Also the time course of methane volumetric fraction proved the acceleration of hydrolysis phase by the ultrasound – in the fermentor with substrate exposed to US the methane volumetric fraction was about 36 % at the fermentation time of 15 h, while in the fermentor without US treatment it was approximately 17 % only. Disintegration transformed various organic compounds into simpler ones that were easily digestible for microorganisms of all phases of anaerobic digestion.

Tab. 1 presents a summary of successful fermentation experiments

The average values of biogas and methane yield for untreated maize silage are approx. 400 Nl/kg_{VS} of biogas and 180 Nl/kg_{VS} of CH_4. Increase of biogas yield due to ultrasonic treatment of biomass is in the range of 13-29.5 % and the CH_4 yield increase is in the range of 16.9-29.5 %. These results should be considered valid only for our experimental system: due to biological nature of the process these numbers may vary in different conditions as well as suitable disintegration parameters .

The ultrasonic treatment enhances the yield of biogas but it also consumes energy for disintegration. Therefore, an energy balance was performed. The estimation of disintegration energy was based on disintegration experiments Assumed methane yield was 180 Nm^3/kg_{VS}. We suppose production of electricity in CHP unit with electrical efficiency $\eta_{el.}$ of 35 %, heating value of methane ΔH_{comb} 35.8 MJ/Nm^3 and increase of Y_{CH4} by US treament of 30 %. In such case, resulting electric energy balance value of approximately 467 kJ/kg_{VS} was determined and should be perceived as the key number for assessment of ultrasonic treatment feasibility. The amount of electrical energy generated from untreated substrate is approximately $E_{el} = Y_{CH4}.\Delta H_{comb}.\eta_{el}$ =2255 kJ/kg_{VS}. Therefore, it might be expected that the electricity production of biogas plant would rise by approximately 20.7 % (467/2130), which is iteresting from both environmental and economical view point.

Table 1: Summary of pilot scale experiments with maize silage.

M mechanical pretreatment, US...sonication of the whole substrate, N...no treatment.

Experiment No.	I		II		III	
Fermentor	A	B	A	B	A	B
Disintegration method	M, US	M	M, US	N	M, US	N
Specific power P_V [kW/m^3]	238.2	—	275.3	—	252.8	—
Power P [W]	141.3	—	250.3	—	202.3	—
Intensity I [W/cm^2]	49.9	—	88.4	—	71.3	—
Degree of disintegration DD [%]	4.09	N/A	4.67	—	4.01	—
Biogas yield Y_{BG}[Nl/kg_{VS}]	526.6	452.1	392.4	347.4	529.4	408.9
Methane yield Y_{CH4}[Nl/kg_{VS}]	201.2	172.1	168.4	143.9	286.2	221.0
Theor. CH_4 yield Y_{CH4_theor} [Nl/kgVS]	318		318		468	
Biological efficiency η [%]	63.3	54.1	53.0	45.3	61.2	47.2
Increase of biogas yield [%]	16.5		13.0		29.5	
Increase of methane yield [%]	16.9		17.0		29.5	

4. Conclusions

Convenient parameters of disintegration process can be roughly estimated by measurements of COD increase in supernatant of samples before and after treatment. Values of both degree of disintegration *DD* and specific disintegration energy e_{dis} were taken as representative (see Eq. 1 and Eq.2 for definition). Results of sets of experiments with ultrasonic treatment and combined mechanical and ultrasonic treatment of maize silage samples proved that the latter mentioned combined method of substrate treatment is more efficient. In case of mechanically pretreated samples, these values of ultrasound were identified as suitable for given system of ultrasonic device and substrate: low frequency of 20 kHz (Tiehm et al., 2001), I > 40 $W \cdot m^{-2}$ and $P_V \approx 250$ $W \cdot m^{-3}$. With these parameters of sonication and treatment time of 25 s, values of feasible *DD* are approximately 8%.

Effect of substrate treatment on biogas production was studied in two simultaneously operated batch fermentors *Bioengineering 75L*. Disintegrated maize silage was used for cultivation in one digester while in the other control sample was fermented. Both reactors were operated at mesophilic temperature of 40°C and pH value was kept higher than 6.5. Biogas and methane yields were determined from continuous measurement of biogas flow and periodic measurement of biogas composition. Cultivation time was set to approximately 500 hours. Observed biogas yield increase was 13 – 29.5% and methane yield enhancement reached 16.9 – 29.5%. Positive electric energy balance of the process was calculated according to experimental results, proving the feasibility of the treatment process

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