Biogas Production Enhancement by Ultrasonic Disintegration of Biomass

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Abstract

Cílem práce je prokázaní pozitivního vlivu ultrazvukové dezintegrace biomasy na navýšení a urychlení produkce bioplynu ve srovnání s konvečními systémy. Aplikací ultrazvukových vln dochází k buněčné lyzi, zvětšení specifického povrchu částic substrátu a k sonochemickému rozštěpení složitých organických látek obsažených v biomase (tuků, bílkovin, polysacharidů) na látky jednodušši. Výsledkem je pak účinnější a rychlejší přeměna biomasy na bioplyn. Pro posouzení vlivu sonikace na proces anaerobní digesce byly prováděny paralelní fermentační experimenty v CSTR bioreaktorech BIOENGINEERING 75l, efektivita samotného dezintegračního procesu pak byla posuzována na základě měření nárůstu $CHSK_{Cr}$ *v kapalné fázi vzorků používaného substrátu (v našem případě kukuřičné siláže). Na závěr bylo provedeno zjednodušené zhodnocení procesu z energetického hlediska.*

Key words

biogas; ultrasonic disintegration of biomass; anaerobic digestion;

1. Introduction

In the 20^{th} century, together with the increase of humankind energy demand and fears from possible exhaustion of its "conventional" resources (oil, coal, uranium etc.), a search for the so-called renewable sources of energy started. One of them was identified in biomass, which could be used generally in three different energy-producing ways: i) burning, producing directly heat ii) alcoholic fermentation, producing ethanol for burning and iii) anaerobic digestion producing biogas for burning. The last mentioned way is very attractive due to the form of energy source it provides: after some modifications of biogas (cleaning, drying etc.) we may obtain the so-called Substitute Natural Gas (SNG) with guaranteed composition and properties.

The main disadvantage of anaerobic digestion may be found in relatively slow degradation rate of the biomass. In conventional digesters, the residence time is typically about 3 weeks and more (depending on the digester type, fermentation temperature etc.), resulting in necessity of large bioreactors' volumes. To improve the biodegrability of input substrate, various pre-treatment methods were tested: thermal treatment, addition of enzymes, ozonation, mechanical disintegration etc. Most of them brought undoubtedly positive effects on biogas production, but usually were found unsuitable for application in industrial scale due to high operating and investment costs (Anders, 2005, Climent, 2007).

One of the possible methods is also ultrasonic treatment of biomass. Cavitation, which occurs during the sonication, causes large shear stresses leading 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 and increase of specific area of substrate particles (Straka, 2006), making thus the biodegradation of biomass faster and more effective.

2. Theoretical background of Anaerobic Digestion and Sonication of Biomass

2.1. Biochemical Principles of Biogas Formation

The process of biological transformation of organic matter into methane and carbon dioxide in the absence of oxygen is called anaerobic digestion. Its main features in macro scale are production of biogas as a possible source of energy, volume and mass reduction of input material which makes it very attractive and often used in the field of sustainable energetics and waste water treatment. It is a highly complex and complicated process: anaerobic digestion is a series of consequent biochemical sub-processes, which are performed by various microorganisms' groups cooperating in symbiosis. Even nowadays, this biochemical path is still not described in detail. In general, it could be divided into four stages (see Fig. 1 for a schematic depiction):

1) Hydrolysis – the first phase of the process and according to microbiologists' research results (Malina, 1992, Boone, 1993) the most time demanding one. During this phase, biomass macromolecules (proteins, polysaccharides and lipids) are split into simpler compounds (saccharides, amino acids, fatty acids and their oligomers) by extracellular hydrolytic enzymes produced by hydrolytic bacteria and then dissolved into solution.
2) Acidogenesis - further breakdown of the remaining components by acidogenic (fermentative) bacteria. These produce volatile fatty acids along with alcohols, carbon dioxide, hydrogen and other by-products. This phase is accompanied by decrease of pH due to production of acids and protonic acidification. If the reactor is overloaded, low pH value may inhibit the process.
3) Acetogenesis – acetic acid, hydrogen and carbon dioxide production from compounds formed in previous phases.
4) Methanogenesis – during this terminal stage, products of the preceding phases are converted into methane, carbon dioxide and water by methanogens. These bacteria are sensitive to low as well as to high pH, which must be kept within a range of 6.5 - 8. Depending on the microorganism species, three components are used to produce methane: i) mixture of CO_2 and H_2 ii) acetic acid CH_3COOH and iii) methanol CH_3OH.

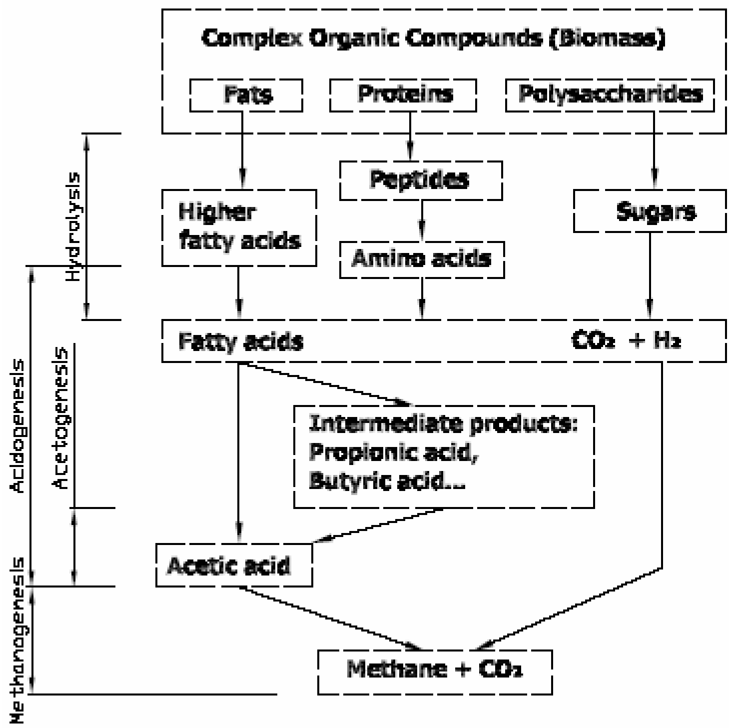


Figure 1: *Biochemical scheme of biogas production from biomass. Each arrow represents a microbiologically driven transformation (Straka, 2006).*

The biological nature of the process further more complicates its application: microorganisms are very sensitive to temperature and pH. Also, presence of biotoxic substances like antibiotics, biocides and disinfectants in the substrate may lead to a functionality failure of a biogas plant. Anaerobic digestion of substrates with high content of nitrogen N and sulfur S (both elements are contained in proteins' chains) is complicated due to formation of ammonia NH_3 and hydrogen sulphide H_2S. Therefore, such substrates are mixed with ones with low protein content (usually of vegetable origin) to keep a ratio of C:N within an optimal range of 25:1 – 30:1.

2.2. Mass-Energy Balance of the Process

The stoichiometry of anaerobic digestion is described by the following formula (Buswell, 1979):

$$C_nH_aO_b + (n - a/4 - b/2)H_2O \rightarrow (n/2 - a/8 + b/4)CO_2 + (n/2 + a/8 - b/4)CH_4 \qquad (1)$$

However, this formula does not include the influence of chemically bound nitrogen. Therefore, another approach described in (Minkevich, 1973) was applied to anaerobic digestion in (Sobotka, 1983). Basic mass balance was supplemented by ion balance. The ions act as donors or acceptors of free electrons in redox reactions. C, H, P and Fe are the donors of 4, 1, 5 and 3 electrons, respectively, whereas O, N, and S are the acceptors of 2, 3 and 2 free electrons, respectively. The electron balance of the redox conversion of a substrate with a general formula $C_nH_aO_bN_z$ (other elements are usually negligible in case of organic materials) is then described by the expression 4n + 1a - 2b - 3z which, referred to 1 C atom, represents the so-called degree of reducibility of a substrate γ.

$$\gamma = 4 + a/n - 2b/n - 3z/n \qquad (2)$$

This variable is an equivalent of available electrons in the organic material per atom of C. The maximum of degree of reducibility is $\gamma_{CH4}=8$ and minimum $\gamma_{CO2}=0$. The degrees of reducibility of all organic substrates γ_{sub} are within the range given by these two limits and are very important - the higher this value the higher energy could be obtained from the substrate. To determine a formula in form of $C_nH_aO_bN_z$, the elementary analysis must be carried out.

2.3. Sonication of Biomass

The most time demanding phase of the complex process of anaerobic digestion is the hydrolysis (Malina 1992, Boone 1993), during which the organic macromolecules are degraded to simpler substances extracellulary by hydrolytic bacteria and their enzymes. The ultrasonic treatment of biomass provides similar results from the chemical point of view. Its main advantage is significant decrease of time of the breakdown of macromolecules and consequent reduction of residence time in the digester. Also, the accessibility of nutrients in the substrate increases, resulting in more effective conversion into biogas of them and consequent overall increase of production. On the other hand, an additional amount of energy needed for this operation has to be taken into account. It should be emphasized that the positive energy balance is the key condition of the treatment feasibility.

The acting of ultrasound on heterogeneous mixtures of particles (in our case pieces of biomass) and liquid (water and dissolved organic substances) has two effects: i) mechanical disintegration and ii) sonochemical reactions.

Both of them are caused by a phenomenon called cavitation, which is defined as the formation of vapor bubbles of a liquid in an area where the pressure of the liquid falls below its vapor pressure and following implosive collapse of bubbles when the pressure increases again.

These pressure jumps are caused by ultrasonic waves. Bubble collapse in liquids results in a significant concentration of energy from the conversion of the kinetic energy of liquid motion into heating of the contents of the bubble (see Fig. 2). High local temperatures and pressures combined with extraordinarily rapid cooling cause enormous shear stresses in bulk liquid, which mechanically destroy cells' walls and decrease size of particles contained in the liquid. Cavitation collapse produces local heating (up to temperature of ~5000 K), high pressures (~1000 atm.) and liquid jet streams (~400 $km \cdot h^{-1}$). (Suslick, 1999). But as stated before, not only mechanical effects are observed: inside the bubbles, the water vapor molecules are splitted into radicals that chemically react with substances dissolved in the liquid on the liquid-gas interface (Parsons, 2004).
Disintegration of cellular structures is most significant at low frequencies, because the bubble radius is inversely proportional to the frequency and large bubbles mean strong shear forces (Tiehm, 2001). Therefore, the ultrasound frequency of 20 kHz is considered the most appropriate.
Other parameters of ultrasonic treatment are mainly:

1) Intensity I [$W \cdot m^{-2}$] – energy flux per unit of emitting area. The cavitation threshold value for water is approximately 40 $W \cdot cm^{-2}$ (Thiem, 2001).
2) Treatment time t [s]
3) Power P [W] –energy consumed during sonication per unit of time.
4) Specific US power P_V [$W \cdot m^{-3}$] – Power input per unit of sonicated volume.

Due to specific properties of every substrate-ultrasound generator system it is necessary to determine the sonication parameters experimentally.

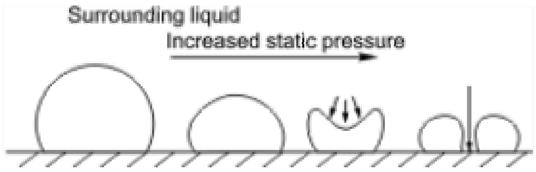


Figure 2: *Cavitation and its effect on a fixed surface (http://en.wikipedia.org/wiki/Cavitation, 28/7/2008)*

3. Experimental Materials and Methods

3.1. Inoculum and Substrate

Inoculum (seeding sludge) contains a mixed microbial culture. In our case, it was taken from two sources, depending on the substrate to be fermented: i) from a biogas plant (Kněžice) in a form of fermenting sludge and ii) from the waste water treatment facility (Česká Lípa) in form of digested sludge from the anaerobic stabilization tank. Both facilities operate at mesophilic temperatures, so that during the fermentation experiments the temperature was maintained at 40 - 41˚C.
To eliminate the influence of endogenous production of biogas (due to residual organic material contained in the sludge), the inoculum was stored for 24 hours at optimal temperature under anaerobic conditions.
Various substrates were used for the anaerobic digestion batch experiments. Maize silage has the best C: N ratio and also the highest value of degree of reducibility (see Table 1). This makes it the most convenient substrate for anaerobic digestion from the group of investigated materials. The other materials were fermented as well, but usually the inhibition of bioprocess was observed due to elevated nitrogen content, mainly in case of poultry manure. Therefore, the maize silage only was used in further work.

Table 1: *Characteristics of substrates used for the experiments.*

Substrate	Formula	C:N ratio	γ [-]
Poultry Slurry	$CH_{1.685}O_{1.262}N_{0.083}$	11.98	2.91
Poultry Manure	$CH_{1.872}O_{1.208}N_{0.162}$	6.17	2.97
Grass	$CH_{1.780}O_{0.915}N_{0.068}$	14.72	3.75
Mixture: P. manure+ Grass	$CH_{1.793}O_{0.956}N_{0.081}$	12.35	3.64
Maize Silage	$CH_{2.172}O_{1.157}N_{0.034}$	29.00	3.76

3.2. Experimental Design – Sonication

The solution with biomass particles is pumped into a glass continuous flow process cuvette with maximum volumetric flow of 30 l/hr, where it is exposed to the ultrasonic waves. The ultrasound is generated by US generator SONOPLUS 3400 of maximal power 400W at frequency of 20 kHz (see Fig. 3). Both the cuvette and the generator are products of Bandelin Co.

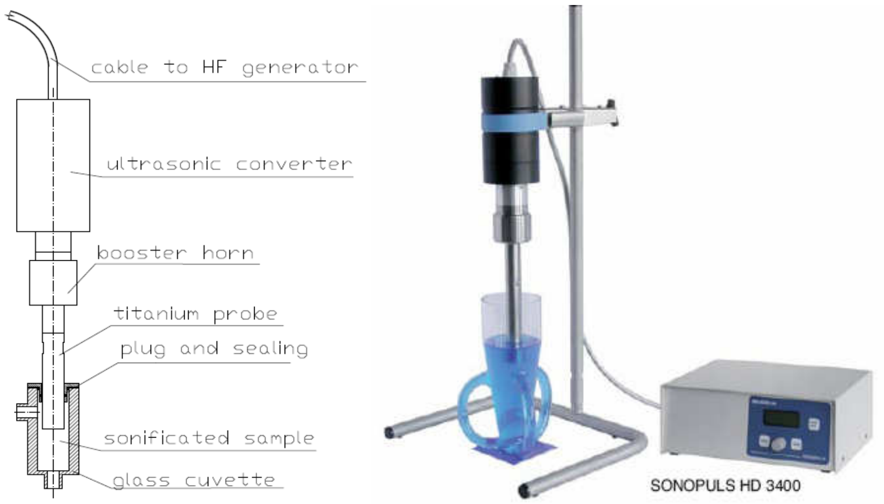


Figure 3:*Depiction of ultrasound generator and description of its parts.*

This procedure is applicable for substrates which do not contain larger pieces of solids. Biomass of vegetable origin (grass, maize silage etc.) is usually formed by fibres that complicate the pumping at the laboratory scale mainly, where the diameters of piping are very small (in our case the inner diameter of rubber tubes is 8 mm) and the pipelines get stuck. Therefore, the substrate was mixed with water to reach the dry-weight content of 8% and then mechanically pre-disintegrated by a mixer. The liquid phase of the mixture was separated (dry-weight content of approximately 5%) and then disintegrated by ultrasound.

Above mentioned problem with pumping should disappear in larger scale, where the pipeline diameter is much greater. On the other hand, the pre-disintegration by mechanical means could also improve the disintegration effect of ultrasonic treatment because larger pieces of biomass are not disintegrated by ultrasound (cavitation takes place only on their surfaces). The mechanical pre-disintegration consumes energy, which must be included in energy balance of the process.

The quantitative evaluation of disintegration is based on the idea that there is a direct relation 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 Chemical Oxygen

Demand *COD* measurements. Degree of disintegration *DD* is then defined as a ratio of increase of dissolved organic matter in liquid phase released into solution by disintegration process to total organic matter in the substrate. Following relation holds (Straka, 2006):

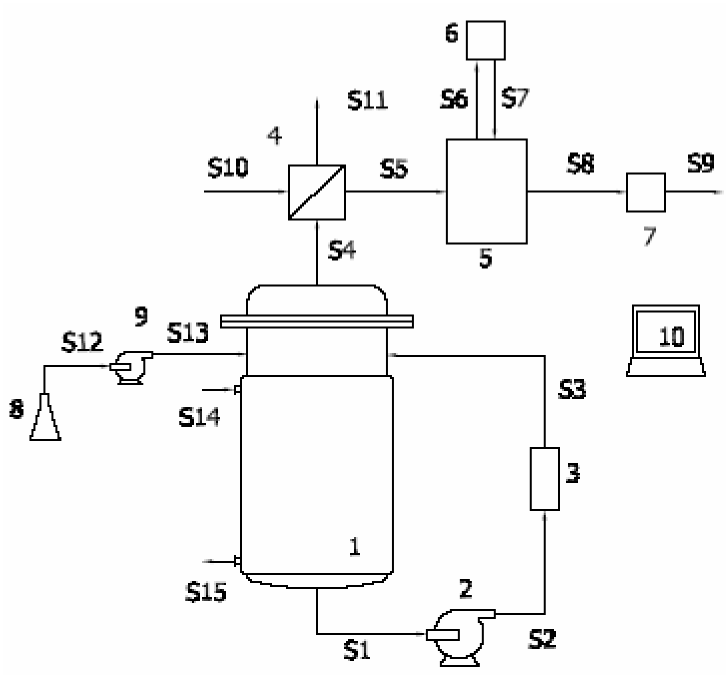
$$DD = \frac{COD_{dis\ (liq)} - COD_{0\ (liq)}}{COD_{0\ (\mathrm{hom})} - COD_{0\ (liq)}} \tag{3}$$

To determine the COD in the liquid phase, the samples are centrifuged at 7000 r/min for 5 minutes at centrifuge Hettich Zentrifugen UNIVERSAL 320R.
Evaluation of disintegration would be incomplete without consideration of its energy demand. Therefore, specific disintegration energy e_{dis} (amount of disintegration energy per increase of DD by 1% and per kg of solids in the material) was defined as follows:

$$e_{dis} = \frac{E}{DD \cdot m_{sol}} \tag{4}$$

3.3. Experimental Design – Fermentation

The fermentation experimental facility consists of two fermentation units to carry out parallel experiments. These are necessary in order to minimize the differences not-caused by ultrasonic treatment (e.g. changeable composition of inoculum and substrate). The *Bioengineering 75 L* CSTR bioreactors were utilized, sensors for quantitative measurements were inserted, digital biogas monitoring subsystem was designed and implemented and ultrasound device for batch treatment installed. Both of the fermentors were equipped with precise gas flow meters Ritter TG01. For measurement of biogas composition, a gas analyzer Aseko AIR LF was used. A schematic depiction of the fermentation unit supplemented by the US loop for substrate sonication is in the Fig. 2.



Units	
1	Fermentor
2	Pump
3	Ultrasound generator
4	Condenser
5	Vessel for BG accumulation
6	Gas analyzer
7	Gas flow meter
8	NaOH solution supply
9	Dosing pump
10	Monitoring, process control

Streams-Piping	
S1, S2	Untreated substrate
S3	Sonicated substrate
S4	Moist biogas
S5 - S9	Dry biogas
S10, S11	Cooling water
S12, S13	NaOH solution
S14, S15	Hot water

Figure 4: *Scheme of the experimental facility, description of units and streams*

The main part of the bioreactor is a cylindrical vessel with hemispherical bottom, made from stainless steel. The vessel with maximum working volume of 50 liters is equipped by various slots in the shell, designed for pH electrode, thermometer and other measuring probes. Jacketed kettle is used to heat up the batch which is necessary to keep the temperature in the optimal range of mesophilic microorganisms. The agitation system consists of an electro motor (nominal power input 0.55 kW), transmission and a shaft with three impellers. Two of them are normalized Rushton turbines, i.e. the impellers of radial type; the upper one is not-normalized Ruax impeller of axial type, which was installed to prevent problems with formation of the flotation layer.
The anaerobic fermentation of real substrates is highly complex bioprocess: both the substrate and inoculum compositions are usually not precisely known, the process is carried out by a microbial consortium with many metabolic characteristics. This fact makes the implementation of a monitoring system and process control very important. In our case, these variables are monitored:

- pressure, pH and temperature in the fermentors
- pressure, temperature and relative humidity of moist and dry biogas
- dry biogas volumetric flow rate and composition.

The composition of biogas was measured periodically by the gas analyzer with minimal input gas flow rate of 0.5 liters/min. This demand is not possible to fulfill during all phases of the bioprocess, because at the beginning and at the end the biogas production is too low. Therefore, the biogas was accumulated in an auxiliary vessel of volume of approximately 25 liters. From this vessel the gas is pumped continuously into the analyzer and then returned back. The immediate composition of biogas is thus slightly distorted at low flow rates (at high flow rates the content of the auxiliary vessel is refreshed quickly), but due to relatively slow dynamics of the process this imprecision is negligible. The analyzer is able to determine volumetric fractions of four most important gases in biogas: CH_4, CO_2, O_2 and H_2S. The content of first two gases is evaluated by IR method, for O_2 and H_2S electrochemical sensors are implemented. One analyzing unit was used for both parallel experiments, so the switching of channels was driven by the monitoring system. The H_2S assay consumes the chemical sensor of the analyzer, so this value was measured once per 6 hours only.
Total biogas and methane volumetric yield could be calculated from experimental data by numerical integration or by simple summation:

$$\begin{aligned} V_{biogas} &= \int \dot{V}\, dt \doteq \sum_i \dot{V}_i\, \Delta t_i \\ V_{CH4} &= \int \dot{V}\, x_{CH4}\, dt \doteq \sum_i \dot{V}_i\, x_{CH4\,i} \Delta t_i \end{aligned} \tag{5}$$

4. Experimantal Results

4.1. Disintegration Experiments

From the point of view of financial and time demand, disintegration experiments are more favorable than fermentation batch tests. Disintegration process characteristics (mainly specific disintegration energy e_{dis}) are useful for determination of suitable disintegration process parameters. However, it is not possible to determine the overall biogas production increase from their results, which only illustrate the suitability of disintegration method for given substrate.
Disintegration experiments were performed with all the substrates mentioned in Tab. 2. However, successful fermentations were carried out with maize silage only because for all other substrates inhibition by ammonia was observed. Therefore, only maize silage disintegration is described.

These tests were aimed mainly at determination of optimal specific power in the ultrasonic chamber P_V. This characteristics is very important also from the economical point of view: the larger the treated volume, the shorter the overall treatment time (the volumetric flow rate increases, keeping the residence time in the process cuvette constant) and consequently also lower sonication energy.
First set of experiments was done with whole pieces of maize silage. The results show very little effect of ultrasonic treatment on the disintegration of maize silage (see Tab.2). The peak value of *DD* is 5.7 %, but should be considered an error of measurement more than an optimal point of disintegration – the feasible value of *DD* is lower than 4%. The explanation could 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 before exposing the biomass to the ultrasonic waves. This procedure would also solve problems with pumping mentioned above.

Table 2: *Ultrasound parameters and results of sonication with maize silage, sonication time 20 s.*

V_{sample} [ml]	E [kJ]	P [W]	P_V [kW/m^3]	I [W/cm^2]	DD [%]	e_{dis} [kJ/(%DD kg$_{TS}$)]
44.6	3.23	161.3	3616.6	56.9	3.2	284.2
87.1	3.26	162.9	1870.0	57.5	2.8	165.9
130.9	3.35	167.65	1280.7	59.1	3.1	103.6
200.0	3.24	162.1	810.5	57.2	5.7	35.4
300.7	3.37	168.45	560.2	59.4	3.7	37.6
511.9	3.37	168.25	328.7	59.3	2.5	33.5
628.0	3.39	169.4	269.7	59.7	3.4	20.0
822.8	3.31	165.55	201.2	58.4	2.6	19.1
1650.0	3.40	169.95	103.0	59.9	3.9	6.6

For another set of experiments the substrate had been pre-disintegrated mechanically first (by a kitchen mixer of nominal power of 400 W) and consequently the liquid phase only (with dry-weight content of 4.73% was sonicated. Results are in the Tab.3 and Fig.5. The feasible *DD* is approximately 8 % and further increase of specific power P_V does not induce significant improvement of disintegration effect. The value of approximately 250 kW/m^3 is the most convenient one from the energetic point of view, because the specific energy of disintegration e_{dis} is very low.
Once again, it is necessary to emphasize that these values could be recommended only for a system of given substrate and ultrasonic device and should be determined experimentally for different conditions.

Table 3: *Ultrasound parameters and results of sonication with maize silage extract, treatment time 25 s.*

V_{sample} [ml]	E [kJ]	P [W]	P_V [kW/m^3]	I [W/cm^2]	DD [%]	e_{dis} [kJ/(%DD kg$_{TS}$)]
44.6	3.60	144.1	3231.4	50.8	8.4	202.2
87.1	3.51	140.5	1613.1	49.6	8.7	97.8
130.9	3.62	144.6	1104.7	51.0	8.2	71.4
200.0	3.55	142.1	710.4	50.1	7.9	47.5
300.7	3.53	141.2	469.4	49.8	7.1	35.0
511.9	3.53	141.1	275.7	49.8	6.3	23.1
822.0	3.59	143.5	174.5	49.8	2.0	45.3

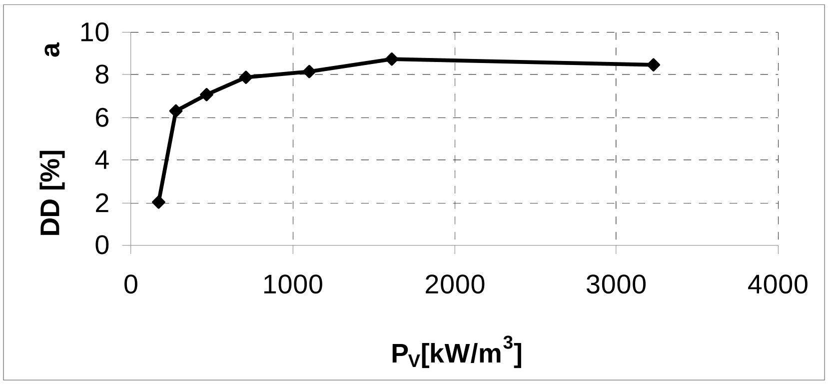


Figure 5: *Degree of disintegration DD with dependence on the specific power in the ultrasonic chamber P_V.*

4.2. Fermentation experiments

Parallel batch fermentation experiments with various substrates were carried out to evaluate the effect of biomass ultrasonic disintegration on biogas production. Nevertheless, with all examined substrates except maize silage inhibition of the process by ammonia NH_3 was observed and so this only substrate was chosen for further research.

First of all, it was necessary to determine maximum load of the reactor. If there is too much organic material in the fermentor, acetogenous microorganisms generate a high amount of fatty acids which induces an abrupt decrease of pH, resulting in the inhibition of methanogens – batch buffering capacity is too low. This fact was visible from the time course of the first set of experiments: no CH_4 production was observed, although in early phases of the anaerobic digestion the CO_2 volumetric fraction reached almost 97% and pH value was approximately 3.5.

Therefore, the maximum load was determined by tests in laboratory scale prior to use larger fermentor volumes. According to the results of these tests the load ratio of the fermentor was set to 20 : 1 in terms of total mass (ratio of maize silage to the inoculum in form of a fermenting sludge from the waste water treatment facility) which equals to 1.2 : 1 in terms of volatile solids. Also, a system of automatic pH control was installed: in case of its decrease under 6.5 a dosis of 30% NaOH solution was automatically pumped into the bioreactor.

After determination of the maximum bioreactor load the parallel batch experiments were carried out. The cultivation conditions are summarized in Tab. 4, Fig 6,7 & 8 present results of one of the successful fermentation experiments.

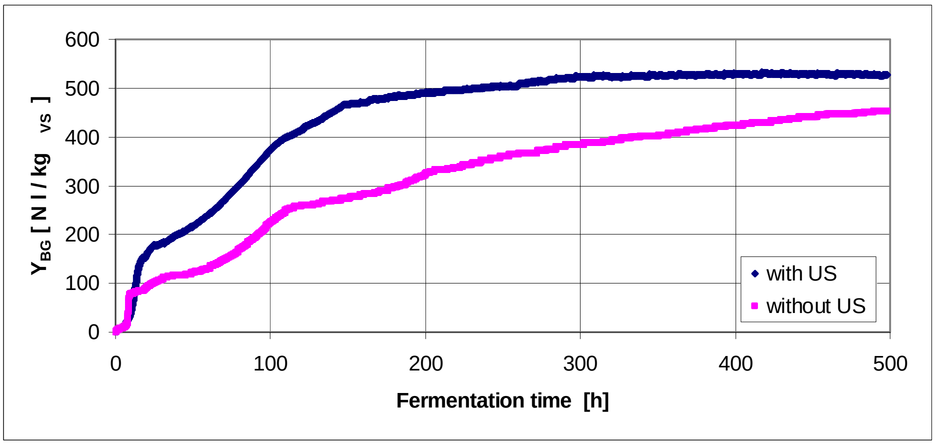


Figure 6: **Biogas yield**

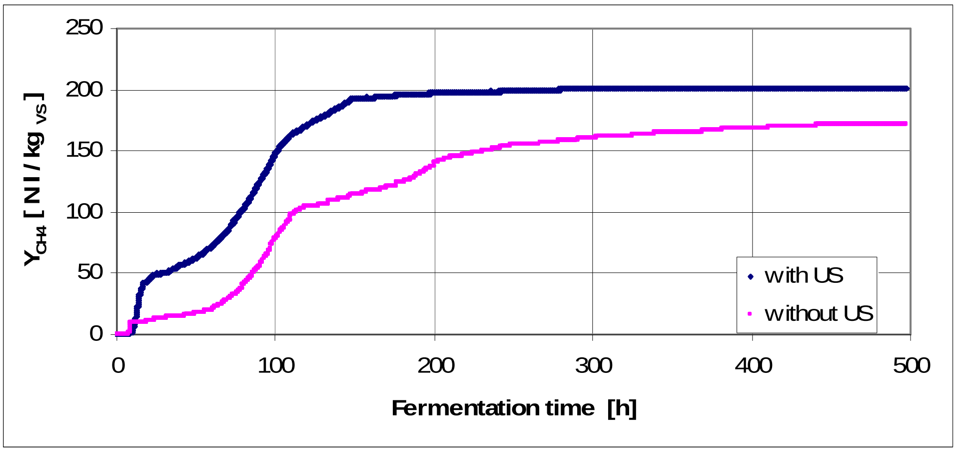


***Figure 7**: Methane yield*

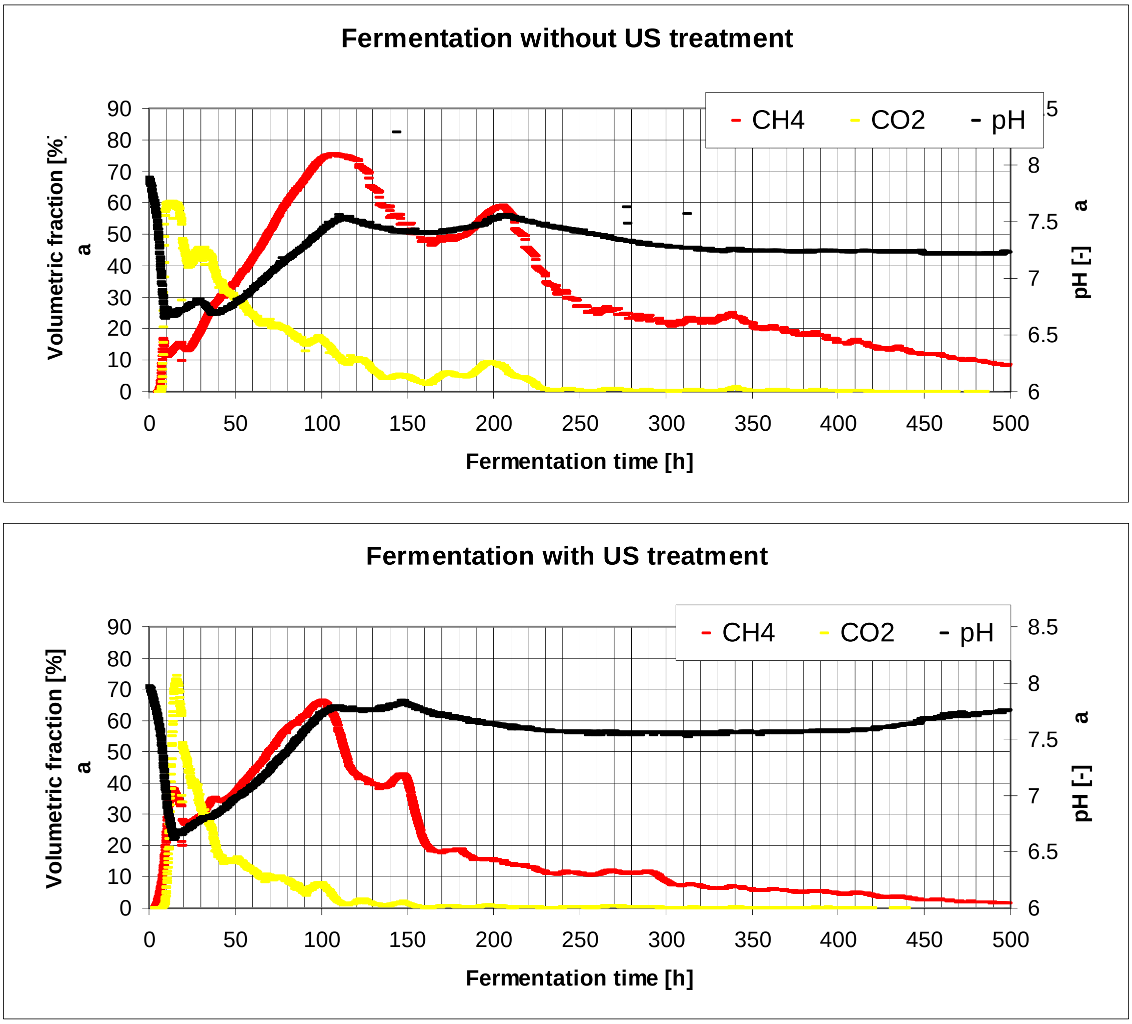


***Figure 8:** Time courses of biogas composition and pH.*

The time course of methane volumetric fraction proves the acceleration of hydrolysis phase by the ultrasound – in the fermentor with biomass liquid phase exposed to US the methane volumetric fraction is about 36% at the fermentation time of 15 hours, while in the fermentor without US treatment it is approximately 17% only (see Fig. 8). It shows the disintegration transformed various organic compounds into simpler ones that are easily digestible for microorganisms of all phases of anaerobic digestion. Following composition time course also implies this assumption: the maximum value of methane fraction is slightly lower for batch with US treated biomass, which is caused by the fact that a significant part of nutrients was transformed into methane already at the beginning of the fermentation, while in the untreated batch there is a lot of digestible substrate still present.

For batch with US treatment, the production ceases after approximately 300 hours and further, the biogas gain is negligible (Fig. 6 and Fig. 7) – all the organic substrate is already biodegraded. On the other hand, in the untreated batch a slight increase is still visible even at the end of the fermentation (i.e. after approximately 3 weeks).

Another interesting effect of sonication on the anaerobic digestion process is visible from the pH time course. In case of fermentation without US treatment, pH decreased almost to reach the critical value 6.5 (below which the conditions become inconvenient or even lethal for the methanogenous bacteria) and did not increase until approximately 45 hours of fermentation time. Slow biological conversion of higher fatty acids into simpler fatty acids and acetic acid, which are (together with hydrogen) transformed into methane during the final stage of anaerobic digestion process, could have lead to inhibition of methanogenous bacteria if the pH control system had not been implemented. pH value also decreased during fermentation with substrate US treatment, but its reverse increase was very fast: the simpler compounds were transformed into methane much faster (also proved by significantly higher CH_4 volumetric fraction mainly during the initial phases of the process), thus preventing an abrupt drop of pH. This should be mentioned as a very interesting conclusion: the US treatment of the biomass could have positive effect not only on the improvement of the biogas yield, but may also improve the stability of the process.

Following table presents a summary of both successful fermentation experiments carried out in parallel in fermentors of type BIOENGINEERING 75l. According to the working volume of the facility, these experiments should be considered as pilot scale tests.

Table 4: *Summary of successful pilot scale experiments with maize silage.*
Legend: M…mechanical pretreatment, US-L…ultrasonication of liquid phase, N…no tretment.

Experiment No.	I		II	
Disintegration method	M, US-L	M	M, US-L	N
US treatment parameters				
Frequency [kHz]	20	—	20	—
Treatment time [s]	40	—	2x20	—
Processing time [min]	54	—	55.1	—
Dissipated energy [kJ]	457.8	—	827.5	—
Power [W]	141.3	—	250.3	—
Intensity [W/cm^2]	49.9	—	88.4	—
Results of disintegration				
Mechanical pretreatment energy consumption [kJ]	40	40	40	—
Degree of disintegration [%]	4.09	N/A	4.67	—
Specific disintegration energy [kJ/(%DD kg$_{VS}$)]	206.1	N/A	294.0	—
Fermentation experiments results				
Biogas yield [Nl/kg$_{VS}$]	526.6	452.1	448.9	401.3
Methane yield [Nl/kg$_{VS}$]	201.2	172.1	188.4	148.3
Maximum methane volumetric fraction [%]	66.3	75.4	78	78.2
Increase of biogas yield [%]	16.5		11.9	
Increase of methane yield [%]	16.9		27	

Unfortunately, other experiments were unsuccessful because of problems with leakage in case of one of the reactors.
The average values of biogas and methane yield for untreated maize silage are approximately 427 Nl/kg_{VS} of biogas and 160 Nl/kg_{VS} of methane. The average increase of biogas and methane yield by ultrasonic treatment of biomass is 14.2 %/ 22.0 %, respectively. However, these results should be still considered valid only for our experimental system: due to biotechnological nature of the process these numbers may vary in different conditions. Also, the optimization of US treatment parameters must be done for given geometry, substrate and US generator. The estimated increase of both biogas and methane productions in case of long-term application in industrial scale is 15-20%.

5. Energy Balance

As was stated in previous section, the ultrasonic treatment enhances the yield of biogas. On the other hand, it also consumes additional energy. Therefore, an energy balance must be performed to assess the process.
Increase of electrical energy could be calculated as follows:

$$\Delta E_{el} = (\delta \cdot Y_{CH4}) \cdot \Delta H_{comb} \cdot \eta_{turb} \qquad (6)$$

The estimation of disintegration energy is based on disintegration experiments carried out with maize silage : feasible value of *DD* was set to 8% and the specific disintegration energy e_{dis} was set to 22 $[J \cdot kg_{VS}^{-1}]$.
Two alternatives were investigated: i) “optimistic” (increase of methane production by 20%, lower disintegration energy consumption) and ii) “pessimistic” (increase of methane production 12%, higher disintegration energy consumption). Results of the calculation are in the following table.

Table 5: *Electric energy balance of biomass sonication*

Production	**optimistic**	**pessimistic**
CH_4 yield [Nl/kgVS]	160	160
Increase of CH_4 production δ [%]	20	12
Lower heating value [kJ/Nl]	35.8	35.8
Turbine effieciency [%]	35	35
Energy increase $[kJ/kg_{VS}]$	401.5	240.9
Disintegration		
DD [%]	8	8
$e_{dis}[kJ/(\%DD\ kg_{TS})]$	22.0	25.0
Disintegration energy $[kJ/kg_{VS}]$	176	200
Additional energy (pumping etc.) $[kJ/kg_{VS})]$	30	50
Energy balance $[kJ/kg_{VS}]$	**195.5**	**-9.1**

Although in case of “pessimistic” alternative the overall electric energy balance is negative, we still have to take into account another important fact: heat is considered as a waste, although it is almost always used at least for heating of the content of the bioreactor. Therefore, the overall energy balance would be positive even in this case.

6. Conclusions

The main aim of this project was to verify the validity of the hypothesis of possible biogas yield increase by ultrasonic treatment of biomass. This process has two effects: i) mechanical disintegration ii) sono-chemical conversion of complex organic macromolecules into simpler ones. Both of them are caused by cavitation, during which extremely high shear stresses are generated as a result of bubble implosions.

Disintegration

The quantitative evaluation of the disintegration process was implemented, based on measurements of COD increase in the liquid phase of samples. For experiments with maize silage following values were determined: the feasible degree of disintegration DD is 8 %, recommended specific power in ultrasonic chamber P_V is 233 W/m^3. With these parameters, the average specific disintegration energy $e_{dis}$is c. 23 $kJ/(\%DD \cdot kg_{TS})$.

The maize silage disintegration process in industrial scale should consist of two main steps:

1. mechanical pre-disintegration - increase of the specific surface.
2. ultrasonic treatment – disintegration of biomass by cavitation

Parameters of ultrasonic treatment in industrial scale should comply with two basic rules: i) US intensity must be higher than 40 W/cm^2 (threshold of cavitation) and ii) the frequency of ultrasound should be 20 kHz (size of bubbles formed during cavitation is inversely proportional to the frequency and large bubbles mean strong shear forces). The other characteristics should be determined experimentally for given substrate, US generator and geometry.

Fermentation Experiments

Parallel fermentation experiments were carried out to minimize the differences caused by variable biocenose activity, laboratory conditions etc. The facility was successfully assembled and tested in pilot scale in fermentors *Bioengineering 75l*.

After problems with inhibition of bio-process by ammonia due to elevated nitrogen content, the C:N ratio was controlled and kept within a range of 25-30:1. This value should be determined before any anaerobic digestion experiment by means of elementary analysis of the substrate.

Also, pH value monitoring and control system is essential. The minimal pH was set to 6.5 and was controlled automatically by dosing of NaOH solution. During the experiments, another positive effect of US treatment was observed: faster conversion of acids and all simpler compounds into methane prevented the pH value from dropping bellow tolerable value. This should be interpreted as an improvement of bioprocess stability.

Successful parallel batch experiments with maize silage as a substrate and digested sludge from waste water treatment facility used for inoculation were carried out. Average increase of biogas and methane yield was **14.2** and **22.0 %,** respectively. However, it should be emphasized that this value is valid only for given substrate, inoculum, geometry etc. In case of industrial scale, this value could be estimated within a range of 12 to 20 % for both biogas and methane yield increase.

Acknowledgements:

This work was supported by EU project BIOWELL (Increased Renewable Energy Recovery from Biomass by Highly Efficient Disruption Process). Project coordinator CUTEC - Institut GmbH, Germany.

List of symbols

COD	chemical oxygen demand	[$kg \cdot m^{-3}$]
DD	degree of disintegration	[-]
e_{dis}	specific disintegration energy	[$J \cdot kg^{-1}$]
E	energy	[J]
ΔH_{comb}	lower heating value of CH	[$J \cdot m^{-3}$]
I	ultrasound intensity	[$W \cdot m^{-2}$]
m	weight	[kg]
P	power	[W]
P_V	specific power	[$W \cdot m^{-3}$]
t	treatment time	[s]
V	volume	[m^3]
$\dot{V}$	volumetric flow rate	[$m^3 \cdot s^{-1}$]
x	volumetric fraction	[-]
Y	yield	[$m^3 \cdot kg^{-1}$]
γ	degree of reducibility	[-]
δ	coefficient of CH_4 production increase	[-]
η	biological efficiency	[-]
η_{turb}	turbine efficiency	[-]

Indexes

0	untreated sample
el	electric
dis	disintegrated
hom	homogenized
liq	liquid
sol	solid
VS	volatile solids

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