THE STUDY OF EFFECTIVENESS OF DISINTEGRATION OF BIOMASS INTENDED TO METHANE FERMENTATION PROCESS

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Summary

Production of biogas in the methane fermentation process is complicated and requires optimisation, among others, with better use of biomass by bacteria. One of the applied solutions is an introduction to the process of the pre-treatment stage – disintegration, the aim of which is the fragmentation of the substrate's cellular structures before it goes to the digester. The result of the process is the increase of the raw material's susceptibility to biological degradation of the substrate, the increase of speed of the methane fermentation process and efficiency of the obtained biogas. This article presents an overview of the available methods of disintegration, and provides the results of the effectiveness of pre-treatment of biomass of the agricultural origin, conducted with the use of selected chemical, thermal and physical methods.

Key words: disintegration, biomass, biogas

1. Introduction

The definition of biogas is determined by the Directive of the European Parliament and of the Council 2009/28/WE of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC. According to the contents of this document, the biogas is "gas from landfills, sewage treatment plants and from biological sources", "produced from biomass and/or the biodegradable part of waste that can be purified to the level of the natural gas quality, to be used as biofuel".

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In accordance with the definition, biogas is a gaseous product formed during methane fermentation, of organic substances decomposed by microorganisms. After proper cleaning, dependent on the target intended use, it can constitute the fuel for boilers, cogeneration engines, or the substitute of natural gas, e.g. for the transport applications.

The methane fermentation process involves several phases: the hydrolysis, acidogenesis, acetogenesis, and methanogenesis phases. The phase, which determines the speed of anaerobic decomposition is the hydrolytic phase, in which water insoluble organic compounds (e.g.cellulose, protein, fats) are decomposed to their mono- or dimers by bacteria [5]. Due to a variety of substrates used in the process, and their vulnerability to microbial degradation (availability for bacteria), hydrolysis of the raw material can last from a few hours (e.g. carbohydrates), to several days (e.g. proteins, fats). It may also end in the incomplete degradation of the raw material, as in case of substrates containing high amounts of lignocellulose and lignin. The effectiveness of hydrolysis can be increased by the use of appropriate methods of pre-treatment of the substrate (disintegration) that enhances the availability of raw materials resistant to degradation and the biodegradability of organic substances [5].

Disintegration is the process of degradation of the solid phase of biomass through the destruction of their cell structures. The intensity of the process is dependent on the type of the used method, energy inputs and properties of biomass. Destruction of cells results in the increase of susceptibility to biological degradation by increasing the active area of the substrate's particles available for microorganisms, involved in the methane fermentation process and thus intensifying the biogas production.

Depending on the method of conducting the pre-treatment, methods of disintegration can be divided into [23]:

1. mechanical, in which the action of various kinds of shearing forces or changes in pressure are used;
2. non-mechanical:
   - physical (factors influencing the cellular destruction of the substrate is high or low temperature and the treatment with detergents);
   - chemical (including oxidation processes, acid or alkaline hydrolysis);
   - biological (the use of enzymes produced by microorganisms for the hydrolysis of organic compounds).

The effectiveness of disintegration is mostly measured by the change in chemical oxygen demand (COD). This parameter informs about the content of organic compounds in the sample, thus their potential for biogas production, but it does not specify their ability to biological degradation. Degradation of organic compounds to simpler causes the release of these compounds into a liquid and also increase of soluble COD value. The effectiveness of disintegration may also be characterised by other chemical parameters such as the content of phosphate, ammonium and proteins [14]. During the evaluation of the effectiveness of disintegration, the selection of an appropriate method depending on the type of biomass and its susceptibility to biodegradability is particularly significant problem.

Studies on impact of selected disintegration methods to improve efficiency of methane fermentation have been carried out for several years. On the basis of several studies conducted using excess sludge from sewage treatment plants, it was found that the mechanical disintegration process with the use of cavitation causes destruction of active sludge flocks and the destruction of the sorted morphological systems of the germ tube microorganisms [23]. The destruction of bacterial cells of the sludge led to the release of accumulated organic compounds, as shown by the change of parameters: COD, ammonia nitrogen and phosphates in the liquid of disintegrated sludge [23]. This resulted in a 41% increase in biogas efficiency compared to the activated sludge, which is not subject to the cavitation disintegration. Moreover, exposing the excessive sludge to homogenisation improves the efficiency of biogas. The studies conducted by the authors [9] have shown that the sludge subject to the 60 second homogenisation in a laboratory homogeniser, after 48 days of fermentation, showed an increase of the coefficient of the biogas release from 0.07 to 0.14 m^3/kg s.m.o. introduced to the fermentation. The most beneficial – the 43.94% COD increase in the sludge was achieved at a pressure of 80 MPa and 4 cycles of homogenisation [27]. Another method of the pre-treatment of biomass is the use of ultrasounds. The use of the ultrasonic method of disintegration in the Chemnitz-Heinesdorf sewage treatment plant resulted in, among others, the increase in biogas production by 15.5%. The best results were obtained with frequencies in the range of 20-50 kHz [4,5].

Microwaves also show the destructive effect on flocks cells and microorganisms of the activated sludge [13]. These studies have shown that the largest increase of the COD value occurred in the initial period followed by samples subject to the microwaves effect, i.e. the period from 0 to 3 minutes.

Brooks [1] studied the hydrolysis processes of organic substances of the excess sewage sludge and their mixtures with primary sludge. The best results were achieved by holding sludge at the temperature of 165-180 °C for 10-30 min. The hydrolysis products were readily degradable in the fermentation process. Conducting the process at lower temperatures (60-80°C), has a beneficial effect on the composition of the obtained hydrolysate, but it requires longer reaction times (60-120 minutes) [9]. The hydrolysis phase is also accelerated by freezing and thawing of biomass. The studies conducted by Franceschini [2] have shown that the best results are obtained using one cycle of freezing and thawing, at the freezing temperature below 10°C. The process is the most effective, when the temperature during freezing is reduced at the rate of 1-3°C per minute [7,8].

In the case of materials resistant to the biodegradation processes e.g. lignocellulosic biomass [19], the lack of proper pre-treatment makes the hydrolytic phase slow and incomplete [5]. It can also be the cause of the formation of toxic compounds that inhibit metabolism of methanogenic bacteria [1]. Disintegration of the lignocellulose biomass allows (by braking lignin structure) to hydrolysis of cellulose and hemicellulose to monosaccharides [3].

There is a lot of methods used for lignocellulosic biomas treatment, which allows to fibers degradation and reducing the degree of polymerisation and crystallisation of lignocellulose [22]. For example hemicellulose degradation occurs in 90% yield using acid hydrolysis as pretreatment method [18]. The process is typically carried out with the use of the sulfuric acid in concentrations of 0.5-10% under increased pressure at a temperature of 140-190°C [26].

The biological pre-treatment of cellulose can be performed with the use of fungi producing enzymes capable of the degradation of lignin and hemicellulose: *Phanerichataete chrysosporium*, *Phlebia radiata*, *Dichmitus squalens*, *Rigidosporus lognosus* and *Jungua separabilima.* However, the depolymerisation of lignin requires several weeks to achieve satisfactory results [16].

One of the most widely studied methods of the physico-chemical treatment of lignocellulosic biomass is the steam explosion. In this process the biomass is treated with hot steam at a temperature of 160 to 240°C, under pressure 0.7 to 4.8 MPa. This process causes degradation of hemicellulose and transformation of lignin, without the necessity of using chemical agents [12]. As indicated in [4], a good method for the pre-treatment of lignocellulosic biomass is also the hydrothermal method with dosing of NaOH, which precedes the process. As a result of treatment the straw and rice husks with the 5% NaOH, and then reaction at a temperature of 200°C for 10 minutes, the 222% increase in methane production [4] was achieved.

The review of literature performed by the authors of this paper showed that there is little information on the effectiveness of disintegration in case of substrates other than sewage sludge.

In view of the above, in this paper, the results of studies on the effects of selected methods of disintegration of maize silage on the content of organic substances available for microorganisms were presented. The effectiveness of the process was estimated on the basis of the value of the chemical oxygen demand.

2. Materials and methods

The material used for the study was the maize silage, collected from the farm, from the Mazowieckie province. The biomass was initially mechanically shredded to the particle size of 4 cm. The most important physical and chemical parameters of maize silage are summarised in Table 1.

Table 1. The physical and chemical parameters of maize silage used for the studies

The studied parameter	Maize silage
The content of dry matter d.m. [%]	31.4
The content of dry organic matter [% d.m.]	95.9
Total COD [mgO_2 g^{-1}]	285
LKT [mg HOC/dm^3]	34,000
The content of potassium [mg K/dm^3]	3,500
The content of phosphorus [mg P/dm^3]	595
The content of total organic carbon TOC [mg C/dm^3]	40,770
The content of ammonia nitrogen [mg NH_4+/0.4dm^3]	150
The content of total nitrogen [mg N/0.4dm^3]	2,000
C:N ratio	20.4
pH	6,88

Prior to studies, the test sample of biomass was hydrated in the ratio 1:8 (the maize silage mass to the mass of distilled water). Nine the same test samples (9 variants of disintegration), each in duplicate, were studied.

Disintegration of the biomass was conducted by the following methods: thermal, mechanical, physical and chemical.

The thermal method was realized in two variants: the low-temperature variant, by freezing in the laboratory refrigerator, and the high-temperature variant by heating in the pressurised reactor. The disintegration of biomass, with the mechanical method, was conducted by using the Zelmer disintegrator, Type 32Z012, of 600W power with two-stage control of cutting knives.

As a physical method, the ultrasonic method was used. It was conducted in three testing variants, with the use of the Elma laboratory sonicator of the Elmesonic S60 (H) type.

In case of chemical methods, there were applied the acid hydrolysis with concentrated sulfuric acid in the amount that enables to obtain pH below 1.5, and the alkaline hydrolysis with the 10% NaOH solution, which was added in the amount resulting in the increase of the pH above 12.7. The samples were kept at ambient temperature for 24 hours, then they were neutralised. In table 2, the methods of disintegration,selected for studies, as well as conditions for conducting individual processes were listed.

Table 2. Conditions of performing the processes of biomass disintegration

Number of sample	Method of disintegration	Conditions of performing the process
1	blank sample	the lack of treatment
2	thermal	T=(-15,5)˚C, t= 24h
3		T=170˚C,P= 6,3 bars, t=30 min
4	mechanical	fragmentation, t=2 min
5	chemical	acid hydrolysis (conc. H_2SO_4), t=24 h
6		alkaline hydrolysis (10% NaOH), t = 24 h
7	physical	ultrasounds, t_1= 5 min
8		ultrasounds, t_2= 10 min
9	physical and thermal	ultrasounds, t_1= 5 min, T=60˚C

The effectiveness of each method was assessed on the basis of changes in the values of the COD parameter. The value of this parameter was determined for the water-soluble organic compounds, present in the filtrate (before and after application of the chosen method of disintegration). For this purpose, the studied sample was filtered under reduced pressure on on the filter paper. Determination of the the chemical oxygen demand was performed by the miniaturised NANOCOLOR COD 1500 method (method No. 0-28). This method is based on the photometric (wavelength 620 nm) determination of the concentration of chromium (III), after oxidation of the sample with the addition of potassium dichromate solution, sulfuric acid and silver sulfate at the temperature of 148°C for 2 h.

3. Results

Figure 1 and table 3 show averaged COD values for two samples, obtained for the individual test samples.

Table 3. The averaged COD values obtained for individual test samples

Number of sample	ChZT [mg/l]
1	1769
2	2064
3	19735
4	3144
5	2540
6	6779
7	2969
8	2541
9	3017

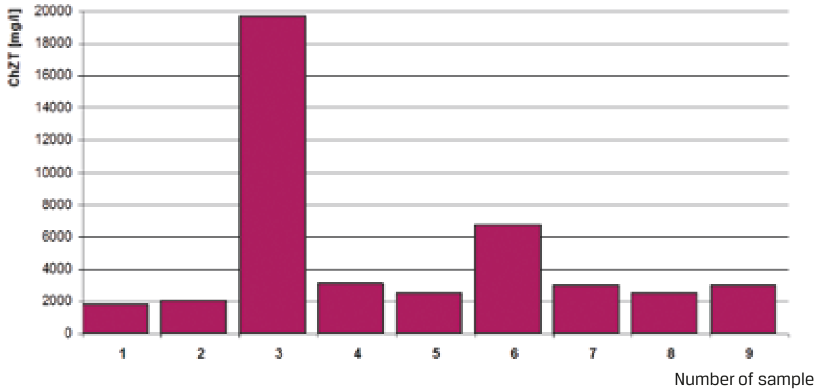

Fig. 1 The averaged COD values obtained for individual test samples

On the basis of the obtained results, it was found that all the methods used for pre-treatment of maize silage resulted in the increase in the COD values, compared to the not pretreated sample. Among the applied techniques, the most effective method was that one where the biomass in reactor was treated with high temperature and pressure (sample No. 3). This method allowed to more than the 10-time increase in the COD value in relation to the blank sample. The method, the effectiveness of which was also singled out among the others, was alkaline hydrolysis, where in case of the sample No. 6 almost the 3.5-time increase in the COD value was obtained. Other methods of disintegration resulted in the increase of COD in the range from 17% (freezing and thawing – sample No. 2) to 80% (fragmentation – sample No. 4). The prolonged exposure time of the maize silage to the ultrasound effect from 5 minute (sample No.7) to 10 minutes (sample No. 8) resulted in the reduction of value of the analysed parameter. Moreover, additional heating of the sample during treatment with ultrasounds has not significantly changed COD.

4. Conclusion

The studies of effectiveness of the selected methods of disintegration of biomass, intended to the methane fermentation process, were conducted. In an experiment, the changes of the COD values of the nine test samples of maize silage, undergoing thermal, mechanical, chemical and physical disintegration, were compared. It was found that the best results, from the selected ones, were obtained due to the high-temperature method. The low-temperature method (freezing and thawing of the sample) was characterised by the lowest effectiveness. In case of this method, only a slight increase in the value of COD was found.

According to the authors' opinion, the works should be extended with additional studies of the effectiveness of other variants of the individual disintegration methods (e.g. different times, temperatures), and their combinations (e.g. fragmentation and hydrolysis or high-temperature processing). The achieved results need to be assessed in terms of the impact of the chosen method of disintegration on the course of the methane fermentation process, in particular, on the quantity and quality of the achieved biogas. These works are currently the authors' subject of study. The obtained experimental results will be published in a separate publication.

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