Effectiveness of using physical pretreatment of lignocellulosic biomass

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Abstract: Pretreatment is aimed at making lignin structures, which in turn causes decrystallisation and depolymerisation of cellulose. This treatment allows to increase the energy potential of substrates. A properly selected method allows for obtaining larger amounts of biogas with a high content of biomethane. The aim of the study was to analyse selected pretreatment methods (ultrasonic and hydrothermal) for biogas yield, including biomethane, and to demonstrate the effectiveness of obtaining additional electricity and heat from these methods. It was based on the literature data. On basis the study, the following information was obtained: average yield of biogas and biomethane before and after treatment, difference in yield of biogas and biomethane after treatment, and the effect of treatment on the substrate used.

Moreover, an estimate was made of the effectiveness of obtaining additional electricity and heat from selected pretreatment methods compared to hard coal. Based on the analysis of the ultrasonic treatment analysis, it was shown that the best result was obtained with the ultrasound treatment of the mixture of wheat straw and cattle manure with the following parameters: frequency 24 kHz, temperature 44.30°C, time 21.23 s. This allowed a 49% increase in biogas production. The use of pretreatment would therefore allow the production of more electricity and heat capable of replacing conventional heat sources such as coal.

Keywords: biogas yield, biomass conversion, energy and thermal efficiency, lignocellulosic biomass, ultrasonic and hydrothermal pretreatment

INTRODUCTION

Biomass is the largest primary renewable energy carrier. Converted by unit processes such as combustion, gasification, esterification or fermentation, it is a valuable source of energy in the industrial sector and can be used in refrigeration, electricity, heating and transport, among others.

Based on the available analyses of biomass potential, it can be concluded that biomass has a very high energy potential and can be an alternative to conventional, so-called fossil fuels. The calorific value of biogas is similar to hard coal and much higher than that obtained from firewood. Tomaszewska-Krojańska (2016) states that the calorific value for: diesel is 41.9, natural gas – 33.0, coal – 23.4, biogas – 20.0–26.0, pellets from digestate –

15.0, firewood – 13.3 and gas from gasification – 5.0 MJ·m^{-3}. According to Ginalski (2012), 9.4 kWh of electricity can be obtained after biogas purification. This value is equal to the electricity that can be obtained from 0.93 m^3 of natural gas or 1.25 kg of coal, respectively. Research by Jarosz (2017) shows that Poland has a plant biomass potential of 305.8 TJ per year, which can be used for energy purposes without reducing the supply of feed and food products. Harnessing the resources can bring tangible benefits. It will allow to increase energy security, improve the condition of the environment and diversify energy sources.

Various types of biomass (substrates) can be used for biogas production. However, a necessary condition is the content of biodegradable organic matter at the level of at least 30% (Lewandowski, 2007; Korycińska, 2009; Bartoszewicz-Burczy,

2012). The factors determining the energy efficiency of the methane fermentation process include, first of all, the type of substrate used, the content of organic dry matter and charge dry matter (Czekała *et al.*, 2016).

Lignocellulosic biomass is a commonly available source of biological resources. About 181.5 Pg ($181.5 \cdot 10^{15}$ g) of it is produced annually in the world (Kumar, Singh and Singh, 2008). The biomass rich in lignocellulose includes waste from, among others, from the agri-food, wood and paper industries. Due to its chemical structure and high calorific value, this material is used for the production of biogas and biodiesel. However, due to its characteristic structure, its use in biogas plants is ineffective.

The cell wall of lignocellulosic biomass is made of three polymers: cellulose (40–55% DM), hemicellulose (24–40%) and lignin (18–25%). The remaining elements of the biomass structure include extracts and inorganic compounds, the so-called ash (Robak and Balcerek, 2017; Sun *et al.*, 2021). Among the polymers mentioned, the greatest energy potential is stored in cellulose, which is surrounded by elements of lignin and hemicellulose. Such a structure makes it difficult to access cellulose decomposition and, consequently, the energy stored in it (Mosier *et al.*, 2005; Michalska and Ledakowicz, 2013). Hemicelluloses present in the cell walls are responsible for the function of matrix and sticking substances. On the other hand, the content of lignin (tree wood) largely determines the possibility of biomass hydrolysis. The phenolic compounds formed during the processing of lignin slow down the hydrolysis of the remaining polymers and may act as an inhibitor on methanogenic microorganisms. The main product of lignin decomposition is vanillin, an organic chemical compound composed of a benzene ring. The tree is resistant to hydrolysis, therefore the content of vanillin in the resulting hydrolysate indicates possible partial degradation of lignin. The transformation of lignin allows to increase the potential of the deeper cellulose subject to hydrolysis (Baudel, Zaror and De Abreu, 2005; Sołowski, 2016).

Pretreatment is used to break down the lignin structure, and consequently decrystallisation and depolymerisation of cellulose (Kumar, Singh and Singh, 2008; Agbor *et al.*, 2011; Paul and Dutta, 2018; Zhang *et al.*, 2019). It allows to increase the yield of fermentable sugars and its higher reactivity. Technologies should be adjusted first of all to the technical possibilities of the biogas plant and the composition of the substrate from which the biogas is produced. The separation of cellulose from lignin and hemicellulose allows more surface area for enzymes that hydrolyse the polysaccharides. As a consequence, it is also possible to use a lower dose of hydrolytic enzymes.

Among the many pretreatment methods, physical methods are frequently used, including mechanical ones, with the use of ultrasound and thermal ones (Izumi *et al.*, 2010).

Mechanical methods of substrate pre-treatment are to reduce the particle size. Primarily, this reduction allows the rate of enzymatic degradation to be increased, and may also solve the problems associated with floating layers. It also reduces the viscosity in fermentation chambers and, consequently, facilitates mixing of the substrate. Another undoubted advantage of this method is the lack of the possibility of creating inhibitors (furfural and hydroxymethylfurfural – HMF), i.e. compounds that inhibit the course of methane fermentation. In turn, the greatest disadvantage of mechanical pretreatment is the high failure rate of mills, due to the possibility of the occurrence of materials such as stones or pieces of metal in the substrate (Taherzadeh and Karimi, 2008; Salihu and Alam, 2016). According to research conducted by Fuerstenau and Abouzeid (2002), wet grinding is more effective and more cost-effective than dry grinding. This is due to lower energy expenditure to carry out wet mechanical treatment and better pulverisation of the substrate. Several factors have an impact on the energy consumption of lignocellulosic biomass, mainly the density, humidity and chemical composition of the substrate. It is also important to choose the right machine for the type of substrate.

There are many methods of physical pretreatment, including ultrasonic, thermal and thermohydrolysis.

Currently, material decompression with the use of ultrasound is successfully used in the food industry and in the treatment of liquid wastewater and sludge. The use of ultrasound produces sinusoidal acoustic waves and small gas bubbles in the liquid. This is due to the drop in local pressure below the vapour pressure of the liquid. Bubbles arise and grow until a critical size is reached, and then cavitation occurs. The phenomenon of a violent implosion is caused by the created extreme local conditions, i.e. shock waves, liquid jets and high pressure. The phenomenon of sonication is a complex process as it involves many processes: combustion, pyrolysis, shear and chemical degradation with radicals (Clodoveo, Durante and La Notte, 2013; Amirante *et al.*, 2017). In terms of frequency, ultrasound can be divided into:
– high frequency ultrasounds 100 kHz–1 MHz,
– diagnostic ultrasound, low energy 1–10 MHz.

Only high-frequency ultrasound can be sufficiently energetic for efficient pretreatment. However, low-energy ultrasound can improve the conversion of sugars to ethanol during fermentation (Rehman *et al.*, 2013).

Thermal treatment is carried out at an appropriate temperature while maintaining a certain pressure. One of the most popular methods is heating with steam at a temperature of 133°C while maintaining a pressure of 0.3 MPa for 20 min (Keep *et al.*, 2000). Some of the substrates (including slaughterhouse remains) cannot be subjected to methane fermentation without appropriate thermal treatment, i.e. hygienisation. The process consists in heating the charge at a temperature of at least 70°C (Kwaśny, Banach and Kowalski, 2012). Hendriks and Zeeman (2009) report that destabilisation of lignocellulosic biomass may take place only from 140°C. However, in the literature, attempts are made to process at lower temperatures. The need to heat the substrate to high temperatures increases processing costs.

Thermohydrolysis is an effective chemical-free treatment to increase the enzymatic digestibility of a given lignocellulose-rich biomass. The method consists in using water under increased pressure (about 1.5 MPa) at a temperature of 200–230°C for several minutes. The biomass is completely immersed in the water and then placed in the bottom of the batch reactor. There is also a similar method where steam is used instead of water and then the biomass is placed at the top of the reactor. Both methods involve the mechanical destruction of the cell structure and the breakdown of complex sugars into simple ones. The advantage of the method is the ability to increase the availability of cellulose for enzymes, while minimising the formation of products that inhibit the growth of microorganisms responsible for the course of fermentation. The effectiveness of the performed pretreatment in the case of LHW and the steam method is measured on the basis

of the percentage of polysaccharides conversion to monosaccharides (Kardaś, Klein and Polesek-Karczewska, 2014; Zhuang *et al.*, 2016).

The aim of the work is to analyse selected methods of pretreatment in terms of biogas yield, including biomethane, and to demonstrate the effectiveness of obtaining additional electricity and heat from these methods.

MATERIALS AND METHODS

Based on the literature data, the analysis of two methods of physical pretreatment with the use of different substrates was carried out.

The first of the analysed methods performed by Zieliński *et al.* (2019b) concerned pre-treatment with ultrasound of a mixture of cattle manure and wheat straw. Ultrasounds with a frequency of 24 kHz were used in 10 different variants, differing in temperature and time of exposure to ultrasound A mixture of wheat straw and cattle manure was used as a substrate. The manure was collected directly from a temporary storage facility located in a field belonging to the Research Station of the University of Warmia and Mazury in Olsztyn in Bałdy (Poland). Wheat straw was harvested from five random bales of the same terrain. The equipment used in the processing of cattle manure and wheat straw is the UP400S Hielschero 100W ultrasonic horn. The statistical analysis of results was carried out with Statistica 10.0 PL package (Statsoft, Inc.). In all tests, the level of significance was adopted at $p = 0.05$ (Zieliński *et al.*, 2019b).

Another of the analysed studies concerned hydrothermal treatment of rice straw in the temperature range from 900 to 1300°C. The substrate was collected in the city of Dyang, China, dried and then cut into particles with a size in the range of about 30–50 mm The inoculum was obtained from a biogas plant dealing with mesophilic anaerobic fermentation of straw. The pretreatment was carried out in a 1 dm³ stainless steel reactor. The heat source was an electric wire wrapped around the reactor, which heated the liquid inside the device by exchanging heat on the wall. A probe installed in the centre of the reactor provided the ability to continuously read temperature data. When the desired temperature of the liquid was reached, such conditions were maintained for a certain time, and then cooled down by washing the device with tap water. The statistical significance of each parameter was evaluated using modified ANOVA (Luo *et al.*, 2019).

On their basis, the following information was obtained: average yield of biogas and biomethane before and after treatment, difference in yield of biogas and biomethane after treatment, and the effect of treatment on the substrate used.

Moreover, an estimate was made of the effectiveness of obtaining additional electricity and heat from selected pretreatment methods compared to hard coal.

RESULTS AND DISCUSSION

COMPARATIVE ANALYSIS OF PRETREATMENT
Ultrasonic treatment

Studies using the ultrasonic method of pretreatment of a mixture of cattle manure with wheat straw were carried out by Zieliński *et al.* (2019b) – Table 1. All versions had a positive effect on biogas production. The best result was obtained on day 20 for sample 5 (exposure at 44.3°C for 21.23 s). What is equally important, the use of ultrasound at a higher temperature and for a long time gave lower results than the test described above. This study revealed the best conditions for improving biogas production. Moreover, the energy needed to apply ultrasound in trial 5 was 4,034 kJ·kg⁻¹ dry weight, while for trial 10 as much as 8,064 kJ·kg⁻¹ dry weight was needed. However, ultrasound did not significantly increase the biomethane content in biogas. In each sample, the biogas yield was slightly above 50% and 1–2% of biomethane.

The use of ultrasound also influenced the solubilisation of organic matter. The solubility increased with increasing duration

Table 1. Analysis of pretreatment with ultrasound of cattle manure and wheat straw at the frequency of 24 kHz

Pre-treatment parameter (temperature and time)	Average biogas yield		Average biomethane yield		Difference in biogas yield after treatment	Difference in biomethane yield after treatment
	before treatment	after treatment	before treatment	after treatment		
	cm³		%			
23.1°C 4.41 s	345	400	51	52	14 ↑	1 ↑
30.0°C 8.82 s	345	495	51	53	30 ↑	2 ↑
44.8°C 13.07 s	345	532	51	52	35 ↑	1 ↑
51.3°C 16.81 s	345	622	51	52	45 ↑	1 ↑
44.30°C 21.23 s	345	682	51	53	49 ↑	2 ↑
52.5°C 25.95 s	345	678	51	53	49 ↑	2 ↑
56.5°C 31.92 s	345	650	51	52	47 ↑	1 ↑
67.2°C 42.47 s	345	645	51	51	47 ↑	0
69.0°C 47.71 s	345	625	51	53	45 ↑	2 ↑
71.3°C 54.14 s	345	639	51	52	46 ↑	1 ↑

Source: own study based on Zieliński *et al.* (2019b).

and temperature, up to trials 5–7. In this range, the value increased by approx. 30%, followed by a decrease in solubility. Tests were also carried out on the same substrate (cattle manure with wheat straw) in a small agricultural biogas plant in order to check the effect of ultrasound on a real scale. Biogas production was monitored over a period of 330 days. It was shown that the use of sonication increased the production by about 25%, but also did not have a significant effect on the content of biomethane ($p > 0.05$) (Zieliński *et al.*, 2019a). Equally good results were obtained in the studies by Chen *et al.* (2011) treating with ultrasound at a frequency of 20–24 kHz cellulose nanofibres from poplar wood. This allowed for the dynamic removal of lignin and hemicellulose, and thus faster and more complete achievement of the energy potential of the plant rich in lignocellulose. Zou *et al.* (2016) also decided to research cattle manure, albeit in combination with corn straw. However, they used a method with different assumptions than those described above. They treated manure and straw as two separate components, not as a mixture. They only sonicated one substrate. The best results were obtained when sonication was applied at the intensity of 284.09 kJ for 30 min on corn straw, without cattle manure treatment. This resulted in an increase in biogas production by over 40%. It was also concluded that the use of ultrasound creates a more suitable environment for the methane fermentation to take place. Moreover, by reducing the initial pH value, it allowed the acidification stage to be reached more quickly.

Hydrothermal treatment

Hydrothermal treatment requires a lot of energy to heat the water. The use of higher temperature is considered to be the most effective method of lignin removal, but more expensive. However, there are reports suggesting that the temperature already above 90°C may loosen the compact structure of lignocellulose and improve the dissolution of lignin (Vassilev, Baxter and Vassileva, 2013; Dasgupta and Chandel, 2019).

Accordingly, Luo *et al.* (2019) decided to carry out a hydrothermal treatment with rice straw at lower temperatures (90–130°C) – Table 2. The content of hemicellulose, cellulose and lignin did not change significantly after applying the pretreatment. This is in line with the studies by Yu *et al.* (2010), according to which the solubilisation of cellulose and hemicellulose started at a temperature of about 150 and 160°C. However, lignin did not dissolve in this temperature range. Similarly, the highest results of biomethane yield were tested for the test heated at 100 and 130°C,

which were respectively 22.0 and 19.8% more than in the control sample. It can be seen that in the treatment with the temperature of 100°C, the biomethane production process was the most stable. There was a sharp increase at first, then reaching 50% on the 9th day, it stabilised at this level until the end of the process. This method is more effective because it achieved over 12% higher net energy production than the untreated sample. However, in the final balance sheet, the surplus energy did not cover the costs needed to carry out the pretreatment. You can consider using excess heat from other biogas plant processes, or using other renewable energy sources, e.g. installing photovoltaic panels. This would reduce the cost of pretreatment while making better use of the energy potential of the rice straw.

Chandra, Takeuchi and Hasegawa (2012) also decided to use the hydrothermal treatment of rice straw. After applying this method at 200°C for 10 min, they achieved accelerated hydrolysis, which resulted in increased efficiency in the production of biogas and biomethane. They recorded a very high increase in biogas production, by over 200% and by over 220% in biomethane production in relation to the untreated sample.

On the other hand, He *et al.* (2017) in their research on the hydrothermal treatment of rice straw, concluded that the use of the temperature of 210°C in different time variants had a negative effect on the course of methane fermentation. The best effect of hydrothermal treatment on safflower (*Carthamus tinctorius* L.) – an annual plant from *Asteraceae* – was observed at the application of 120°C for 1 h. As a result of decompression, a solid fraction (consisting mainly of cellulose) and a liquid fraction (main component: hemicellulose monomers) were obtained. In the case of the solid fraction, the treatment process increased the biogas production by as much as 98% compared to the control sample (Hashemi, Karimi and Mirmohamadsadeghi, 2019).

He *et al.* (2017) conducted a similar study also taking into account the net energy profit. They assessed the energy factor by the difference between the energy used to apply the treatment and the energy obtained from combustion (compared to the combustion of rice straw without the applied treatment). The best result was obtained when the temperature was 150°C for 20 min. Cao *et al.* (2012) obtained a very high lignin removal rate (91%) by treating sorghum pomace at a temperature of 121°C for 60 min. Hydrothermal treatment is not suitable for every type of substrate, it can be counterproductive, as in the case of processed food waste (Qiao *et al.*, 2011). In this type of treatment, the most important turned out to be the selection of the appropriate

Table 2. Analysis of the hydrothermal pre-treatment of rice straw

Pretreatment temperature (°C)	Average biogas yield		Average biomethane yield		Difference in biogas yield after treatment	Difference in biomethane yield after treatment
	before treatment	after treatment	before treatment	after treatment		
	cm^3		%			
90	5525	6141	52	55	10 ↑	3 ↑
100	5525	6259	52	59	12 ↑	7 ↑
110	5525	5641	52	56	2 ↑	4 ↑
120	5525	5303	52	52	4 ↑	0
130	5525	6247	52	58	12 ↑	6 ↑

Source: own study based on Luo *et al.* (2019).

temperature of the process allowing to increase the production of biomethane with a simultaneous good energy balance of the entire utilisation system.

PRETREATMENT EFFICIENCY

It was assumed that after purifying biogas from 1 m^3, even 9.4 kWh of electricity can be obtained (Ginalski, 2012), while the calorific value is in the range of 20–26 MJ (Tomaszewska-Krojańska, 2016). For the following calculations, an average value of 23 MJ was adopted. Data on the calorific value and energy value of biogas are very divergent, depending on many factors, including on the type of substrate subjected to methane fermentation, the technology used and the conversion efficiency achieved by cogeneration systems (CHP).

In the studies (Zieliński et al., 2019b), the use of ultrasound allowed for a 49% increase in biogas production compared to the untreated sample. After conversion, it allowed to generate more electricity by 0.0031678 kWh and an increase in heat production by 0.007751 MJ. Due to the fact that the tests were carried out in laboratory conditions, small samples were used for the production of biogas. Therefore, it was decided to estimate the production in real scale, referring to the data obtained in laboratory tests. It should be taken into account that the obtained data are estimates. It is impossible to say with certainty how a given substrate would behave during methane fermentation with an increased amount. It is necessary to take into account the possible occurrence of such phenomena as inhibition, which would inhibit the entire biogas production process. Transferring the estimated data to the real scale will allow you to check whether the pre-treatment can bring tangible benefits from both an economic and environmental point of view. This is especially important now when there is a risk of reducing the availability of conventional fuels. In addition, climate change is starting to make itself felt more and more. It is necessary to maximise and best use the potential of available renewable energy sources (Garuti et al., 2018; Zieliński et al., 2019b; Khan et al., 2022).

Assuming that 80 Mg of substrate per day are needed to power an exemplary biogas plant with a capacity of 0.8 MW, and assuming that 2 kg of manure and wheat straw dissolved in water were used for the tests. When converted to real conditions, it will allow for the production of approx. 13.8 m^3 more biogas per day. This is equivalent to producing 129 kWh of electricity and 317 MJ of heat. Monthly 3,870 kWh of energy and 9,510 MJ of heat. The use of pretreatment would replace approx. 484 kg of hard coal per month. An investment in an ultrasound installation would certainly increase the energy potential of the substrate. Using the same amount of charge after pretreatment would allow more electricity and heat to be produced. The data presented above are only estimates in order to check the cost-effectiveness of the pretreatment.

Long-term research in an exemplary biogas plant would be necessary to be sure of the legitimacy of using such a technology. However, good results from both laboratory tests and estimates can encourage more extensive research and real-scale analysis. However, it should be remembered that an incorrectly selected pretreatment can produce effects opposite to the intended one. An example is the subjecting of rice straw to hydrothermal pretreatment (Luo et al., 2019). Initially, heating at 90–110°C allowed for a 2–10% increase in biogas production. However, the

application of the temperature at the level of 120°C resulted in a reduction of production by 4% in relation to the control sample (Tab. 3). The use of such technology resulted in a reduction in production. Assuming that the energy required for heating was 0.127 kWh, it was shown that the treatment resulted in a loss of approximately 0.129 kWh of energy. In the described case, the heating temperature turned out to be an important parameter influencing the treatment efficiency. Even fluctuations of several dozen degrees can affect production. The use of laboratory tests may allow the exclusion of tests that already at this stage turn out to be unprofitable, bringing losses after their application (Wu et al., 2018; Kasinath et al., 2021; Mozhiarasi, 2022; Suthar et al., 2022).

Table 3. Effectiveness of selected methods of pretreatment

Type of treatment	Effectiveness of method	
	ultrasounds	hydrothermal
Average biogas yield before treatment (cm^3)	345	5525
Average biogas yield after treatment (cm^3)	682	5303
Difference in biogas yield after treatment (%)	49 ↑	4 ↓
Energy yield after treatment (kWh)	0.0031678	−0.129
Heat yield after treatment (MJ)	0.0031678	−0.005106

Source: own study based on Luo et al. (2019) and Zieliński et al. (2019b).

CONCLUSIONS

From a comparative analysis of the various pretreatment methods, it should be stated that one ideal treatment cannot be selected for each type of substrate. It should also be noted that the individual pretreatment techniques have certain technical limitations when used on a large scale. In biogas plants, first of all, those methods that have been thoroughly tested and have produced good results should be used. Physical pretreatment methods are common. In the conducted analysis, the best results were obtained with ultrasound treatment (24 kHz ultrasound at 44.30°C for 21.23 s) of a mixture of wheat straw and cattle manure. This allowed for a 49% increase in biogas production. However, it was noticed that in the case of physical methods, the biomethane production was lower. Alternatively, pretreatment methods may allow the use of materials that are easier and cheaper to obtain and that could not be subjected to methane fermentation without pretreatment (high in lignocellulose). The most important component of biogas is biomethane, because it is this compound that affects the calorific value of biogas. Situations where pretreatment can lead to a reduction in the biomethane content of the resulting biogas are undesirable. By analysing the obtained results, it can be concluded that a properly selected pretreatment is an effective way to increase the production of biogas with a high biomethane content. The increase in temperature and duration of ultrasound operation only up to a certain point resulted in an increase in production. After reaching the maximum efficiency on the fifth attempt, the

production started to drop gradually in subsequent analyses. Research on the application of hydrothermal treatment is often found in the literature. They are often combined with chemical treatment. Treatment with hot water gives promising results, it allows the dissolution of the lignin. However, it is very important to choose the right temperature for the process and the substrate used. Too high temperature may inhibit the process, e.g. by reducing cellulose crystallisation.

It often happens that the pretreatment is the only possibility of subjecting a given material to methane fermentation. Due to the high content of lignocellulose and the complex structure, it is not possible to use many potential materials for energy purposes, for example untreated sorghum.

Pretreatment can bring many tangible benefits to high-calorie biogas. It would certainly allow to increase the energy potential of the substrate. The use of the same amount of charge after pretreatment would allow for the production of more electricity and heat, which could replace conventional heat sources such as hard coal. However, it should be remembered about the complexity of this process, poorly selected or carried out may result in the formation of inhibitors that negatively affect the methane fermentation process. During processing, they produce, among others lignin derivatives – phenols and furan aldehydes. The lignin remaining after the process (especially in solids) reduces the availability of active cellulase for cellulose hydrolysis by adsorbing cellulases. On the other hand, phenols, which are products of the degradation of sugars and weak acids, negatively affect the activity of microorganisms that carry out methane fermentation. There are also reports that pretreatment with alkali leads to the formation of free phenols (e.g. ferulic acid), which when the plant structure is intact, are esterified to polysaccharides of the cell wall. Before selecting the best treatment, it is important to understand the structure of the substrate and how the method works in order to be able to make the best choice.

An additional aspect in favour of the justified use of pretreatment is the often-encountered fibrous form of plant material (e.g. grass, alfalfa). In the case of such plants, the lack of fragmentation into smaller particles may lead to problems during methane fermentation, when the feed is mixed. Pretreatment may, apart from a significant improvement in the efficiency of the biogas production process, also have a positive effect on the final product of methane fermentation, i.e. digestate. The increase in biomethane content in the produced biogas will reduce the concentration of this gas in the digestate mass. As a result, sterile digestate with an appropriate composition can become an even more valuable agricultural fertiliser, with no negative impact on the environment. Pretreatment may result in a sterile mass free from pathogenic microorganisms.

REFERENCES

Agbor, V.B. *et al.* (2011) "Biomass pretreatment: Fundamentals toward application," *Biotechnology Advances*, 29, pp. 675–685. Available at: https://doi.org/10.1016/j.biotechadv.2011.05.005.

Amirante, R. *et al.* (2017) "Acoustic cavitation by means ultrasounds in the extra virgin olive oil extraction process," *Energy Procedia*, 126, 201709, pp. 82–90. Available at: https://doi.org/10.1016/j.egypro.2017.08.065.

Bartoszewicz-Burczy, H. (2012) "Potencjał i energetyczne wykorzystanie biomasy w krajach Europy Środkowej [Potential and energy use of biomass in Central European countries]", *Energetyka*, 65, 12, pp. 860–865.

Baudel, H.M., Zaror, C. and De Abreu, C.A. (2005) "Improving the value of sugarcane bagasse wastes via integrated chemical production systems: An environmentally friendly approach," *Industrial Crops and Products*, 21(3), pp. 309–315. Available at: https://doi.org/10.1016/j.indcrop.2004.04.013.

Cao, W. *et al.* (2012) "Comparison of the effects of five pretreatment methods on enhancing the enzymatic digestibility and ethanol production from sweet sorghum bagasse," *Bioresource Technology*, 111, pp. 215–221. Available at: https://doi.org/10.1016/j.biortech.2012.02.034.

Chandra, R., Takeuchi, H. and Hasegawa, T. (2012) "Hydrothermal pretreatment of rice straw biomass: A potential and promising method for enhanced methane production," *Applied Energy*, 94 (C), pp. 129–140. Available at: https://doi.org/10.1016/j.apenergy.2012.01.027.

Chen, W. *et al.* (2011) "Individualization of cellulose nanofibers from wood using high-intensity ultrasonication combined with chemical pretreatments," *Carbohydrate Polymers*, 83(4), pp. 1804–1811. Available at: https://doi.org/10.1016/j.carbpol.2010.10.040.

Clodoveo, M.L., Durante, V. and La Notte, D. (2013) "Working towards the development of innovative ultrasound equipment for the extraction of virgin olive oil," *Ultrasonics Sonochemistry*, 20 (5), pp. 1261–1270. Available at: https://doi.org/10.1016/j.ultsonch.2013.02.001.

Czekała, W. *et al.* (2016) "Produkcja biogazu z odpadów komunalnych [Biogas production from municipal waste]," *Technika Rolnicza, Ogrodnicza, Leśna*, 5, pp. 21–25.

Dasgupta, A. and Chandel, M.K. (2019) "Enhancement of biogas production from organic fraction of municipal solid waste using hydrothermal pretreatment," *Bioresource Technology Reports*, 7, 100281. Available at: https://doi.org/10.1016/J.BITEB.2019.100281.

Fuerstenau, D.W. and Abouzeid, A.Z.M. (2002) "The energy efficiency of ball milling in comminution," *International Journal of Mineral Processing*, 67(1–4), pp. 161–185. Available at: https://doi.org/10.1016/S0301-7516(02)00039-X.

Garuti, M. *et al.* (2018) "Monitoring of full-scale hydrodynamic cavitation pretreatment in agricultural biogas plant," *Bioresource Technology*, 247, pp. 599–609. Available at: https://doi.org/10.1016/j.biortech.2017.09.100.

Ginalski, Z. (2012) *Substraty dla biogazowni rolniczych [Substrates for agricultural biogas plants]*. Radom: CDR O. Radom. Available at: https://cdr.gov.pl/pol/OZE/substraty.pdf (Accessed: October 2, 2012).

Hashemi, S.S., Karimi, K. and Mirmohamadsadeghi, S. (2019) "Hydrothermal pretreatment of safflower straw to enhance biogas production," *Energy*, 172, pp. 545–554. Available at: https://doi.org/10.1016/j.energy.2019.01.149.

He, Y. *et al.* (2017) "Lipid production from dilute alkali corn stover lignin by *Rhodococcus* strains," *ACS Sustainable Chemistry & Engineering*, 5(3), pp. 2302–2311. Available at: https://doi.org/10.1021/acssuschemeng.6b02627.

Hendriks, A.T.W.M. and Zeeman, G. (2009) "Pretreatments to enhance the digestibility of lignocellulosic biomass," *Bioresource Technology*, 100(1), pp. 10–18. Available at: https://doi.org/10.1016/j.biortech.2008.05.027.

Izumi, K. *et al.* (2010) "Effects of particle size on anaerobic digestion of food waste," *International Biodeterioration & Biodegradation*,

64(7), pp. 601–608. Available at: https://doi.org/10.1016/j.ibiod.2010.06.013.

Jarosz, Z. (2017) "Potencjał energetyczny biomasy roślinnej i możliwości wykorzystania do celów energetycznych [The energy potential of plant biomass and the possibility of using it for energy purposes]," *Zeszyty Naukowe Szkoły Głównej Gospodarstwa Wiejskiego w Warszawie – Problemy Rolnictwa Światowego*, 17(32), 2, pp. 81–92.

Kardaś, D., Klein, M. and Polesek-Karczewska, S. (2014) "Termochemiczne metody przetwarzania lignocelulozy na surowiec do produkcji biogazu [Thermochemical methods of processing lignocellulose into a raw material for biogas production]," in I. Wojnowska-Baryła and J. Gołaszewski *Konwersja odpadów przemysłu rolno-spożywczego do biogazu – podejście systemowe [Conversion of agri-food industry waste to biogas – a system approach]*. Olsztyn: Wydawnictwo UWM, pp. 104–121.

Kasinath, A. *et al.* (2021) „Biomass in biogas production: Pretreatment and codigestion," *Renewable and Sustainable Energy Reviews*, 150, 111509. Available at: https://doi.org/10.1016/j.rser.2021.111509.

Keep, U. *et al.* (2000) "Enhanced stabilization of sewage sludge through thermal hydrolysis – three years of experience with full-scale plant," *Water Science and Technology*, 42, pp. 89–96. Available at: https://doi.org/10.2166/WST.2000.0178.

Khan, M.U. *et al.* (2022) "A review of recent advancements in pretreatment techniques of lignocellulosic materials for biogas production: Opportunities and limitations," *Chemical Engineering Journal Advances*, 10, 100263. Available at: https://doi.org/10.1016/j.ceja.2022.100263.

Korycińska, A. (2009) "Stan rozwoju sektora biogazowni [The state of development of the biogas plant sector]," in *Odnawialne źródła energii nowym wyzwaniem dla obszarów wiejskich w Polsce [Renewable energy sources a new challenge for rural areas in Poland]*. Warszawa: Fundacja Programów Pomocy dla Rolnictwa FAPA, pp. 6–16.

Kumar, R., Singh, S. and Singh, O.V. (2008) "Bioconversion of lignocellulosic biomass: Biochemical and molecular perspectives," *Journal of Industrial Microbiology & Biotechnology*, 35(5), pp. 377–391. Available at: https://doi.org/10.1007/s10295-008-0327-8.

Kwaśny, J., Banach, M. and Kowalski, Z. (2012) "Przegląd technologii produkcji biogazu różnego pochodzenia [Review of biogas production technologies of various origins]," *Chemia. Czasopismo Techniczne*, 17, pp. 83–102.

Lewandowski, W.M. (2007) *Proekologiczne odnawialne źródła energii [Pro-ecological renewable energy sources]*. Warszawa: Wydaw. WNT.

Luo, T. *et al.* (2019) "Hydrothermal pretreatment of rice straw at relatively lower temperature to improve biogas production via anaerobic digestion," *Chinese Chemical Letters*, 30(6), pp. 1219–1223.

Michalska, K. and Ledakowicz, S. (2013) "Alkalipre-treatment of Sorghum Moench for biogas production," *Chemical Papers*, 67(9), pp. 1130–1137. Available at: https://doi.org/10.2478/s11696-012-0298-0.

Moiser, N. *et al.* (2005) "Features of promising technologies for pretreatment of lignocellulosic biomass," *Bioresource Technology*, 96, pp. 673–686. Available at: https://doi.org/10.1016/j.biortech.2004.06.025.

Mozhiarasi, V. (2022) "Overview of pretreatment technologies on vegetable, fruit and flower market wastes disintegration and bioenergy potential: Indian scenario," *Chemosphere*, 288(3),

132604. Available at: https://doi.org/10.1016/j.chemosphere.2021.132604.

Paul, S. and Dutta, A. (2018) "Challenges and opportunities of lignocellulosic biomass for anaerobic digestion," *Resources, Conservation and Recycling*, 130, pp. 164–174. Available at: https://doi.org/10.1016/j.resconrec.2017.12.005.

Qiao, W. *et al.* (2011) "Evaluation of biogas production from different biomass wastes with / without hydrothermal pretreatment," *Renewable Energy*, 36(12), pp. 3313–3318. Available at: https://doi.org/10.1016/j.renene.2011.05.002.

Rehman, M.S.U. *et al.* (2013) "Use of ultrasound in the production of bioethanol from lignocellulosic biomass," *Energy Education Science and Technology, Part A. Energy Science and Research*, 30(2), pp. 1391–1410.

Robak, K. and Balcerek, M. (2017) "Rola obróbki wstępnej biomasy lignocelulozowej w produkcji bioetanolu II generacji [The role of pretreatment of lignocellulosic biomass in the production of bioethanol of the second-generation]," *Acta Agrophysica*, 24(2), pp. 301–318.

Salihu, A. and Alam, M.Z. (2016) "Pretreatment methods of organic wastes for biogas production," *Journal of Applied Sciences*, 16(3), pp. 124–137. Available at: https://doi.org/10.3923/jas.2016.124.137.

Skibko, Z. *et al.* (2021) "Use of pellets from agricultural biogas plants in fertilisation of oxytrees in Podlasie, Poland," *Journal of Water and Land Development*, 51, pp. 124–128. Available at: https://doi.org/10.24425/jwld.2021.139022.

Sołowski, G. (2016) "Obróbka lignocelulozy – pierwszy etap zielonej energii, chemii wraz z wodorem [Lignocellulose processing – The first stage of green energy, chemistry together with hydrogen]," in K. Kropiwiec and M. Szala (eds.) *Wybrane zagadnienia z zakresu ochrony środowiska i energii odnawialnej [Selected issues in the field of environmental protection and renewable energy]*. Lublin: Wydaw. Nauk. TYGIEL pp. 54–72.

Sun, X. *et al.* (2021) "Recent advances in hydrodynamic cavitation-based pretreatments of lignocellulosic biomass for valorization," *Bioresource Technology*, 345, 126251. Available at: https://doi.org/10.1016/j.biortech.2021.126251.

Suthar, S. *et al.* (2022) "Enhanced biogas production in dilute acid-thermal pretreatment and cattle dung biochar mediated bio-methanation of water hyacinth," *Fuel*, 307, 121897. Available at: https://doi.org/10.1016/j.fuel.2021.121897.

Taherzadeh, M.J. and Karimi, K. (2008) "Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: A review," *International Journal of Molecular Sciences*, 9, pp. 1621–1651. Available at: https://doi.org/10.3390/ijms9091621.

Tomaszewska-Krojańska, D. (2016) "Zagospodarowanie odpadów z biogazowni rolniczych Wybrane zagadnienia z zakresu ochrony środowiska i energii odnawialnej [Management of waste from agricultural biogas plants]," in K. Kropiwiec and M. Szala (eds.) *Wybrane zagadnienia z zakresu ochrony środowiska i energii odnawialnej [Selected issues in the field of environmental protection and renewable energy]*. Lublin: Wydawnictwo Naukowe TYGIEL, pp. 195–196.

Vassilev, S.V., Baxter, D. and Vassileva, C.G. (2013) "An overview of the behaviour of biomass during combustion: Part I. Phase-mineral transformations of organic and inorganic matter," *Fuel*, 112(3), pp. 391–449. Available at: https://doi.org/10.1016/j.fuel.2013.05.043.

Wu, J. *et al.* (2018) "Release of cell wall phenolic esters during hydrothermal pretreatment of rice husk and rice straw," *Biotechnology for Biofuels*, 11, 162. Available at: https://doi.org/10.1186/s13068-018-1157-1.

Yu, G. *et al.* (2010) "Pre-treatment of rice straw by a hot-compressed water process for enzymatic hydrolysis," *Applied Biochemistry and Biotechnology*, 160(2), pp. 539–551. Available at: https://doi.org/10.1007/s12010-008-8420-z.

Zhang, K. *et al.* (2019) "A sustainable approach for efficient conversion of lignin into biodiesel accompanied by biological pretreatment of corn straw," *Energy Conversion and Management*, 11(199), 111928. Available at: https://doi.org/10.1016/j.enconman.2019.111928.

Zhuang, X. *et al.* (2016) "Liquid hot water pretreatment of lignocellulosic biomass for bioethanol production accompanying with high valuable products," *Bioresource Technology*, 199, pp. 68–75. Available at: https://doi.org/10.1016/j.biortech.2015. 08.051.

Zieliński, M. *et al.* (2019a) "Cavitation-based pretreatment strategies to enhance biogas production in a small-scale agricultural biogas plant," *Energy for Sustainable Development*, 49, pp. 21–26. Available at: https://doi.org/10.1016/j.esd.2018.12.007.

Zieliński, M. *et al.* (2019b) "Comparison of ultrasonic and hydro-thermal cavitation pretreatments of cattle manure mixed with straw wheat on fermentative biogas production," *Waste and Biomass Valorization*, 10(4), pp. 747–754. Available at: https://doi.org/10.1007/s12649-017-9977-y.

Zou, S. *et al.* (2016) "Enhancement of biogas production in anaerobic co-digestion by ultrasonic retreatment," *Energy Conversion and Management*, 112, pp. 226–235. Available at: http://dx.doi.org/10.1016/j.enconman.2015.12.087.