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Energy Efficiency of Comminution and Extrusion of Maize Substrates Subjected to Methane Fermentation

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Abstract: The production of methane in the anaerobic digestion process is a proven technology, but it is characterized by low cost-effectiveness. The pretreatment of substrates seems to be a promising technology, which may increase the cost-effectiveness of biogas installations. The aim of the study was to investigate the influence of the comminution and extrusion of maize silage and maize straw silage on the course and yield of anaerobic digestion. The use of a pretreatment (comminution, extrusion) is justified when its energy balance is positive. The greatest increase in the methane yield per dry matter (12.4%) was observed after the extrusion of maize straw silage at 175 °C. The change in the methane yield resulting from the extrusion of maize silage and maize straw silage at 150 °C was small and amounted to 6.4% and 9%, respectively. The comminution caused an increase in the methane yield and accelerated the fermentation of substrates. The methane yield from maize silage was 38.4%, whereas the yield from maize straw silage was only 8.3%.

Keywords: pre-treatment; comminution; extrusion; lignocellulose biomass; anaerobic digestion

1. Introduction

The global economy needs to use waste and by-products to generate renewable energy in order to achieve sustainable development and to protect the climate and natural resources [1]. Anaerobic digestion (AD) is a proven technology of handling organic waste, which yields high-energy products such as methane and digestate [2]. Apart from that, the use of biodegradable waste significantly reduces the emissions of greenhouse gases and odors resulting from uncontrolled fermentation [3].

AD is a promising technology of lignocellulose waste management. During this process, biogas is produced. Its main components are methane—CH_4 (50%–75%), carbon dioxide—CO_2 (25%–50%), and the following volatile compounds in trace amounts: water vapor (H_2O), hydrogen sulfide (H_2S), ammonia (NH_3), hydrogen (H_2), and oxygen (O_2). Another product of anaerobic digestion is digestate pulp, which is a valuable fertilizer [3].

The production of methane in the anaerobic digestion process is a proven technology, but it is characterized by low profitability. Biogas installations without financial initiative in the form of green and yellow certificates or fixed feed-in tariffs for the sale of electricity and heat would not be cost-effective and could not compete with conventional fuels such as coal or natural gas [4]. There are a lot of factors causing this state of affairs, e.g., the high costs of substrates for biogas production, a limited supply of local raw materials, and limited availability of innovations that would make biogas energy production cost-effective [5]. Therefore, innovative solutions are being sought to improve the efficiency of anaerobic digestion. They may consist of improvement of biogas quality (product innovations), the biogas production process (technological innovations), production economics (marketing innovations), and production organization (organizational innovations) [6]. The introduction of new solutions in biogas installations consists of making a technological innovation which results in a new or significantly improved production method in the field of technology, devices, or software [7].

Unfortunately, there are too few innovative biogas technologies with commercial potential that could have significant impact on the economy. There were a large number of studies aimed at increasing the cost-effectiveness of biogas installations, but most of them are characterized by a low technological readiness level (TRL) [8]. The cost-effectiveness of biogas installations can be increased via biological, mechanical, or chemical pretreatment of substrates [9]. These processes are currently applied in the production of bioethanol and biogas from hardly decomposable substrates [10]. Pretreatment is applied to waste substrates, mainly those that are rich in lignocellulosic fibers, fats, and long-chain proteins [11]. Many of these compounds can be found in agricultural waste, the agri-food industry, sewage sludge, and biodegradable municipal waste, i.e., second-generation biofuels.

Agricultural waste includes lignocellulose substrates, very large quantities of which are produced on farms. The annual availability of biomass in the world is over 220 billion tons of dry matter [12]. So far, biomass is used as an organic fertilizer and as a substrate for the production of pellets and briquettes [13].

The following substrates were used in our study: maize silage (MS) and maize straw silage (MSS). Maize silage was used in our research due to its common application in agricultural biogas plants in Poland. In 2017, the area of maize silage in Poland was about 596 hectares, with an average productivity of 55 $Mg{\cdot}ha^{-1}$, giving a mass for fodder and energy purposes of 32.78 million Mg per year [14]. Maize straw in farms is a waste product used as fertilizer in the form of crop residue [15]. In 2017, the area of maize grown for grain in Poland was as high as 562.1 hectares [14], with an average straw yield of 22 $Mg{\cdot}ha^{-1}$, which annually gives about 12.37 million Mg of waste biomass.

Lignocellulose fibers contain lignins, which are hardly decomposable polymers. Cellulose biopolymers and hemicellulose can be easily decomposed by hydrolyzing bacteria. Therefore, lignocellulose biomass, which is difficult to decompose, has a high energy potential. Lignocellulose fibers are the main building blocks of plant cell walls [16].

In order to increase the biogas and biomethane yield of substrates, it is necessary to apply appropriate pre-treatment. There are four basic types of processing: mechanical treatment, chemical treatment, biological treatment, and combined treatment [17].

This study compares two pretreatment methods: comminution and extrusion. Both methods are characterized by high technological readiness level due to the availability of devices such as mills and extruders, which can be successfully used in biogas installations.

The aim of pretreatment of substrates is to give fermentation bacteria easier access to decomposable compounds. This can be done by greater fragmentation of substrates and by the extrusion [18]. Comminution is the process via which the size of particles of the material to be processed is reduced. In consequence, the degree of cellulose crystallization and polymerization is reduced, and there is a larger specific surface area of the substrate which can be affected by microorganisms [19]. Extrusion is a pressure-thermal process in which the raw material (lignocelluloses, fats, proteins) is affected by mechanical forces (shearing, compression), high temperature (40–200 °C), and changing pressure (from several to several dozen MPa) [20].

The aim of the study was to investigate the influence of the comminution and extrusion of maize silage and maize straw silage on the course and yield of anaerobic digestion. In addition, the pretreatment energy input was compared with the increase in energy generated by the AD yield.

2. Materials and Methods

2.1. Lignocellulose Substrates

Maize silage came from the Experimental Agricultural Farm in Przybroda (Poland), belonging to the Poznań University of Life Sciences (PULS). The maize of Monsanto cultivar was harvested with a John Deere self-propelled forage harvester, and then it was ensiled.

Maize straw silage came from a farm in Chodów (Poland). The maize was harvested with a Claas self-propelled forage harvester (theoretical chaff length = 3 cm), and then it was ensiled.

2.2. Pretreatment of Substrates

The lignocellulose substrates were comminuted with an MUT-160A impact milling machine (Metalchem Gliwice, Gliwice, Poland) at the Micronization Laboratory, Inorganic Chemistry Division in Gliwice. As a result of comminution, different fractions of individual substrates were obtained.

The lignocellulosic substrates were extruded with an S45-12 series extruder (Metalchem Gliwice, Gliwice, Poland) [21] at the Cereal Technology Unit, Institute of Plant-Derived Food Technology, Poznań University of Life Sciences. Table 1 shows the technical specification of the extruder.

Table 1. The technical specification of the S45-12 extruder.

Technical Specification	Parameter Value
Year of manufacture	1989
Drive motor power (kW)	10
Heater power (kW)	3
Length/Diameter screw ratio	12:1
Endless screw rotational speed (rpm)	60
Die plate nozzle diameter (mm)	12.6
Mass efficiency (kg·h^{-1})	70–100

Each substrate was extruded at two temperatures, i.e., 150 °C and 175 °C. The selection of temperature was governed by the properties of lignocellulosic compounds and their susceptibility to thermal hydrolysis. The dissolution of hemicelluloses starts already at 150 °C [22]; thus, the lower temperature limit was set at 150 °C. The upper temperature limit of the extruder chamber was set at 175 °C because, above this temperature, the lignocellulosic biomass burns due to a change in the organic dry matter content. There were differences in the durability of individual substrates in the extruder chamber. It was not subject to settings but was measured. The residence time of maize silage extruded in the chamber at 150 °C and 175 °C (MS150 and MS175) was 58 and 62 s, respectively. The residence time of maize straw silage extruded in the chamber at 150 °C and 175 °C (MSS150 and MSS175) was 70 and 72 s, respectively.

The extrusion was conducted when the humidity content in the substrates was 25%–35%, which corresponds to a dry matter content of 65%–75%. If the humidity was lower, the substrate was burnt. If it was higher, the substrate was boiled. The burnt substrate caused the extruder chamber to bung up, while the boiling material prevented the substrate from moving within the chamber.

2.3. Physicochemical Tests of Substrates

The following physicochemical parameters of the substrates were measured: dry matter content, dry organic matter content, pH value, granulometric composition, and chemical composition of the lignocellulosic raw material (lignin, cellulose, holocellulose, and hemicellulose).

The dry matter content was measured according to the PN-EN 12880: 2004 standard "Sewage Sludge Characteristics. Measuring Dry Residue and Water Content". Samples of the substrates were dried in an SUP-18G laboratory dryer at 105 ± 5 °C until their weight was constant.

The dry organic matter content in the substrates was measured according to the PN-EN 12879: 2004 standard, "Sewage Sludge Characteristics. Measuring Loss on Ignition of Sludge Dry Matter". Samples of the substrates were burnt in a Lenton AF 11/6b muffle furnace at a temperature of 550 ± 25 °C until their weight was constant.

The pH value was measured with the potentiometric method, according to the PN-EN 12176: 2004 standard "Sewage Sludge Characteristics. Measuring the pH Value". The pH value of the substrate samples was measured with an Elmetron CP-411 pH-meter with an ERH-111 combination electrode and a temperature sensor with a Pt-1000B resistor in order to compensate for the pH value depending on the temperature of the sample.

The granulometric composition of the comminuted lignocellulosic materials was determined according to the PN-R-04032: 1998 standard "Soils and Mineral Sediments. Sampling and Determination of Granulometric Composition". Individual fractions of the comminuted plant material were determined with the sieve method, which consists of separating the material sample into granulometric fractions by means of a set of sieves placed on a mechanical vortex mixer. Due to the physicochemical properties of the materials (low density), each sample weighed 100 g. The mesh sizes of the sieves were 1.25 mm, 0.8 mm, 0.25 mm, 0.1 mm, and 0.045 mm.

The chemical composition of the lignocellulosic raw material (lignin, cellulose, holocellulose, and hemicellulose) was determined according to the Polish standard PN-92/P-50092. The following methods were used to measure the physicochemical parameters of the plant material [23,24]: humidity—the oven-drying method; the lignin content—the TAPPI method; the cellulose content—the Seifert method; the holocellulose content—with sodium chlorite in a Soxhlet extractor; the hemicellulose content—by subtracting the cellulose content from the holocellulose content; the mineral content—in accordance with the DIN 51731 standard.

The results of measurements of dry matter, dry organic matter, and the chemical composition of the lignocellulosic material were given as the average of three measurements. Additionally, the content of lignocellulose compounds and dry organic matter was calculated in relation to the dry matter of the raw material (including humidity in each case).

2.4. Methane Fermentation

The substrates for anaerobic digestion were tested at the Institute of Biosystems Engineering, Poznań University of Life Sciences. The anaerobic digestion process consisted of batch and wet digestion. The basic physicochemical parameters of the substrates were determined at the BW QUARK Environmental Research and Implementation Laboratory, Poznań, Poland. The experiments were carried out according to the German standard DIN 38 414-8 [25] and technical guidelines of VDI 4630 [26].

The biogas mixture was prepared according to the technical guidelines of VDI 4630, allowing for the ratio of the dry organic matter of the substrate to the dry organic matter of the graft. This quotient cannot be greater than 0.5. The organic mass of the graft must be within 1.5%–2% of the fresh mass (m/m).

$$\frac{\text{dry organic matter of substrate}}{\text{dry organic matter of graft}} \leq 0.5. \quad (1)$$

Table 2 shows the composition of the biogas mixture of comminuted and extruded substrates.

Table 2. The composition of the biogas mixture of comminuted and extruded substrates.

Substrate	Substrate Weight (g)	Graft Weight (g)	pH Value
Checking test	-	1200	7.67
Maize silage (MS)	15	1185	7.31
Comminuted maize silage (MSC)	14	1186	7.87
Maize silage—150 °C (MS150)	12	1188	7.45
Maize silage—175 °C (MS175)	12	1188	7.51
Checking test	-	1200	7.67
Maize straw silage (MSS)	15	1185	7.28
Comminuted maize straw silage (MSSC)	15	1185	8.12
Maize straw silage—150 °C (MSS150)	13	1187	7.26
Maize straw silage—175 °C (MSS175)	13	1187	7.48

The biogas and biomethane yields from the comminuted and extruded substrates were tested with biodigesters at the Institute of Biosystems Engineering, Poznań University of Life Sciences. Glass biodigesters with a capacity of 2 dm^3 were placed in a water jacket, which enabled adjustment of the temperature to mesophilic digestion at 39 ± 1 °C. The produced biogas was stored in Plexiglas cylinders filled with a neutral liquid (preventing the dissolution of gases—mostly carbon dioxide). The capacity of the gas tanks was 5 dm^3. The biogas from the tanks went to an apparatus, which analyzed the gas composition for the content of methane, ammonia, hydrogen sulfide, carbon dioxide, and oxygen. A side view of the biodigester chambers is shown in Figure 1.

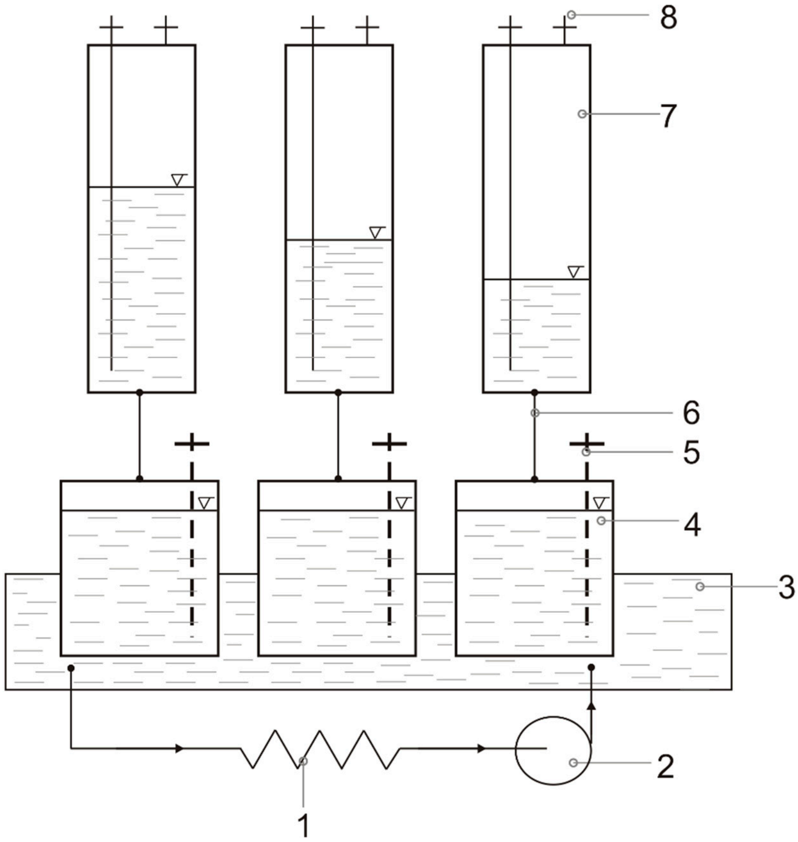

Figure 1. A scheme of the digester for testing biogas production (redrawn from Reference [27]): 1. water heater with temperature controller (20–70 °C); 2. water pump; 3. water jacket (39 ± 1 °C); 4. biodigester (2 dm^3); 5. notch for sampling biogas mixture; 6. tube for transporting produced biogas; 7. calibrated tank for biogas; 8. gas sample valve.

The biogas mixture was prepared according to the technical guidelines of VDI 4630. The concentration of methane, carbon dioxide, hydrogen sulfide, ammonia, and oxygen in the biogas was measured with a certified Geotech GA5000 gas analyzer. The cumulated biogas and methane yields were calculated in an Excel spreadsheet, and converted from $dm^3 \cdot g^{-1}$ into $m^3 \cdot Mg^{-1}$ and then expressed as $m^3 \cdot Mg^{-1}$ in relation to the fresh weight, dry matter, and dry organic matter. The test of the biogas efficiency of substrates was carried out in three replicates.

2.5. Methods for Calculating Energy Efficiency

Biogas is used as a fuel for cogeneration engines, the main purpose of which is to generate electricity. In order to prepare the energy balance of the digestion of treated substrates, the amount of electricity obtained from one megagram of dry organic matter (DOM) of untreated and pretreated biomass is calculated as follows:

$$E_N / E_C / E_E = E_{CH4} \times V_{CH4} \times \mathrm{n} \tag{2}$$

where $E_N/E_C/E_E$ ($kWh \cdot Mg^{-1}$) is the amount of electricity obtained from dry organic matter of non-pretreated/comminuted/extruded biomass, E_{CH4} ($kWh \cdot m^{-3}$) is the methane energy value (9.56 $kWh \cdot m^{-3}$), V_{CH4} ($m^3 \cdot Mg^{-1}$) is the amount of methane obtained from one megagram of dry organic matter of non-pretreated/comminuted/extruded biomass, and n is the electric efficiency of the cogeneration engine (based on the specifications of cogeneration engines available on the Polish market, n = 45% (range 32%–48.7%).

The difference between the amount of electric energy obtained from the dry matter of non-pretreated organic biomass and the amount of electric energy obtained from the dry matter of pretreated organic biomass is an additional energy yield. To calculate the energy balance of the pretreatment and anaerobic digestion, the amount of electricity uptake used by the machine for pretreatment must be deducted from the energy yield.

Due to the low efficiency of the laboratory equipment (disintegrating mill—2 kg/h and laboratory extruder—70 kg/h), the energy balance was always negative. Therefore, industrial machines were used to calculate the energy balance.

In order to calculate the energy efficiency of comminution, an MB11C hammer mill was used. Its technical specification is shown in Table 3.

Table 3. The technical specification of the MB11C hammer mill.

Technical Specification	Parameter Value
Mass efficiency (straw) ($kg \cdot h^{-1}$)	400
Maximum weight (kg)	350
Drive motor power (kW)	15
Power supply (V)	400
Supported sieves (mm)	1–4
Dimensions (mm)	1100 × 900 × 1100

In order to calculate the extrusion energy efficiency, a Presoil E-1000 extruder (Extruder for grain Olejpress, Charkov, Ukraine) was used. Its technical specification is shown in Table 4.

Table 4. The technical specification of the E-1000 extruder.

Technical Specification	Parameter Value
Mass efficiency ($kg \cdot h^{-1}$)	1000
Drive motor power (kW)	90
Endless screw rotational speed (rpm)	400–750
Die plate nozzle diameter (mm)	16

The calculation of electricity consumption of the pretreatment machine would require measurement of electricity consumed each time. In order to calculate the energy balance without taking measurements, the maximum energy consumption of the machine under unfavorable conditions can be assumed. Therefore, the maximum energy consumption and minimum efficiency of both devices (hammer mill, extruder) was assumed according to their power listed in the specification.

The performance of the devices was calculated in relation to dry organic matter as follows:

$$W_{d.o.m} = W_p \times X_{\ d.m.} \times X_{\ d.o.m.} \tag{3}$$

where $W_{d.o.m.}$ ($Mg{\cdot}h^{-1}$) is the device efficiency related to dry organic matter, W_p ($Mg{\cdot}h^{-1}$) is the device efficiency (according to the manufacturer), $X_{d.m.}$ (%) is the percentage of dry matter in total weight of the product, and $X_{d.o.m.}$ (%) is the percentage of dry organic matter in dry matter of the product.

Performance of the hammer mill and extruder with respect to the dry matter of the organic substrates is presented in Table 5.

Table 5. The performance of the MB11C hammer mill and E-1000 extruder in relation to the dry organic matter of the substrate.

Substrate	Extrusion Temperature (°C)	$X_{d.m.}$ (%)	$X_{d.o.m.}$ (%)	$W_{d.o.m.}$ ($Mg{\cdot}h^{-1}$)
Comminuted maize silage (MSC)	-	93.74 ± 3.32	95.36 ± 4.38	0.36 ± 0.02
Comminuted maize straw silage (MSSC)	-	88.70 ± 3.14	92.78 ± 4.26	0.33 ± 0.02
Extruded maize silage	150 ± 3.0	90.97 ± 3.22	95.55 ± 4.38	0.87 ± 0.04
	175 ± 3.5	95.64 ± 3.39	96.05 ± 4.41	0.92 ± 0.05
Extruded maize straw silage	150 ± 3.0	73.63 ± 2.61	93.87 ± 4.31	0.69 ± 0.04
	175 ± 3.5	77.35 ± 2.74	95.41 ± 4.38	0.74 ± 0.04

The electricity consumed by the machine was calculated according to the following equation:

$$E_m = \frac{P}{W_{d.o.m.}}, \tag{4}$$

where E_m ($kWh{\cdot}Mg^{-1}$) is the electricity consumed by the machine, P (kW) is the machine power, and $W_{d.o.m.}$ ($Mg{\cdot}h^{-1}$) is the device efficiency related to the organic dry matter of biomass.

2.6. Uncertainty, Statistics, and Measurement Error

2.6.1. Measurement Uncertainty

Due to technological progress, the significance of the results of analyses is increasing; thus, they need to be of top quality. Measurement uncertainty is a component of individual sections of analytical procedures. Therefore, it is very important to determine the source and types of uncertainty at individual stages of analytical procedures [28]. Measurement reliability increases when its uncertainty is determined, because the results can be compared between laboratories. In our study, the measurement uncertainty procedures followed the ISO standards [29].

2.6.2. Measurement Error

The daily biogas production was measured by reading the neutral liquid level on the tank scale. A unit on the scale was 10 cm^3; thus, this was the accuracy of biogas production measurement. At less than 400 cm^3, the gas was not removed because the analysis of its composition would have resulted in a gross error. In order to calculate the daily production on the next day, it is necessary to read the total volume from several days and subtract the volume from the day before. A possible cumulative error in the estimation of the volume of biogas produced should be taken as the product of the reading error and the number of readings followed by biogas removal and its analysis. The error ranged from 0.85% for comminuted maize silage to 1.97% for maize silage extruded at 150 °C.

2.6.3. Data Statistics

The data obtained during the tests were analyzed statistically with ANOVA type III at a significance level p of α = 0.05. The Statistica 13.1 (StatSoft Inc., Tulsa, OK, USA) software was used for the analysis. The values of cumulated methane for each substrate (within the range of dry matter of the substrates) and the temperature level were analyzed.

3. Results

3.1. Comminuted Substrates

The following fractions were obtained as a result of comminution with the MUT-160A laboratory mill (Metalchem Gliwice, Gliwice, Poland):

1. Maize silage:

- >1.25 mm—share 2.58% ± 0.10%;
- 0.8–1.25 mm—share 47.05% ± 1.82%;
- 0.25–0.8 mm—share 43.36% ± 1.68%;
- 0.1–0.25 mm—share 4.80% ± 0.19%;
- 0.045–0.1 mm—share 2.21% ± 0.09%.

The share of the 0.25–0.8 mm and 0.8–1.25 mm maize silage fractions was the largest, i.e., 90.4%.

2. Maize straw silage:

- >1.25 mm—share 45.60% ± 1.76%;
- 0.8–1.25 mm—share 22,80% ± 0.88%;
- 0.25–0.8 mm—share 23.20% ± 0.90%;
- 0.1–0.25 mm—share 5.20% ± 0.20%;
- 0.045–0.1 mm—share 3.20% ± 0.12%.

The share of the >1.25 mm commuted maize straw silage fraction was the largest, i.e., 45.6%, whereas the 0.25–0.8 mm and 0.8–1.25 mm fractions accounted for a total of 46%.

The basic physicochemical parameters of the substrates measured in tests checking the influence of comminution are shown in Table 6.

Table 6. The basic physicochemical parameters of the substrates used for comminution.

Substrate	pH	Conductivity ($mS\cdot cm^{-1}$)	Dry Matter (%)	Dry Organic Matter (%)
Maize silage (MS)	3.90 ± 0.17	2.69 ± 0.12	78.00 ± 2.77	95.17 ± 4.37
Comminuted maize silage (MSC)	4.06 ± 0.17	4.01 ± 0.18	93.74 ± 3.32	95.36 ± 4.38
Maize straw silage (MSS)	8.55 ± 0.36	1.65 ± 0.08	79.38 ± 2.82	78.53 ± 3.60
Comminuted maize straw silage (MSSC)	8.41 ± 0.36	1.47 ± 0.07	88.70 ± 3.15	92.78 ± 4.26

The measurements showed that the mechanical treatment caused an increase in the dry matter content, which was different for individual substrates. The comminuted substrates had a higher content of dry matter due to the evaporation of water as a result of increased temperature in the comminution chamber. The highest increase in the dry matter content, i.e., from 78% to 93.74%, was recorded for maize silage.

The content of lignocellulosic materials (lignins, celluloses, and holocelluloses) in the comminuted substrates was not measured, because, in contrast to extrusion, during the comminution, there was no high temperature or pressure which could cause changes in the chemical composition of the biomass.

3.2. Extruded Substrates

The basic physicochemical parameters of the extruded and non-extruded substrates are shown in Table 7.

Table 7. The basic physicochemical parameters of the extruded substrates.

Substrate	pH	Conductivity ($mS \cdot cm^{-1}$)	Dry Matter (%)	Dry Organic Matter (%)
Maize silage (MS)	4.05 ± 0.17	2.56 ± 0.12	75.08 ± 2.66	95.16 ± 4.37
Maize silage—150 °C (MS150)	4.11 ± 0.18	3.05 ± 0.14	90.97 ± 3.22	95.55 ± 4.38
Maize silage—175 °C (MS175)	4.15 ± 0.18	3.10 ± 0.14	95.64 ± 3.39	96.05 ± 4.41
Maize straw silage (MSS)	4.15 ± 0.18	2.43 ± 0.11	66.21 ± 2.34	93.85 ± 4.31
Maize straw silage—150 °C (MSS150)	4.29 ± 0.18	2.71 ± 0.12	73.63 ± 2.61	93.87 ± 4.31
Maize straw silage—175 °C (MSS175)	4.20 ± 0.18	2.46 ± 0.11	77.35 ± 2.74	95.41 ± 4.38

The measurements showed that the extrusion caused an increase in the dry matter content, which was different for individual substrates due to the evaporation of water as a result of increased temperature in the extrusion chamber. The highest increase in the dry matter content, i.e., from 75.08% to 95.64%, was noted for maize silage extruded at 175 °C.

After the extrusion, the pH value increased in most of the substrates. It is most likely that the effect was caused by the loss of volatile fatty acids (VFAs) from the ensiled substrates due to the high temperature of extrusion and the addition of maize silage.

The content of lignocellulosic materials (lignins, celluloses, and hemicellulose) in the substrates was measured because, during the extrusion, high temperature and pressure may have caused changes in the chemical composition of the biomass.

Table 8 shows the percentage content of lignocellulosic compounds, both unprocessed and extruded at 150 °C and 175 °C. These are the average values of measurements in two replicates.

Table 8. The percentage content of lignocellulosic compounds.

Substrate	Lignin (%)	Cellulose (%)	Hemicellulose (%)
Maize silage	11.99 ± 0.60	34.33 ± 1.72	17.27 ± 0.86
Maize silage—150 °C	10.99 ± 0.55	23.23 ± 1.16	9.67 ± 0.48
Maize silage—175 °C	9.19 ± 0.46	19.49 ± 0.97	7.04 ± 0.35
Maize straw silage	18.04 ± 0.90	41.29 ± 2.06	21.91 ± 1.10
Maize straw silage—150 °C	22.40 ± 1.12	38.92 ± 1.95	14.09 ± 0.70
Maize straw silage—175 °C	17.29 ± 0.86	36.00 ± 1.80	17.63 ± 0.88

The lignin content in the samples before and after extrusion did not change much. The biggest change in the lignin content, i.e., 4.36%, was observed in the maize silage extruded at 150 °C. The lignin content in the other substrates did not change significantly after the extrusion. The cellulose content dropped in all the extrudates (extrusion products). The greatest decrease, i.e., 19.84%, was noted in the maize silage extruded at 175 °C. The hemicellulose content decreased in all the extrudates. The greatest decrease, i.e., 10.23%, was observed in the maize silage extruded at 175 °C.

Apart from the content of CH_4 and CO_2 in the biogas, the maximum concentrations of hydrogen sulfide and ammonia produced during the anaerobic digestion of the extruded and non-extruded substrates were also measured. The maximum concentration of hydrogen sulfide, i.e., 10,000 ppm, was observed during the first days of the digestion. The highest daily concentration of hydrogen sulfide in the biogas was found in maize silage. By contrast, no ammonia was produced during the digestion of extruded substrates.

4. Discussion

4.1. Energy Efficiency of Comminution

Methane is the most important component of biogas, because it determines the energy value of the biogas produced [30,31]. Therefore, pretreatment is applied to increase its yield. Therefore, the analysis of the energy efficiency of pretreatment should be referred to the yield of methane. A change in the yield in relation to fresh weight does not indicate more efficient fermentation of the substrate, but this information is important for biogas installation investors. After the comminution, the dry matter content increased in all the substrates due to the evaporation of water. The digested compounds were components of dry organic matter. Therefore, the total methane yield per fresh weight unit increased by 10%. The methane yield from commuted maize silage and maize straw silage increased by 66.8% and 43%, respectively. However, this does not mean that the substrates were digested more efficiently.

On the other hand, the changes in the yield per dry organic matter content indicate the influence of the pretreatment. The percentage increase in the cumulated yield of methane from the commuted substrates was given for non-pretreated substrates.

Comminution should not cause a "physical" growth or loss of dry organic matter. It should only change the physical structure of the substrate, allowing better access for digestion bacteria [32]. The increase in the digestion efficiency per organic dry matter unit (Figure 2) points to the influence of comminution.

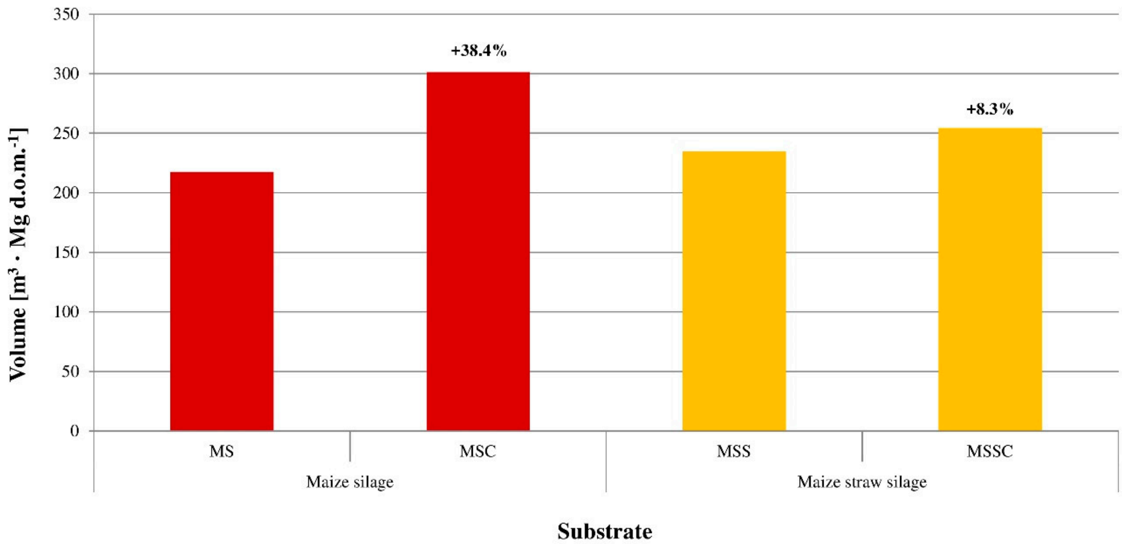

Figure 2. The cumulated yield of methane from comminuted and non-comminuted substrates per dry organic matter content.

The highest increase in methane yield per dry organic matter due to comminution was observed in maize silage.

The course of the anaerobic digestion is shown in daily methane yield diagrams, expressed as cubic meters per megagram of dry organic matter (Figure 3).

As the results show, the comminution of the substrates accelerated the digestion of the substrates and resulted in a higher methane yield. The highest increase in the methane yield, i.e., 38.4%, was recorded for maize silage, whereas the increase in the yield of methane from maize straw silage amounted to only 8.3%. These effects were achieved by increasing the active surface of the biomass, which provided anaerobic bacteria better and faster access to decomposable compounds [33]. Thus, the duration of the anaerobic digestion of comminuted substrates was reduced by five days for maize silage and by four days for maize straw silage. Silva et al. [34] conducted a study on wheat straw and found that the hydrolysis efficiency increased from 6% to 34% due to comminution, which reduced the size of particles and facilitated access to decomposable polymers. Lindner et al. [35] analyzed the effect of the comminution of digestate after separation from a working biogas plant and from a laboratory reactor. The biogas plant used a mixture of the following substrates: slurry, manure, maize and grass silage, and grain. The laboratory reactor was fed with a mixture of hay and maize straw and silage. The mechanical processing increased the methane yield from the biogas plant by 9% and from the laboratory reactor by 17%. Tedesco et al. [36] studied the effect of *Laminaria* spp. algae fragmentation on the biogas yield and observed that the amount of methane increased by as much as 53%.

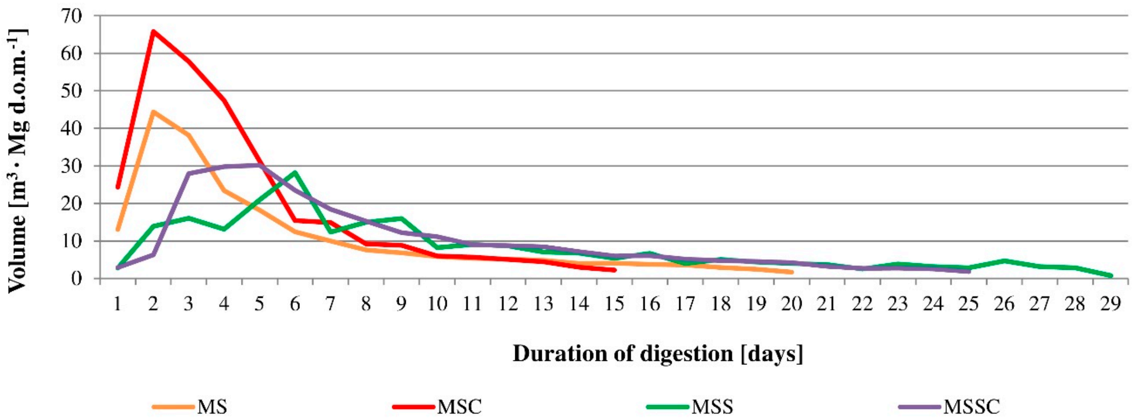

Figure 3. The course of methane production from non-comminuted and comminuted maize silage and maize straw silage.

In order to evaluate the usefulness of comminution, it is necessary to compare the energy consumed by pretreatment with the energy obtained from the increased yield of methane. Equations (1), (2), and (3) were used to calculate the energy yield of comminution and the yield of biomethane per dry organic matter. The energy efficiency of comminution was always calculated per megagram of DOM. The productivity of the mill was taken from Table 3 and the power was 15 kW. The methane energy value was assumed at 9.56 kWh·m^{-3}. The electric efficiency of the cogeneration engine, which is necessary to calculate the electricity generated from dry organic matter, was assumed at 45%. The following equation was used to calculate the yield of additional electricity from the DOM of comminuted substrates, allowing for the energy consumed by pretreatment with a hammer mill:

$$\Delta E = (E_C - E_N) - E_m. \quad (5)$$

The relative percentage increase in energy obtained was

$$\frac{\Delta E}{E_N} \times 100\%. \quad (6)$$

Table 9 lists the amounts of energy generated from the substrates before and after the comminution, as well as the extra energy yield, energy balance, energy consumed by the mill, and the percentage increase in energy.

The most favorable energy balance was noted for maize silage. An additional 318.2 kWh of energy per megagram of DOM was generated after deducting the energy consumed for comminution. This represented as much as a 34.01% increase in energy in relation to the energy obtained from silage without comminution.

Table 9. The energy balance of comminution. DOM—dry organic matter.

Substrate	Electric energy from DOM E_N (kWh·Mg^{-1})	Electric energy from Comminuted DOM E_R (kWh·Mg^{-1})	Extra Energy Yield (kWh·Mg^{-1})	Energy Consumed by Machine E_m (kWh·Mg^{-1})	Energy Balance ΔE (kWh·Mg^{-1})	Energy Increase ΔE/E_N (%)
Maize silage	935.60 ± 42.66	1295.70 ± 59.08	360.10 ± 16.42	41.95 ± 1.91	318.20 ± 14.51	34.01 ± 1.55
Maize straw silage	1010.00 ± 46.06	1094.20 ± 49.90	84.20 ± 3.84	45.57 ± 2.08	38.70 ± 1.76	3.83 ± 0.17

4.2. Energy Efficiency of Extrusion

The extrusion of all the substrates also resulted in a percentage increase in the dry matter content. As the digestion compounds were organic dry matter components, the yield of methane from the fresh weight increased considerably, i.e., by 29.4% and 32.4% from the maize silage extruded at 150 °C and 175 °C, respectively, and by 21.2% and 33.5% from the maize straw silage extruded at the same temperatures. The increase does not mean that the substrates were digested more efficiently.

The extrusion did not cause a "physical" growth or loss of dry matter or dry organic matter, but it may have changed the physical and chemical structure of the substrates, allowing digestion bacteria better access to the compounds formed in the extruder during thermal hydrolysis [37]. This effect was reflected by the cumulated yield of methane (Figure 4) per unit of dry organic matter. An increase in the yield per unit of dry organic matter indicates the real effect of extrusion.

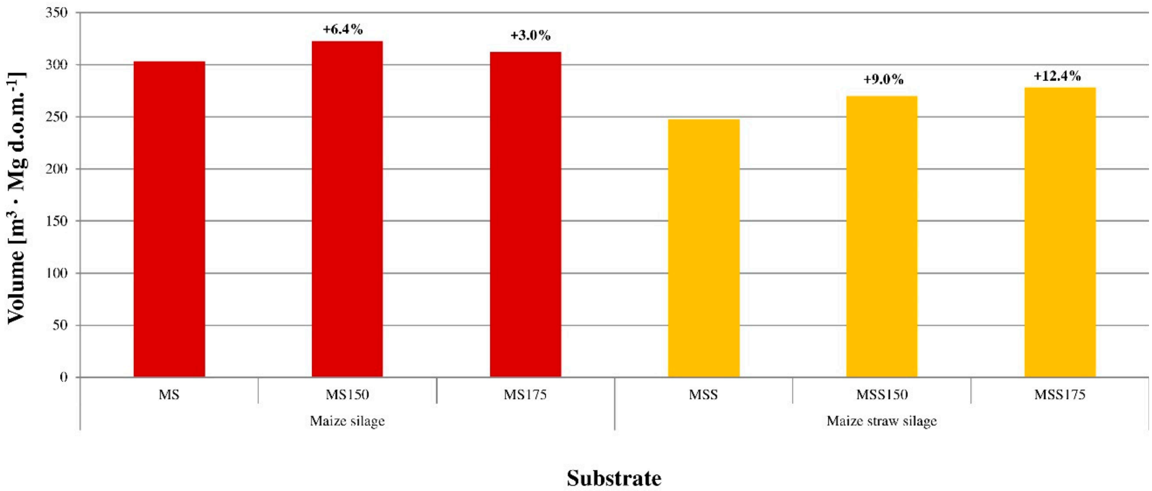

Figure 4. The cumulated yield of methane from extruded and non-extruded substrates per organic dry matter.

The extrusion of the maize straw silage at 175 °C resulted in the greatest increase in methane efficiency per organic dry matter, i.e., 12.4%. However, the extrusion of the maize silage and maize straw silage at 150 °C increased the methane yield by a much lesser extent, i.e., by 6.4% and 9%, respectively.

The plots in Figure 5 show the daily methane yield expressed as cubic meters per megagram of dry organic matter.

The extrusion of the substrates increased the active surface of the biomass. Its initial hydrolysis allowed anaerobic bacteria better access to decomposable compounds and, thus, accelerated the first phase of the AD process [38]. As a result, the anaerobic digestion of the maize extruded at 150 °C and 175 °C was shortened by one day, whereas the digestion of the maize straw silage extruded at both 150 °C and 175 °C was six days shorter. In addition, the increased availability of decomposable compounds and their initial hydrolysis (in addition to maize silage) resulted in a higher pH value than in the corresponding non-extruded substrates.

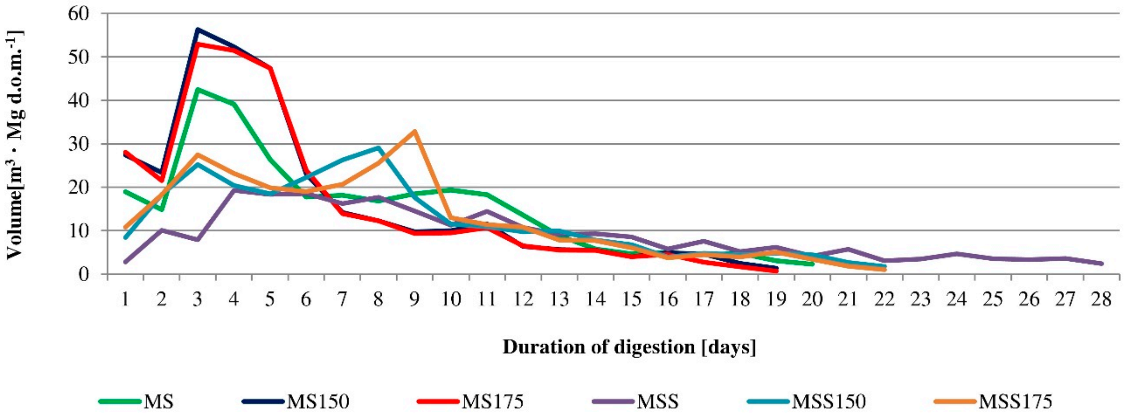

Figure 5. The daily yield of methane from extruded and non-extruded maize silage and maize straw silage.

The energy balance of extrusion was analogous to the energy balance of comminution. The efficiency of extrusion was calculated depending on the dry organic matter of the substrates (Table 10). The power of the extruder was 90 kW. Table 10 lists the amount of energy generated from the substrates before and after the extrusion, as well as the extra energy yield, energy efficiency, including the energy consumed by the extruder, and the percentage increase in the amount of energy.

Table 10. Energy balance of extrusion.

Substrate	Extrusion Temperature (°C)	Electric Energy from DOM E_N (kWh·Mg^{-1})	Electric Energy from Comminuted DOM E_E (kWh·Mg^{-1})	Extra Energy Yield (kWh·Mg^{-1})	Energy Consumed by Machine E_m (kWh·Mg^{-1})	Energy Balance ΔE (kWh·Mg^{-1})	Energy Increase ΔE/E_N (%)
Maize silage	150 ± 3.0	1304.3 ± 59.48	1387.60 ± 63.27	83.30 ± 3.80	103.50 ± 4.72	−20.20 ± 0.92	−1.55 ± 0.07
	175 ± 3.5		1343.20 ± 61.25	38.90 ± 1.77	98.00 ± 4.47	−59.10 ± 2.69	−4.53 ± 0.21
Maize straw silage	150 ± 3.0	1064.8 ± 48.55	1160.70 ± 52.93	95.90 ± 4.37	130.20 ± 5.94	−34.30 ± 1.56	−3.22 ± 0.15
	175 ± 3.5		1197.00 ± 54.59	132.20 ± 6.02	122.00 ± 5.56	10.20 ± 0.47	0.96 ± 0.04

The anaerobic digestion of the maize silage extruded at 150 °C and 175 °C, and maize straw extruded at 150 °C resulted in a negative energy balance. By contrast, the digestion of the maize straw silage extruded at 175 °C resulted in a positive energy balance.

Menardo et al. [39] conducted research to check the susceptibility of rice straw silage, maize silage, and triticale silage to extrusion and came to similar conclusions. Four different blends of these substrates were used in a fermentation bioreactor, where the content of rice straw silage amounted to 10%, 30%, 50%, and 70%. The remaining part of the blend consisted of maize silage and triticale silage mixed at a ratio of 2.5:1. The composition was determined on the basis of the fresh weight of the substrates. Extrusion increased both the degradation of organic substances and the yield of methane by 16%. The mixture containing 10% of rice straw silage resulted in a positive energy balance. By contrast, the energy efficiency of the blend containing 30% of rice straw silage was close to zero [39]. Panepinto and Genon [40] studied the effect of extrusion of maize silage, slurry, and cow manure on biogas yield and also did not observe a significant increase in the amount of biogas produced from these substrates. Additionally, the research showed that the extrusion of maize silage may decrease in the methane yield. However, in most cases, the yield of methane from extruded substrates increased by up to 15%. Pérez-Rodríguez et al. [41] studied the effect of extrusion on the biogas efficiency of maize cobs and observed an increase in the methane yield.

4.3. Comparison of Energy Efficiency of Pretreated Substrates

In order to select the most energy-efficient pretreatment method, the energy balances of the substrates comminuted with the MB11C hammer mill and those extruded with the E-1000 extruder were compared (Figure 6).

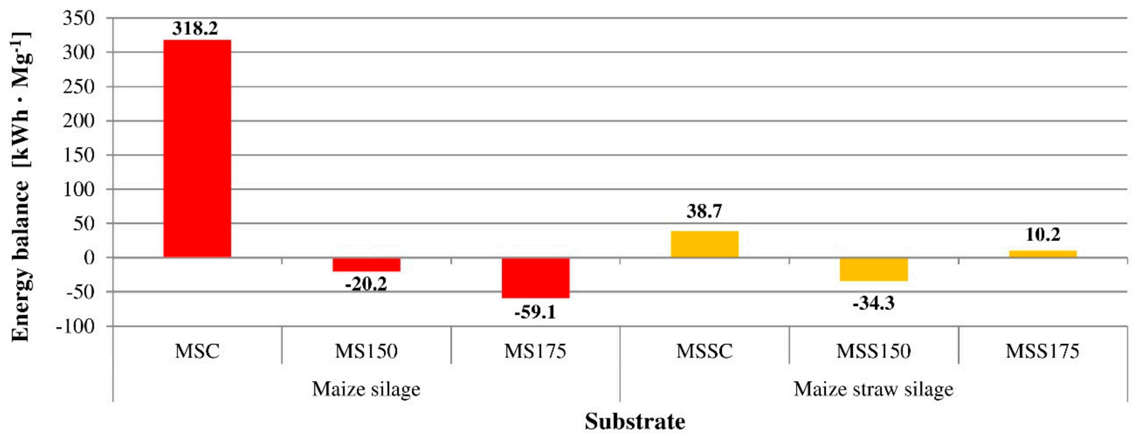

Figure 6. A comparison of the yield of methane in the anaerobic digestion of the substrates comminuted with the MB11C hammer mill and the substrates extruded with E-1000 extruder.

The comparison of the energy efficiency of the comminution and extrusion showed that the comminution of maize silage resulted in a considerable amount of extra energy.

The energy generated in the form of extra biogas yield from half of the substrates compensated for the energy consumed by the mill and extruder in the pretreatment process. The comminution of maize silage resulted in its considerable fragmentation (over 90% with the fraction of 0.25–1.25 mm) and, thus, increased the active surface of the biomass. Lindner et al. [35] analyzed the effect of milling digestate separated from a working biogas plant and a laboratory reactor, and they came to similar conclusions. The biogas plant worked on a mixture of slurry, manure, maize and grass silage, and grain. The laboratory reactor was fed with a mixture of hay, straw, and maize silage. The mechanical treatment increased the methane yield from the biogas plant and the experimental reactor by 9% and 17%, respectively.

The extrusion of silage should also significantly increase the biogas efficiency due to the greater active surface of extruded biomass. The extension of the surface is caused by rapid pressure change (substrate expansion) and thermal hydrolysis of the substrate, as a result of which cellulose and hemicellulose are transformed into simple sugars: xylose, mannose, galactose, and glucose [20]. The research showed that the extrusion of maize silage resulted in negative energy balance. The study conducted by Panepinto et al. [40] showed that the extrusion of maize silage even decreased the methane yield. However, in most cases, the extrusion of substrates increased the methane yield up to 15%.

It is most likely that such a significant difference between the comminuted and extruded substrates was caused by the loss (evaporation) of compounds formed during the ensiling process (lactic and acetic acids) due to the high temperature of extrusion. Moreover, the drop in the energy yield and the increase in temperature in the extruder chamber were caused by the formation of anaerobic digestion inhibitors during extrusion (furfural, hydroxymethylfurfural, levulinic acid, carboxylic acids). This is more likely because extrusion reduced the percentage of cellulose and hemicelluloses. The extrusion of maize silage at 150 °C caused the content of cellulose and hemicellulose to decrease by 11.1% and 7.6%, respectively. The extrusion of maize silage at 175 °C reduced the content of cellulose by as much as 14.84% and the content of hemicellulose by 10.23%. Furthermore, phenolic compounds may have been formed from lignins as a result of high temperatures.

The energy balance of maize straw silage was different. Although the most favorable energy balance was achieved by comminution, the extrusion of maize straw silage at 175 °C also resulted in a positive energy balance. Silva et al. [34] made similar observations in a study, which showed that milling increased the efficiency of wheat straw hydrolysis from 6% to 34%. The mechanical pretreatment reduced the size of particles and, thus, facilitated access to degradable polymers. The fact that the energy balance of comminuted maize straw silage was worse than that of maize silage may have been caused by the poor susceptibility of maize straw to comminution (the share of the largest fraction >1.25 mm was up to 45.6%), which resulted in a lower increase in the active surface. On the other hand, the positive energy balance of the maize straw extruded at 175 °C may have been caused by the formation of products (simple sugars) [42] of thermal hydrolysis as the extrusion temperature process increased (the content of cellulose decreased by more than 5% and the content of hemicellulose decreased by over 4%). Such an increase may also have been caused by the lack or a minimal amount of anaerobic digestion inhibitors in extrudates, thus enabling the acclimation of methanogenic bacteria (the lignin content decreased by only 0.75%). Another cause may have been an increase in the active surface of the substrate extruded at 175 °C. Menardo et al. [39] conducted research on the susceptibility of rice straw silage, maize silage, and triticale silage to extrusion and made similar observations. The extrusion intensified the degradation of organic substances and increased the methane yield by 16%. The mixture containing 10% of rice straw silage resulted in a favorable energy balance. The energy balance of the mixture containing 30% of rice straw silage was close to zero.

The results of the one-way ANOVA type III distribution of the yield of methane from the dry organic matter of all the substrates are shown in Figure 7. The results of the analysis for all the substrates at each temperature level were statistically significant at $\alpha = 0.05$.

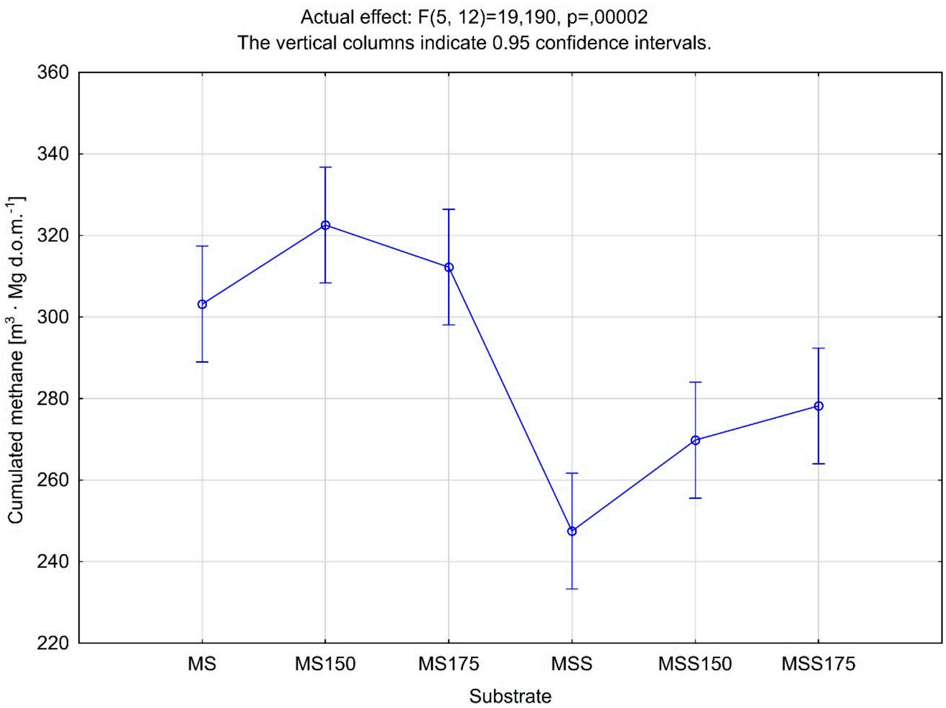

Figure 7. The results of type III one-way ANOVA.

5. Conclusions

The aim of the research presented in this article was to assess the influence of selected pretreatment technologies applied to plant substrates on the course and efficiency of anaerobic digestion. The experiment was conducted to check whether the mechanical pretreatment, as well as the mechanical and thermal pretreatment, of the substrates would increase the anaerobic digestion efficiency sufficiently to produce the amount of electricity exceeding the energy consumed by the pre-treatment machinery. The comparison of the pretreatment methods applied to individual substrates with the devices used in the experiment showed that maize silage should be comminuted, whereas maize straw silage should be extruded at 175 °C.

The comminution and extrusion of maize silage and maize straw silage accelerated the process of their anaerobic digestion. The duration of the process conducted in the laboratory was reduced by one day for the maize silage and by six days for the maize straw.

The extrusion of the maize straw silage at 175 °C resulted in the greatest increase in methane yield per dry organic matter, i.e., 12.4%. The extrusion of the maize silage and maize straw silage at 150 °C increased the methane yield to a lesser extent, i.e., by 6.4% and 9%, respectively.

The comminution of the substrates accelerated their digestion and resulted in a higher yield of methane. The highest increase in the methane yield, i.e., 38.4%, was recorded for maize silage, whereas the increase in the yield of methane from maize straw silage amounted to only 8.3%.

The method used in the study to calculate the pretreatment energy balance makes it possible to check whether the use of any pretreatment device is justified. The method does not determine the cost-effectiveness of pretreatment, because it does not refer to the price of equipment, the costs of its operation, or the costs of its service. However, it indicates that it is irrational to use the devices whose energy consumption is greater than the amount of energy that can be generated by using them. Pre-treatment (comminution, extrusion) is justified if its energy balance is positive.

Extrusion and comminution increase the yield of methane from processed substrates. However, the implementation of these technologies in a biogas plant involves additional costs. Investment costs depend on the efficiency of a particular technology and they range from several dozen to several hundred thousand euros depending on the performance of machines (mill, extruder). The economic balance of such investments should also take the amount of energy consumed by the machine into account—from 30 to even 90 kWh per ton of substrate. Therefore, one should not be guided by cost-cutting when choosing the right technology.

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References

1. Panigrahi, S.; Dubey, B.K. A critical review on operating parameters and strategies to improve the biogas yield from anaerobic digestion of organic fraction of municipal solid waste. *Renew. Energy* **2019**, *143*, 779–797. [CrossRef]
2. Pilarska, A.A.; Pilarski, K.; Waliszewska, B.; Zborowska, M.; Witaszek, K.; Waliszewska, H.; Kolasinski, M.; Szwarc-Rzepka, K. Evaluation of biomethane yields from high-energy organic waste and sewage sludge: A pilot study for a wastewater treatment plant. *Environ. Eng. Manag. J.* **2019**, *18*, 2023–2034. [CrossRef]
3. Chiumenti, A.; Pezzuolo, A.; Boscaro, D.; da Borso, F. Exploitation of mowed grass from green areas by means of anaerobic digestion: Effects of grass conservation methods (drying and ensiling) on biogas and biomethane yield. *Energies* **2019**, *12*, 3244. [CrossRef]
4. Rafique, R.; Poulsen, T.G.; Nizami, A.-S.; Asam, Z.-Z.; Murphy, J.D.; Kiely, G. Effect of thermal, chemical and thermo-chemical pre-treatments to enhance methane production. *Energy* **2010**, *35*, 4556–4561. [CrossRef]
5. Ferella, F.; Cucchiella, F.; D'Adamo, I.; Gallucci, K. A techno-economic assessment of biogas upgrading in a developed market. *J. Clean. Prod.* **2019**, *210*, 945–957. [CrossRef]
6. Patinvoh, R.J.; Osadolor, O.A.; Chandolias, K.; Sárvári Horváth, I.; Taherzadeh, M.J. Innovative pretreatment strategies for biogas production. *Bioresour. Technol.* **2017**, *224*, 13–24. [CrossRef]

7. *Oslo Manual*; The Measurement of Scientific and Technological Activities; OECD: Paris, France, 2005; ISBN 9789264013087.
8. Budzianowski, W.M. A review of potential innovations for production, conditioning and utilization of biogas with multiple-criteria assessment. *Renew. Sustain. Energy Rev.* **2016**, *54*, 1148–1171. [CrossRef]
9. Abraham, A.; Mathew, A.K.; Park, H.; Choi, O.; Sindhu, R.; Parameswaran, B.; Pandey, A.; Park, J.H.; Sang, B.-I. Pretreatment strategies for enhanced biogas production from lignocellulosic biomass. *Bioresour. Technol.* **2020**, *301*, 122725. [CrossRef]
10. Pandiyan, K.; Singh, A.; Singh, S.; Saxena, A.K.; Nain, L. Technological interventions for utilization of crop residues and weedy biomass for second generation bio-ethanol production. *Renew. Energy* **2019**, *132*, 723–741. [CrossRef]
11. Dahunsi, S.O. Mechanical pretreatment of lignocelluloses for enhanced biogas production: Methane yield prediction from biomass structural components. *Bioresour. Technol.* **2019**, *280*, 18–26. [CrossRef]
12. Phuttaro, C.; Sawatdeenarunat, C.; Surendra, K.C.; Boonsawang, P.; Chaiprapat, S.; Khanal, S.K. Anaerobic digestion of hydrothermally-pretreated lignocellulosic biomass: Influence of pretreatment temperatures, inhibitors and soluble organics on methane yield. *Bioresour. Technol.* **2019**, *284*, 128–138. [CrossRef] [PubMed]
13. Erol, M.; Haykiri-Acma, H.; Küçükbayrak, S. Calorific value estimation of biomass from their proximate analyses data. *Renew. Energy* **2010**, *35*, 170–173. [CrossRef]
14. Food and Agriculture Organization of the United Nations (FAO). *FAOSTAT Online Statistical Service*; Food and Agriculture Organization of the United Nations: Rome, Italy, 2019; Available online: http://faostat.fao.org (accessed on 2 December 2019).
15. Mazurkiewicz, J.; Marczuk, A.; Pochwatka, P.; Kujawa, S. Maize straw as a valuable energetic material for biogas plant feeding. *Materials* **2019**, *12*, 3848. [CrossRef] [PubMed]
16. Waliszewska, H.; Zborowska, M.; Stachowiak-Wencek, A.; Waliszewska, B.; Czekała, W. Lignin transformation of one-year-old plants During Anaerobic Digestion (AD). *Polymers* **2019**, *11*, 835. [CrossRef]
17. Li, Y.; Park, S.Y.; Zhu, J. Solid-state anaerobic digestion for methane production from organic waste. *Renew. Sustain. Energy Rev.* **2011**, *15*, 821–826. [CrossRef]
18. Rodriguez, C.; Alaswad, A.; Benyounis, K.Y.; Olabi, A.G. Pretreatment techniques used in biogas production from grass. *Renew. Sustain. Energy Rev.* **2017**, *68*, 1193–1204. [CrossRef]
19. Millati, R.; Wikandari, R.; Ariyanto, T.; Putri, R.U.; Taherzadeh, M.J. Pretreatment technologies for anaerobic digestion of lignocelluloses and toxic feedstocks. *Bioresour. Technol.* **2020**, *304*, 122998. [CrossRef]
20. Duque, A.; Manzanares, P.; Ballesteros, M. Extrusion as a pretreatment for lignocellulosic biomass: Fundamentals and applications. *Renew. Energy* **2017**, *114*, 1427–1441. [CrossRef]
21. Makowska, A.; Baranowska, H.M.; Michniewicz, J.; Chudy, S.; Kowalczewski, P.Ł. Triticale extrudates—Changes of macrostructure, mechanical properties and molecular water dynamics during hydration. *J. Cereal Sci.* **2017**, *74*, 250–255. [CrossRef]
22. Hendriks, A.T.W.M.; Zeeman, G. Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresour. Technol.* **2009**, *100*, 10–18. [CrossRef]
23. Krzyżaniak, M.; Stolarski, M.J.; Waliszewska, B.; Szczukowski, S.; Tworkowski, J.; Załuski, D.; Śnieg, M. Willow biomass as feedstock for an integrated multi-product biorefinery. *Ind. Crops Prod.* **2014**, *58*, 230–237. [CrossRef]
24. Stolarski, M.J.; Krzyzaniak, M.; Waliszewska, B.; Szczukowski, S.; Tworkowski, J.; Zborowska, M. Lignocellulosic biomass derived from agricultural land as industrial and energy feedstock [Dendromasa pozyskana z gruntów rolniczych jako surowiec przemysłowy i energetyczny]. *Drewno* **2013**, *189*, 5–23.
25. Norm DIN 38414-8. *Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung; Schlamm und Sedimente (Gruppe S); Bestimmung des Faulverhaltens (S 8); [German Standard Methods for the Examination of Water, Waste Water and Sludge; Sludge and Sediments (Group S); Determination of the Amenability to Anaerobic Digestion (S 8)]*; Beuth Verlag GmbH: Berlin, Germany, 1985.
26. Technische Regel VDI 4630. *Vergärung organischer Stoffe Substratcharakterisierung, Probenahme, Stoffdatenerhebung, Gärversuche; [Fermentation of Organic Materials Characterization of the Substrate, Sampling, Collection of Material Data, Fermentation Tests]*; Verein Deutscher Ingenieure—German Engineers Club: Düsseldorf, Germany, 2006.

27. Pilarska, A.A.; Pilarski, K.; Witaszek, K.; Waliszewska, H.; Zborowska, M.; Waliszewska, B.; Kolasiński, M.; Szwarc-Rzepka, K. Treatment of dairy waste by anaerobic co-digestion with sewage sludge. *Ecol. Chem. Eng. S* **2016**, *23*, 99–115. [CrossRef]
28. *Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical Measurement*, 3rd ed.; Ellison, S.L.R.; Williams, A. (Eds.) Eurachem/CITAC: London, UK, 2012; ISBN 978-0-948926-30-3.
29. ISO. *Guide to the Expression of Uncertainty in Measurement (GUM)*; ISO: Geneva, Switzerland, 1993.
30. Fischer, M.; Jiang, X. An investigation of the chemical kinetics of biogas combustion. *Fuel* **2015**, *150*, 711–720. [CrossRef]
31. Pilarski, K.; Pilarska, A.A.; Boniecki, P.; Niedbała, G.; Durczak, K.; Witaszek, K.; Mioduszewska, N.; Kowalik, I. The efficiency of industrial and laboratory anaerobic digesters of organic substrates: The use of the biochemical methane potential correction coefficient. *Energies* **2020**, *13*, 1280. [CrossRef]
32. Fjørtoft, K.; Morken, J.; Hanssen, J.F.; Briseid, T. Pre-treatment methods for straw for farm-scale biogas plants. *Biomass Bioenergy* **2019**, *124*, 88–94. [CrossRef]
33. Gallegos, D.; Wedwitschka, H.; Moeller, L.; Zehnsdorf, A.; Stinner, W. Effect of particle size reduction and ensiling fermentation on biogas formation and silage quality of wheat straw. *Bioresour. Technol.* **2017**, *245*, 216–224. [CrossRef]
34. Silva, G.G.D.; Couturier, M.; Berrin, J.-G.; Buléon, A.; Rouau, X. Effects of grinding processes on enzymatic degradation of wheat straw. *Bioresour. Technol.* **2012**, *103*, 192–200. [CrossRef] [PubMed]
35. Lindner, J.; Zielonka, S.; Oechsner, H.; Lemmer, A. Effects of mechanical treatment of digestate after anaerobic digestion on the degree of degradation. *Bioresour. Technol.* **2015**, *178*, 194–200. [CrossRef]
36. Tedesco, S.; Mac Lochlainn, D.; Olabi, A.G. Particle size reduction optimization of Laminaria spp. biomass for enhanced methane production. *Energy* **2014**, *76*, 857–862. [CrossRef]
37. Pilarski, K.; Pilarska, A.; Witaszek, K.; Dworecki, Z.; Żelaziński, T.; Ekielski, A.; Makowska, A.; Michniewicz, J. The impact of extrusion on the biogas and biomethane yield of plant substrates. *J. Ecol. Eng.* **2016**, *17*, 264–272. [CrossRef]
38. Bochmann, G.; Montgomery, L.F.R. Storage and pre-treatment of substrates for biogas production. In *The Biogas Handbook*; Elsevier: Amsterdam, The Netherlands, 2013; pp. 85–103.
39. Menardo, S.; Cacciatore, V.; Balsari, P. Batch and continuous biogas production arising from feed varying in rice straw volumes following pre-treatment with extrusion. *Bioresour. Technol.* **2015**, *180*, 154–161. [CrossRef] [PubMed]
40. Panepinto, D.; Genon, G. Analysis of the extrusion as a pretreatment for the anaerobic digestion process. *Ind. Crops Prod.* **2016**, *83*, 206–212. [CrossRef]
41. Pérez-Rodríguez, N.; García-Bernet, D.; Domínguez, J.M. Extrusion and enzymatic hydrolysis as pretreatments on corn cob for biogas production. *Renew. Energy* **2017**, *107*, 597–603. [CrossRef]
42. Duque, A.; Manzanares, P.; González, A.; Ballesteros, M. Study of the application of alkaline extrusion to the pretreatment of eucalyptus biomass as first step in a bioethanol production process. *Energies* **2018**, *11*, 2961. [CrossRef]