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The Influence of the Pressure-Thermal Agglomeration Methods of Corn Bran on Their Selected Physicochemical Properties and Biogas Efficiency

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Abstract: The article presents the research made on the effects of methods of pressure-thermal agglomeration of corn bran, as well as the influence of processing parameters on selected physicochemical properties and biogas efficiency. Corn bran moistened to four levels of moisture content was used for the tests: 20%, 25%, 30% and 35% of dry matter. The pressure-thermal treatment was carried out with the use of a Brikol SJ25 pellet maker and a TS-45 single-screw extruder. In the tests of the extrusion-cooking process, three rotational speeds of the extruder screw were applied: 70, 90 and 110 rpm. The following characteristics were examined: efficiency of the extrusion-cooking and pelleting process, as well as the energy consumption. The water absorption index (*WAI*), the water solubility index (*WSI*), bulk density, kinetic strength, structure analysis by the *ART/FTIR* method, energy potential and the efficiency of cumulated biogas and cumulated methane per dry mass, as well as fresh mass and fresh organic matter and a series of microscopic pictures were completed. The analysis of the *ATR/FTIR* infrared spectra of the tested pelleted and extruded samples showed clear changes at the molecular level. Biogas production of extruded corn bran increased by several percent, as compared to untreated material.

Keywords: extrusion-cooking process; corn bran; biogas production; fermentation; SME; physical properties; ATR/FTIR spectroscopy

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1. Introduction

Currently, coal-fired power plants and combined heat and power plants are being abandoned as these have a negative impact on the natural environment condition and contribute to the greenhouse effect. One of the ways of obtaining energy and, at the same time, reducing CO_2 emissions is the use of renewable energy resources, including biomass. In Poland, it is estimated that about 10 tons of biomass are obtainable annually from only 1 ha of agricultural land. This is the equivalent of about 5 tons of hard coal [1]. Considering the total area of agricultural land and the possibility of obtaining biomass from state-owned forests, it is possible to obtain biomass amount to the equivalent of 150 million tons of hard coal. Compared to hard coal or lignite, biomass is characterized by a lower calorific value and energy density. Nevertheless, it is an economically viable fuel that can serve as a cheap source of green energy [2]. In addition, agriculture generates many tons of biological wastes or residues each year. Directive 2009/28/EC states that their abundance

reaches 220 billion tons annually [1]. The pro-ecological awareness of many countries is growing, and researchers are looking for alternative energy sources that will allow for a reduction of CO_2 emissions into the atmosphere. The management of waste from the agri-food industry is of increasing importance. One of the most effective ways of using biomass for energy production is its processing via methane fermentation in order to obtain high-energy biogas.

The selection of substrates used in agricultural biogas plants is, however, of great importance for the effectiveness of the process. The composition and quality of the feed mixture determines the quantity and quality of the obtained biogas [3]. Most biogas plants in Europe use plants that are intentionally cultivated for energy purposes. The basic waste sub-losses are mixtures of agricultural and animal origins [4,5].

The most common crop for fodder, food and energy purposes is corn/maize. It is characterized by a high yield of green mass and the fact that many varieties are adaptable to changing agroclimatic conditions [6,7]. Another important aspect in the use of maize is a very favorable composition in terms of methane fermentation [8,9]. Maize intended for energy purposes as a targeted crop should not have major impact on food production. This is due to the different characteristics of crops—in the food industry, starch or waxy maize varieties containing one type of starch are more acceptable [10,11]. However, the occupation of fertile land by energy crops may be controversial.

Currently, a dynamic increase in the demand for corn grain for food applications is observed on the Polish market. The growing interest in gluten-free products made from domestic raw materials compels food producers to buy corn grits and flour from Polish producers. For the production of starch, the wet grinding method is applied, in which fully developed, healthy and undamaged corn grains are the base stock. The effect of soaking the grains and the degree of their damage have a significant impact on the size of the obtained starch granules [12–14]. Grinding removes some of the outer layers of corn, named bran, which are rich in vitamins and minerals, but as a by-product they are used only as animal feed [15–17]. Corn bran contains cellulose (150–200 g kg^{-1}), hemicellulose (400–500 g kg^{-1}) and lignin (80–130 g kg^{-1}). The high content of arabinoxylan (70%) makes them a good source for the production of xylooligosaccharides and other soluble dietary fibers [18,19]. The use of the extrusion-cooking process as a pretreatment increases the content of soluble fibers in bran and breaks the cellulose fraction [20]. Corn is processed not only for its grain, but also for its remaining parts. It is exploited in its entirety for the production of silage, which, due to its high energy value and digestibility, is used in feeding pigs. Another application of maize silage is its use as input for agricultural biogas plants [4]. Due to the high sugar content, it is one of the most common additives.

Unfortunately, more and more frequent droughts, as well as the mass occurrence of pests and diseases of maize are not conducive to increasing the area of its cultivation. Moreover, high demand for raw materials for biogas plants may result in the emergence of maize monocultures, which has a negative impact on agroecosystems [21]. Thus, as an alternative biogas substrate, it was decided to use corn wastes, but still those derived from crops grown for food purposes in the form of corn bran. Similar studies have already been carried out [22], but not with the use of extrusion-cooking pretreatment to break up difficult-to-ferment cellulose fibers.

Therefore, the study investigated the possibility of forming corn bran into an easy-to-transport fuel by assessing the conditions of their processing for best physicochemical properties and biogas profitability. In doing this, attenuated total reflectance Fourier transform infrared spectroscopy (*ATR/FTIR*) measurements were applied to evaluate changes at the molecular level after pelleting and extrusion-cooking processes. Herein, *FTIR* gives the possibility to identify the marker bands responsible for sample structure modification as a result of the employed processing factors of variable rotational speed of the screw or changes in sample moisture content. The aim of the research was to compare the methods of pressure-thermal agglomeration of corn bran and the influence of processing conditions

on selected physicochemical properties of the obtained products in the form of extrudates and pellets.

2. Materials and Methods

The research was carried out on extrudates made of corn bran obtained from Pol-Foods Sp. z o.o. (Prostki, Poland). The corn bran was moistened to an initial moisture content (*MC*) of 20%, 25%, 30% and 35%. In the experiment, a TS-45 single-screw extruder (Meacham, Gliwice, Poland) and a Brikol SJ25 pellet press (PPHU Brikol Marcin Poźniak, Człuchów, Poland) with comparable nominal capacity depending on the type of raw material processed were used. The temperature of the extrusion-cooking process was within the range of 130–145 °C, and a die diameter of 8 mm was employed. Three rotational screw speeds of the extruder were used in the research (70 rpm, 90 rpm and 110 rpm, marked as extr 70 rpm, extr 90 rpm and extr 110 rpm, respectively). Separately, the pelleting of corn bran (pel) was done with a matrix size of 8 mm.

2.1. Processing Efficiency

Processing efficiency was ascertained by determining the mass of product obtained in a given time for all used raw materials and the assumed processing parameters. The measurements were carried out three times for each test series, taking the mean of the measurements as the final results. The efficiency was determined by the formula:

$$Q = \frac{m}{t} \left[\text{kg h}^{-1}\right] \quad (1)$$

where Q is the processing efficiency, m is the mass obtained during the measurement (kg) and t is the measurement time (h).

2.2. Energy Consumption during Corn Bran Pretreatment

In the case of the pellet making pretreatment, the unit energy inputs *Ej* (kWh kg^{-1}) incurred in the pelleting process were adjudged. Electricity consumption was recorded using the KEW6310 (Kyoritsu Electrical Instruments Works Ltd., Tokyo, Japan) power quality analyzer. First, the energy consumption for the own needs of the device operation to overcome mechanical resistance, *Eo* (kWh), was determined without biomass load. Electricity consumption (gross) *Eb* (kWh) was then measured during the pelleting process with various initial moisture content. After deducting from the gross energy (*Eb*—the energy lost to overcome the resistivity *Eo*), and relating this difference to the mass of produced pellets (*m*) (kg), the energy consumption (net) of the pelletization process *Ej* (kWh kg^{-1}) was subsequently determined by applying the formula:

$$E_j = \frac{E_b - E_o}{m} = \frac{E}{m}\left[\text{kWh kg}^{-1}\right] \quad (2)$$

where *Ej* is the energy consumption, *E* is the net energy inputs (kWh) and *m* is the mass of pellets obtained (kg).

The measurements for each variant were repeated three times and the obtained arithmetic mean value was indicated as the final result.

During extrusion-cooking pretreatment, energy consumption measurements were undertaken with drive parameters (including load) and the efficiency of processing was also taken into account [23–25]. Energy consumption was determined based on the specific mechanical energy (*SME*) value using the formula proposed by Ryu and Ng [26]:

$$SME = \frac{n\ P\ O}{n_m\ Q}\ \left[\text{kWh kg}^{-1}\right] \quad (3)$$

where *SME* is the specific mechanical energy, n is the extruder screw speed (rpm), n_m is the extruder nominal speed (rpm), O is the drive load vs. maximum load (%), P is the nominal power (kW) and Q is the extrusion-cooking efficiency (kg h^{-1}).

2.3. Testing the Water Absorption Index (WAI)

The processed corn bran samples obtained as a result of various pretreatments were ground into particles with a size less than 0.3 mm using a laboratory mill. From each sample, 0.7 g was dissolved in 7 mL of distilled water and the suspension was continuously stirred for 20 min. The obtained suspension was then centrifuged at 15,000 rpm for 10 min in a Digicen 21 (OrtoAlresa, Madrid, Spain) laboratory centrifuge. The filtrate was decanted over the obtained gel, and the obtained gel was weighed. The water absorption index was calculated according to the formula [27,28]:

$$WAI = \frac{m_g}{m_s} \left[\mathrm{g\,g^{-1}}\right] \quad (4)$$

where *WAI* is the water absorption index, m_g is the gel mass (g) and m_s is the sample mass (g).

2.4. Study of the Degree of Water Solubility Index (WSI)

The filtrate obtained during the measurement of the *WAI* was dried at 105 °C until the water was completely evaporated. The water solubility index was calculated according to the formula [25]:

$$WSI = \frac{m_{ds}}{m_s} \times 100\ (\%) \quad (5)$$

where: *WSI* is the water solubility index, m_{ds} is the mass of the sample after drying (g), m_s is the sample mass (g).

2.5. Study of the Bulk Density of Processed Corn Bran

The density was measured according to BN-87/9135-09 [29] by placing the tested material through free fall into a 1000 cm^3 vessel, scraping off the excess material and then weighing the vessel with an accuracy of 0.01 g. The bulk density was calculated from the obtained mass according to the formula:

$$\rho_u = \frac{m_s}{v} \left[\mathrm{kg\,m^{-3}}\right] \quad (6)$$

where ρ_u is the bulk density, m_s is the sample mass (kg) and v is the sample volume (m^3).

The measurements were performed in three repetitions, and the arithmetic mean was taken as the final result.

2.6. Test of the Durability of Pretreated Corn Bran

The durability was measured twice using the Pfost apparatus as source of kinetic strength during rotation in a closed chamber. In undertaking this, 100 g of the sample was placed inside the apparatus chamber and rotated for 10 min. The weight of the uncrushed sample was subsequently determined in relation to the weight of the initial sample. Durability was ascertained through use of the formula:

$$D = \frac{m_u}{m_s} \times 100\ (\%) \quad (7)$$

where: D is the durability (%), m_u is the mass of uncrushed sample (g) and m_s is the sample mass (g).

2.7. Methane Fermentation of the Processed Raw Materials

Biogas efficiency of the tested substrates was evaluated depending on the method of pretreatment and the initial moisture of the corn bran. The tests were conducted in the Laboratory of Ecotechnologies at Poznan University of Life Sciences (PULS). This is the best-equipped laboratory for this type of research in Poland (with over 250 different fermenters), and the scientific team had obtained (the first in Poland) certificates issued by KTBL and

VDLUFA (the Association of German Agricultural Analytic and Research Institutes) in 2017. In our experiment, biogas efficiency was investigated by applying methane fermentation under mesophilic conditions (the most popular technology in Europe), in three replications, using a proprietary biofermenter (Figure 1).

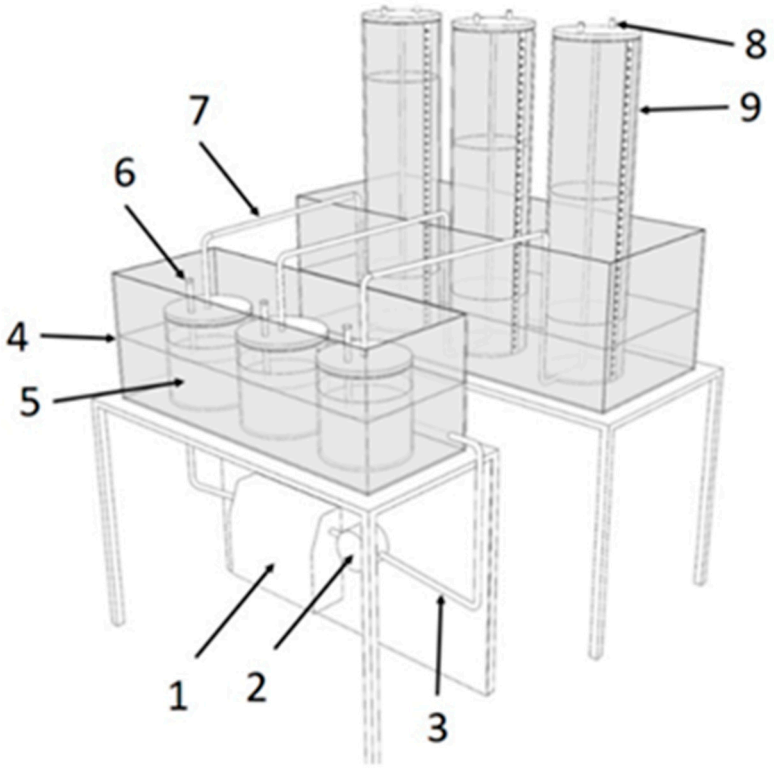

Figure 1. Scheme of research biofermenter for biogas production (three-chamber section): 1—water heater with temperature regulator, 2—water pump, 3—insulated conductors of calefaction liquid, 4—water coat, 5—fermenter with charge capacity 2 dm^3, 6—sampling tubes, 7—biogas transporting tube, 8—gas sampling valve and 9—biogas volume-scale reservoir [30].

The pretreated samples were analyzed for biogas efficiency according to standard methodologies (DIN 38414/S8 and VDI 4630) [21]. The biogas production experiment was carried out under standard methane fermentation conditions in sets of 3 tank biofermenters [31]. Fermentation reactors with a capacity of 2 dm^3 were first filled with the inoculum (a dose of microorganisms from the operating biogas plant) and the corn bran that was processed under various conditions. The content of organic dry matter in the inoculum ranged from 1.5% to 2%. Dry matter and organic dry matter were checked prior to testing, and the substrates were placed in an airtight fermentation reactor. The sample tanks were placed in water at controlled temperature (approx. 39 °C), which simulated the actual operating conditions of commercial biogas installations. The volume and qualitative composition of the produced gases was measured every 24 h. The fermentation process was stopped when the daily biogas production was lower than 1% of the total biogas production during last 24 h. Samples were tested in triplicate. Biogas yield (m^3 Mg^{-1}) was based on fresh mass (corn bran), dry mass and dry organic matter, as described by Dach et al. [32].

2.8. The Energy Potential of the Substrate

The energy potential of pretreated corn bran was evaluated by determining the elemental composition and heat of combustion. Moisture content (M) was assessed using the thermogravimetric method in accordance with the requirements of EN ISO 18134 [33]; volatile compounds (V) were ascertained according to EN ISO 18123 [34], and ash content

(A) was evaluated according to EN ISO 18122 [35] using the LECO TGA 701 thermogravimeter (LECO Corporation, Saint Joseph, MI, USA). Carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) contents were determined with a LECO CHNS 628 elemental analyzer (LECO Corporation, Saint Joseph, MI, USA). The bound carbon (BC) content was defined by difference up to 100%. The elemental composition (C, H, N, S) of the combustible substance was adjudged in samples in the dry state.

The heat of combustion (HHV) was determined on the LECO AC 600 isoperibolic calorimeter (LECO Corporation, Saint Joseph MI, USA) according to EN ISO 18125:2017-07 [36] standard. Based on the heat of combustion (HHV), the calorific value (LHV) was calculated for the selected substrate humidity. Determinations were performed on samples in a dry state in triplicate.

2.9. Infrared Spectra Measurements

Measurements of the infrared spectra of the tested samples were made with the IRSpririt spectrometer (Shimadzu, Kyoto, Japan). An attenuated total reflection (ATR) snap-in was used for the measurements, with a ZnSe crystal with a specific geometry (i.e., truncated at 45°) in order to ensure a 20-fold internal reflection of the absorbed beam. During the measurements, 24 scans of each sample were recorded, and then the program averaged the results for all collected spectra. Before each measurement, the crystal was thoroughly purged using ultra-clear and pure solvents purchased from Sigma-Aldrich. For 1 h before and during the measurement, the measuring chamber was kept under an inert atmosphere of N_2 gas. Spectral measurements were recorded in the range from 500 to 3750 cm^{-1}, with a very good resolution of 0.5 cm^{-1}. Spectra measurements were carried out in the Laboratory of the Department of Biophysics at the University of Life Sciences in Lublin. Finally, the spectra were analyzed and processed with the Grams/AI software (ThermoGalactic Industries, Salem, NH, USA). All spectra were measured at room temperature.

2.10. Microscopic Structure

An Olympus CX41 microscope (Olympus Europa Holding, Hamburg, Germany) equipped with a camera with an Olympus C5060 adapter was used to take the pictures. A 40× magnification of the image was applied, and then pictures were taken using reflected light. The pictures were taken for the control sample (untreated) and for the pelletized and extruded corn bran.

2.11. Statistical Analysis

Statistical analysis was performed using the Statistica 13.1 software (StatSoft, Tulsa, OK, USA). Statistical differences between the mean values were determined using the multiple regression equation. The initial humidity and screw speed used during processing were analyzed as independent variables.

3. Results

In mills dealing with the grinding of corn for food purposes, there is a big problem with the management of wastes in a form of corn bran. The most popular method of corn bran management is fodder production. This research was aimed at determining the possibility of using the corn bran as a substrate for energy purposes. Corn bran consists largely of cellulose, hemicellulose and lignins. The use of pressure-thermal pretreatment allows for the agglomeration of bran. Combined mechanical and enzymatic pretreatment can give satisfactory results in destruction of cellulosic biomass structure to make cellulose more accessible to the enzymes in fermentation process. The most popular is alkali treatment of lignocellulosic substances, which disrupts the cell walls by dissolving hemicellulose and lignin in fibrous raw materials, increasing the biodegradability of the cell walls due to cleavage of the bonds between lignin and cellulose [37]. The extrusion process is successfully used in the treatment of typical waste lignocellulosic materials such as straw or

hay. The application of the extrusion-cooking technique in the processing of lignocellulosic materials in the form of corn or cereal straw allowed for the increase the biogas efficiency by up to 70% compared to non-extruded samples [38]. By means of the conducted research, we were able to obtain new knowledge as to whether the additional energy expenditure incurred for the processing of bran has economic justification. Extruded and pelleted samples were used in the research. The employment of process variables, as well as different moisture content of raw materials allowed for developing guidelines for potential best bran processing practices for energy purposes. During the tests, no major deviations from single measurements were observed.

3.1. Results of Processing Efficiency

The efficiency of the corn bran extrusion-cooking process largely depends on many factors. Among these are the humidity of the mixture subjected to the extrusion process and the rotational speed of the extruder screw. The method of agglomeration of corn bran had a significant impact on the efficiency of the process. The working element in the extruder is a screw rotating in the barrel. The processed material is subjected to high temperature, shear forces and pressure. These conditions result in lower extrusion efficiency compared to the flat die pelleting process. The Table 1 shows the measurement results for the bran subjected to the pelleting process. It was observed that the efficiency of the extrusion and pelleting process of corn bran (Table 1) was significantly affected by the initial moisture of the raw materials. As the moisture content of corn bran increased, the efficiency of the extrusion and pelleting process increased.

Table 1. Results of measurements of the physical properties of pelleted corn bran.

MC (%)	*Q* (kg h^{-1})	*SME* (kWh kg^{-1})	*WAI* (g g^{-1})	*WSI* (%)	ρ_u (kg m^{-3})	*D* (%)
20	68.18	0.0084	2.24	5.16	504.0	99.30
25	75.00	0.0090	2.34	2.94	486.0	99.41
30	73.17	0.0096	2.26	8.44	452.2	99.54
35	78.95	0.0073	2.41	9.78	439.4	99.83

An additional factor determining the increase in the efficiency of the extrusion process is the rotational speed of the extruder screw (Figure 2). The highest efficiency of the corn bran extrusion process was recorded for the samples processed at the screw speed of 110 rpm (50.4 kg h^{-1}) and at a 30% moisture level. Almost double lower efficiency (27.84 kg h^{-1}) was found at the rotational speed of the extruder screw at 70 rpm and at 20% moistening level. Pelletized materials were characterized by significantly higher efficiency. The highest measurement (78.95 kg h^{-1}) was obtained during pelleting of the raw material with a 35% moisture level. The lowest efficiency of pelletized corn bran (68.18 kg h^{-1}) was recorded for the 20% moisture level. This is comparable with the work of Sobota and Rzedzicki [39], who, in applying single-screw extrusion and undertaking similar extruder processing of a mixture of corn semolina with oat bran, achieved the process efficiency of 22 kg h^{-1} with the use of mixtures with a 12% moisture level, but in increasing the moisture level to 16%, the process efficiency decreased to 18 kg h^{-1}. Sobota and Rzedzicki [39] used blends of semolina with oat bran in the experiment, but in our work, only pure corn bran was used. Probably, the application of semolina, which contains a lot of starch, made the blends easy to gelatinize during the extrusion-cooking process, increasing the dough viscosity and thus lowering the efficiency, because the increase in moisture content gives the possibility to gelatinize a higher amount of starch in semolina, causing a high density of the processed dough. Because of the low amount of starch available for gelatinization in pure corn bran, increasing the level of moisture content works as a lubricant, lowering the shearing forces inside the extruded material, thus increasing the ability of the treated material to have easier movement of bran inside the extruder without high-shearing forces

and with a low starch gelatinization level. Additionally, the composition of oat bran is different than corn bran so it can have an effect on processing efficiency. Thus, additional research can be done for an oat bran with similar methodology.

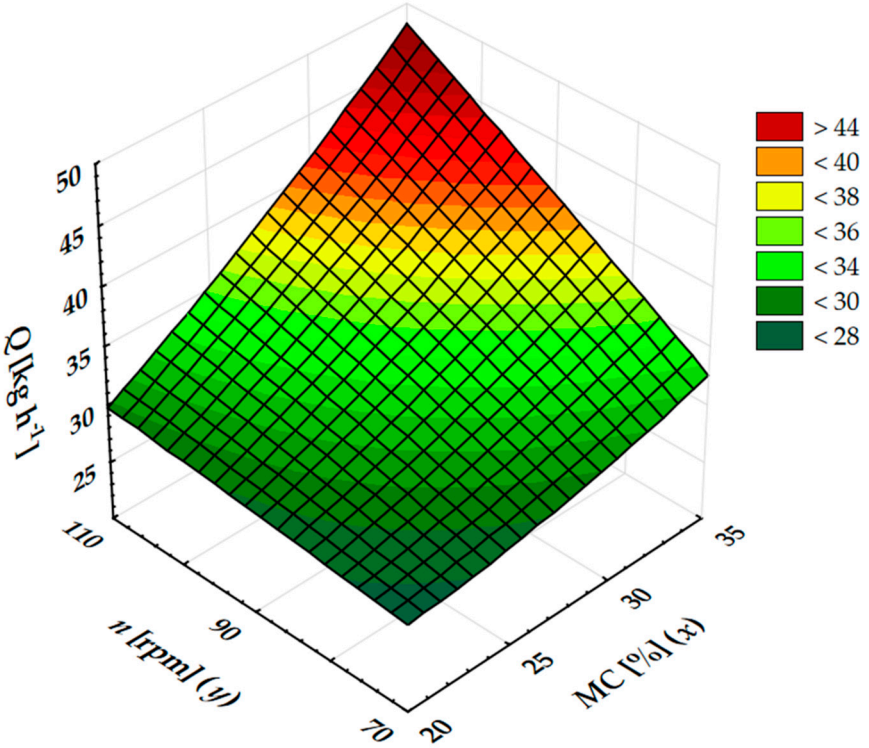

Figure 2. The influence of the rotational speed of the extruder screw and the level of raw material moisture on the efficiency of the extrusion process.

3.2. Results of the Energy Consumption during the Corn Bran Processing

Another important and even basic parameter determining the economic success of the pressure-thermal pretreatment of corn bran is the incurred energy expenditure. Extrusion-cooking processing is much more energy consuming than the pelleting process. However, raw material transformation at temperatures ranging from 130 to 145 °C and high pressure causes destruction of the lignocellulosic structures, which, in the case of fibrous substrates, is translated into an increase in biogas production efficiency [40]. The decisive factor influencing the energy demands, in addition to the extruder screw speed, is the appropriate selection of the moisture content of the raw materials subjected to the extrusion-cooking process. It is thus necessary to find optimal processing conditions related to the possibly highest biogas efficiency of the processed substrates. However, economically, the extrusion-cooking process is a more energy-consuming process compared to pelletization. This is due to the necessity to heat the device at the stage of preparation for operation and the energy expenditure needed to carry out the process itself. During pelleting, there is no need to heat up the device, as heat is generated spontaneously by friction.

In the case of the extrusion-cooking process, the increased moisture level of corn bran induced a decrease in energy consumption in the extrusion pretreatment. The increase in the screw rotational speed enhanced the energy consumption of the process. Figure 3 shows the effects of the rotational screw speed and the level of moistening of corn bran on the energy consumption of the extrusion processing. We observed that the energy consumption of the extrusion cooking of corn bran decreased with the increase of moistening level. The highest energy consumption of the corn bran extrusion process was 0.247 kWh kg^{-1} at the 110 rpm screw speed and the moisture of the raw material at 20%, and the lowest (0.068 kWh kg^{-1}) was found at 70 rpm screw speed and the moisture level of the corn bran at 35%.

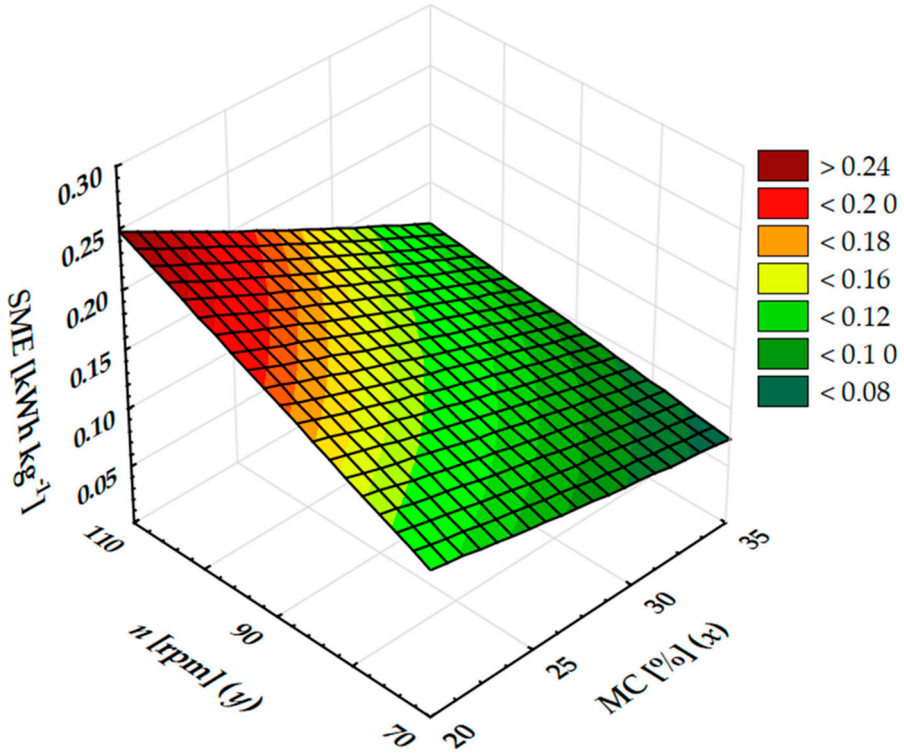

Figure 3. The influence of the rotational speed of the extruder screw and the level of raw material moisture on the energy consumption of the extrusion process.

Due to lower energy expenditure and a different structure of the agglomerating working element, the pelletization tests were characterized by a lower energy consumption during processing. In the case of this pretreatment, the highest measurement (0.0096 kWh kg^{-1}) was recorded for the raw material with a 30% moisture level, and the lowest (0.0073 kWh kg^{-1}) was for the corn bran with a 35% moisture level (Table 1). Pardhi et al. [40] reported the results of measuring the energy consumption of the brown rice extrusion process, where the energy demand ranges from 0.101 to 0.138 kWh kg^{-1}. The obtained energy consumption values are comparable to those obtained during the extrusion cooking of corn bran. Moreover, as reported by Roye [41], the energy consumption of the wheat bran extrusion processing was at the range of 0.026–0.046 kWh kg^{-1}.

3.3. Results of the Water Absorption Index (WAI)

The substrates used in agricultural biogas plants, especially waste lignocellulosic biomass, are subjected to various treatments aimed at accelerating methane fermentation and increasing biogas efficiency [42]. One method is the extrusion process. The destruction of lignocellulosic structures affects the degree of water absorption. A common problem in fermentation chambers is the formation of a scum on their surface, which results in blockage of the fermenter. The value of the *WAI* shows to what extent the processed material absorbs water, which may cause it to sink to the bottom during mixing in the fermentation chamber without causing its retention. A higher water absorption index may also affect the solubility index (*WSI*), thanks to which the charge will be better mixed and dissolved, which should be reflected in improvements in the course of the methane fermentation process.

The highest water absorption index was recorded for extruded corn bran (3.99 g g^{-1}) processed at the rotational screw speed of 110 rpm and at 20% of the initial moisture content (Figure 4). The lowest values of *WAI* (2.20 g g^{-1}) were observed in the case of bran moistened to 35% in the entire range of the rotational speeds of the extruder screw. Such a high initial moisture acts as a solvent and limits the shear forces inside the extruder and, hence, impedes change within the fibrous material. With the increase in the screw speed

in all pretreated raw materials, an increase in the water adsorption index was observed. Corn bran pelleted from mixtures with moisture content of 20% showed the lowest value of the *WAI* index (2.24 g g^{-1}) (Table 1). This demonstrates that the pelleting process will not change sufficiently the structure of corn bran, and therefore the lignocellulose complexes have not been destroyed. These observations are confirmed in the analysis of the microscopic pictures of pretreated samples. In similar work, Żelaziński [43] describes the extrusion of corn whole grains and buckwheat. His research shows higher results of *WAI* (5.04 g g^{-1} for buckwheat and 4.66 g g^{-1} for corn), whereas in the case of brown rice extrusion, the obtained values ranged from 4.72 to 7.81 g g^{-1} [40].

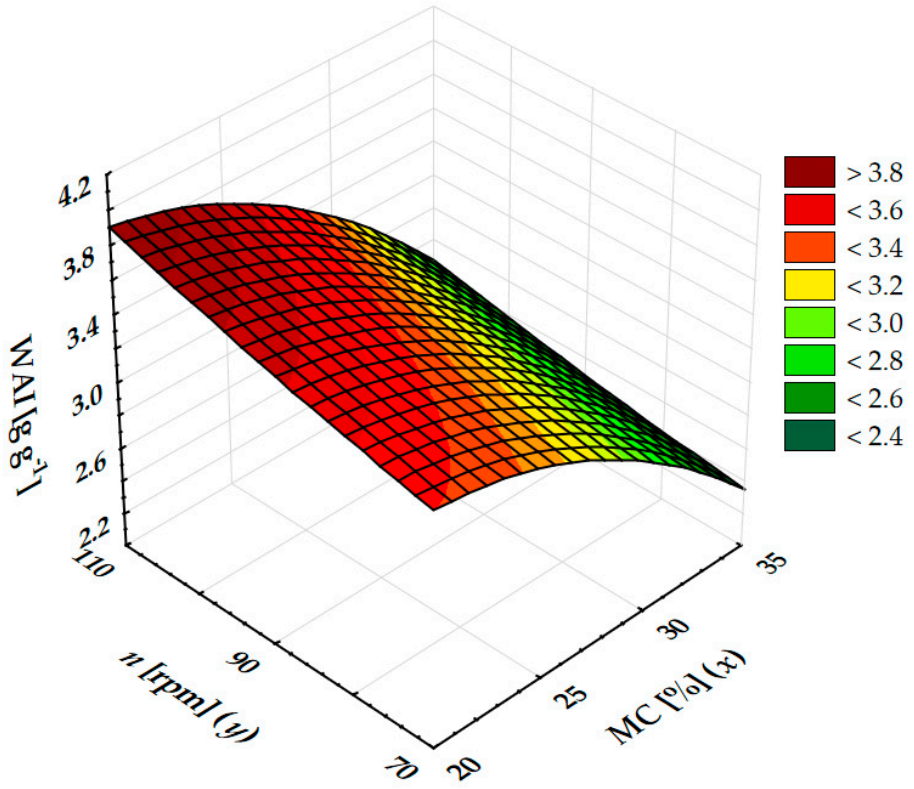

Figure 4. The influence of the rotational speed of the extruder screw and the level of raw material moisture on the water absorption index (*WAI*).

3.4. Results of the Water Solubility Index (WSI)

The *WSI* index determines the extent to which processed corn bran can dissolve in water as the number of soluble particles after moistening. As a result of thermal or pressure pretreatment, the material breaks down into smaller particles, which accelerates the methane fermentation process. The method of raw material pretreatment may be an important factor influencing the value of this indicator. As was shown in the later studies of the analysis with the use of infrared *FTIR* spectroscopy and the analysis of microscopic pictures, the degree of agglomeration of the corn components may be an important factor affecting the degree of solubility. Samples with a compact structure absorb water to a lesser extent, which means that the degree of solubility is lower, and in the case of samples with a non-compacted structure (pelleted and expanded—in the case of extrusion), this process is more effective.

In the case of the extrusion-cooking process, the samples processed at the extruder screw speed of 110 rpm and the 20% level of moisture content were characterized by the highest degree of water solubility (8.88%), as shown in Figure 5. The lowest measurement (4.51%) was recorded for the samples treated with the lowest process variables (70 rpm and 20% moisture level). Both the lowest (2.94%) and the highest degree of solubility (9.78%) were found for pelleted corn bran. The lowest measurements were recorded at a

25% moisture level, and the highest at a 35% moisture level (Table 1). According to pelleted corn bran, the lowest solubility of corn bran could be observed with the bran treated at 25% of initial moisture; this could suggest this level of moisture as the most adequate to bind strongly corn bran pelleted at the conditions and with the equipment used in the experiment. In similar work, extruded buckwheat grains [43] were characterized by a much higher *WSI* index (22.63%). Moreover, samples of brown rice were characterized by almost double lower *WSI* (up to 14.32%) [40], but still higher that observed for fibrous corn bran.

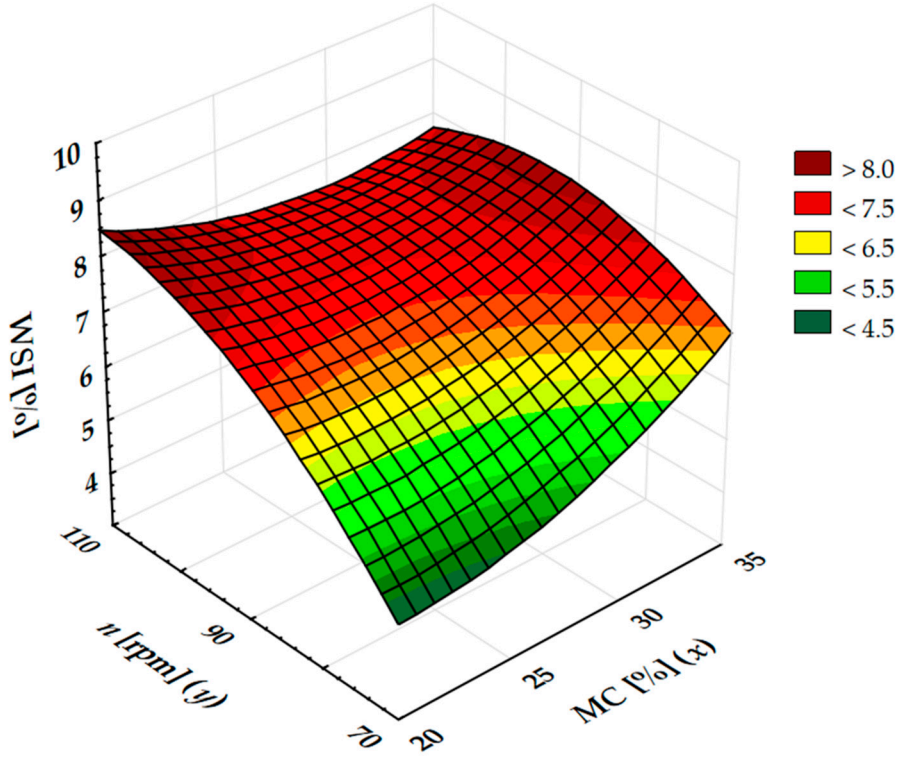

Figure 5. The influence of the rotational speed of the extruder screw and the level of raw material moisture on the water solubility index (*WSI*).

3.5. Results of the Bulk Density of Processed Corn Bran

Another tested parameter was the bulk density of both the extruded and pelleted corn bran. The use of an appropriate pressure or pressure-thermal agglomeration method allows one to significantly reduce the storage area of the loose materials (bran) supplied by the milling industry. The highest bulk density (605.6 kg m^{-3}) was recorded for the bran extruded with the use of 90 rpm screw speed at a 30% moisture level. The lowest value (436 kg m^{-3}) was observed for extruded corn bran with a 20% of moisture level and 110 rpm of the rotational screw speed were applied during pretreatment. Only in the case of 110 rpm, along with an increase in the moistening level, was an increase evident in the bulk density (Figure 6). In the case of pelleted samples, an increase in the initial moisture content brought about a decrease in the bulk density (Table 1). During the pressure pretreatment process, the highest measurement was 504 kg m^{-3} and the lowest was 439.4 kg m^{-3}. The bulk density of extruded instant porridges (50% corn groats: 50% buckwheat groats), according to Wójtowicz [40], was 201–297 kg m^{-3}, which gives much lower results compared to corn bran. This may be due to different granulation and moisture content of the processed material, as well as the higher content of starch in flours other than in bran. These are structural components, so the product was more expanded, which is related to a lower bulk density.

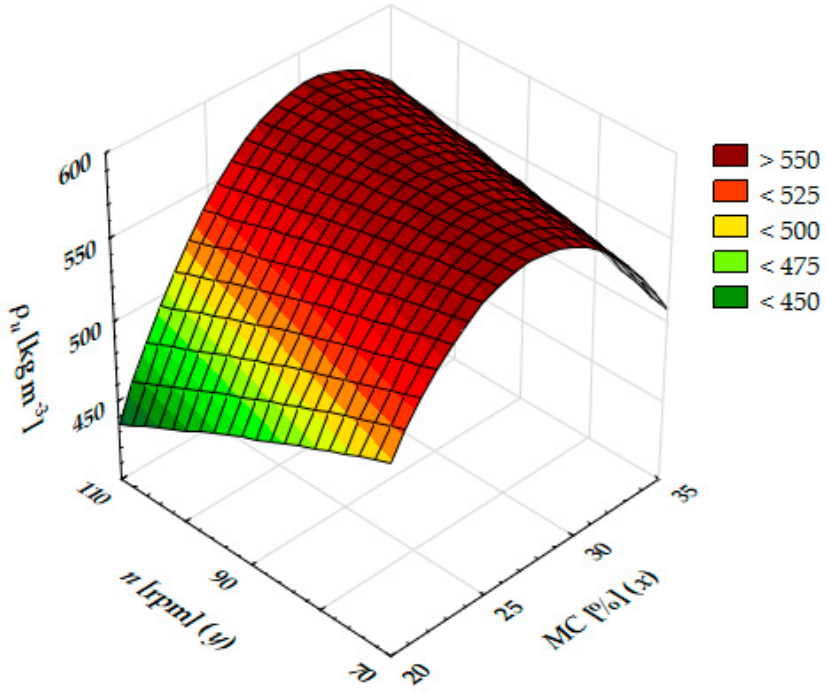

Figure 6. Influence of the rotational speed of the extruder screw and the level of raw material moisture on the bulk density of the extrudate.

3.6. Results of the Durability Measurements of Processed Corn Bran

Measurement of the kinetic strength, called durability, is aimed at determining the resistance of the processed material to the conditions prevailing during transportation and storage. This is an important parameter that determines whether a given substrate will be processed and stored within the biogas plant, or whether it will be processed at, for example, a farm complex and transported to the biogas plant as a ready input to the fermentation chamber. It is important that the processed material achieves higher values of durability during transport, and at the same time it should be brittle enough to delaminate during contact with water. Figure 7 shows the dependences of the rotational screw speeds and the influence of the moisture level on the durability of the obtained extrudates. As indicated in the figure, the durability of the extrudates increased with the increase in moistening level. In contrast, lowering of durability was observed when a higher screw rpm was applied during processing. This indicates that the extrusion-cooking pretreatment process of corn bran with intensive mechanical treatment at higher rotational screw speeds affects durability to a great extent. This outcome is due to the more intensive shear forces and more porous structure induced by the cooking effect at high extrusion speed and low moisture content. In the extruded samples, starch still present in the bran is gelatinizing and binds with the husk, and the cellulose is strongly bound in the starch matrix, especially at increased moisture of raw material. This is reflected to the results of the infrared spectra analysis (Figure 8) and of microscopic structure analysis, which show a continuous cross-sectional structure of the extrudates along with the remaining husk that is characteristic for cereal materials. The highest value of durability (99.35%) was observed in the case of bran extruded at the lowest screw speed of 70 rpm and with a 35% level of moistening. The lowest durability (97.94%) was recorded for the samples processed at a 20% moisture level and at 110 rpm. The results of durability of the pellets are higher compared to the extrudates (Table 1.). During the pelleting process, the raw material is exposed to very high pressure, so the pellets have higher mechanical strength. This situation is also confirmed by the microscopic observations. Samples with test outcomes of 99.83% were characterized by having the highest durability; thus, the highest resistance was recorded for pelleted samples processed at a 35% moisture level. In the case of pelletization,

the lowest measurement of durability (99.30%) was recorded for samples with the lowest level of moisture content (Table 1).

Tables 2 and 3 present the results of the statistical analysis of the influence of the extruder screw speed and the moisture level of the mixtures on the physical properties of the resulting extrudates.

Table 2. Multiple regression equations of process efficiency and energy consumption and physical properties of extruded corn bran.

Parameter	Quadratic RSM Model
Q	$55.4333 - 1.9937{*}x - 0.3356{*}y + 0.014{*}x^2 + 0.0223{*}x{*}y - 0.0003{*}y^2$
SME	$-0.923 + 0.0037{*}x + 0.0061{*}y + 4.6667^{E-5}{*}x^2 - 0.0001{*}x{*}y - 1.25^{E-6}{*}y^2$
WAI	$1.1037 + 0.1753{*}x + 0.008{*}y - 0.0041{*}x^2 - 0.0003{*}x{*}y + 5.9375^{E-5}{*}y^2$
WSI	$-19.9876 - 0.0244{*}x + 0.5411{*}y + 0.0093{*}x^2 - 0.0049{*}x{*}y - 0.0019{*}y^2$
ρ_u	$10.3829 + 56.4577{*}x - 5.2228{*}y - 1.3167{*}x^2 + 0.2171{*}x{*}y - 0.0067{*}y^2$
D	$97.7836 + 0.1337{*}x - 0.0149{*}y - 0.003{*}x^2 + 0.001{*}x{*}y - 0.0002{*}y^2$

Table 3. Results of the ANOVA of the effects of processing conditions and their interactions on the tested properties of extruded corn bran.

Depandent Variable	Independent Variable	Sum of Square Effect	df Effect	Mean Square Effect	F-Test	*p* Value
Q	*x*	763.43	3	254.48	3816.10	0.00
	y	481.52	2	240.76	3610.40	0.00
	x∗*y*	495.92	6	82.65	1239.40	0.00
SME	*x*	0.0454	3	0.0151	10193.70	0.00
	y	0.0402	2	0.0201	13538.30	0.00
	x∗*y*	0.0119	6	0.0019	1333.40	0.00
WAI	*x*	6.8794	3	2.2931	136.65	0.0000
	y	1.0144	2	0.5072	30.22	0.0000
	x∗*y*	1.7105	6	0.2851	16.99	0.0000
WSI	*x*	4.497	3	1.499	1.79	0.1752
	y	36.009	2	18.004	21.54	0.000004
	x∗*y*	26.906	6	4.484	5.36	0.0012
ρ_u	*x*	0.0941	3	0.0314	674.30	0.0000
	y	0.0033	2	0.0017	35.90	0.0000
	x∗*y*	0.0474	6	0.0079	169.80	0.0000
D	*x*	4.90	3	1.60	77.00	0.0000
	y	4.00	2	2.00	94.00	0.0000
	x∗*y*	3.00	6	0.50	24.00	0.0000

x—moisture content; *y*—screw speed.

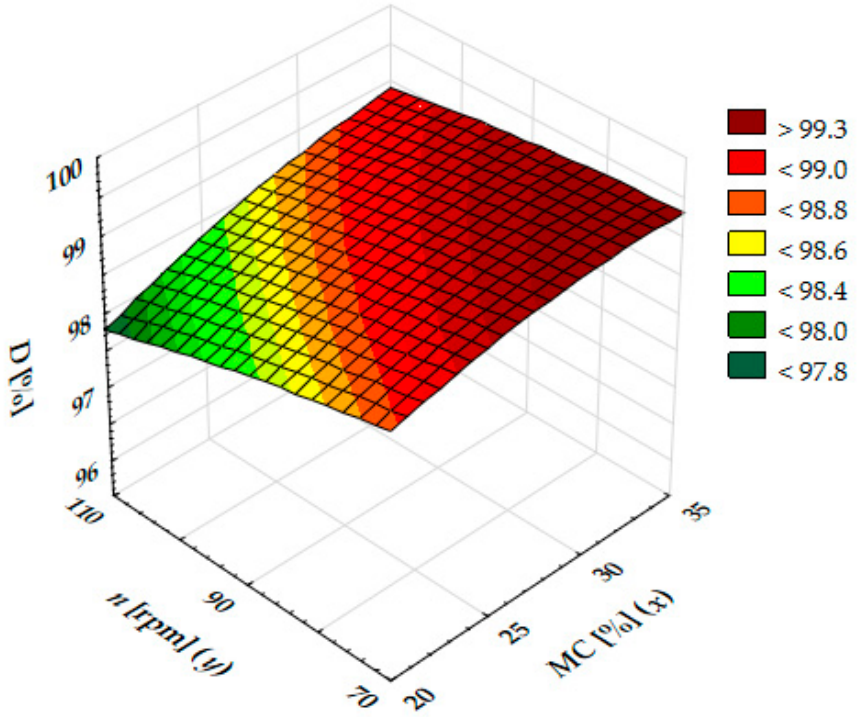

Figure 7. Influence of the rotational speed of the extruder screw and the level of raw material moisture on the durability of the extrudate.

Based on the conducted statistical analysis, it was observed that the level of moistening did not have a significant effect on the parameter under study only in the case of the *WSI* measurement (0.1752). In the case of the remaining measurements, the level of moisture, rotational speed and interactions between them had a significant impact on the tested properties. Based on the *F-test*, it was found that in the case of efficiency, *WAI* and bulk density, the dominant parameter was the moisture content—as it displays the highest values. In the case of the remaining parameters, the screw speed dominated.

3.7. Corn Bran Biogas Yield Results

The next tests were carried out to assess the efficiency of biogas creation as yielded from various samples of both extruded corn bran and pelleted corn bran. This study was aimed at comparing pretreatment methods in the context of their possible use in agricultural biogas plants. The content of methane during production of biogas in all samples was at similar levels: the control sample was 50.29%, and in the treated samples, it ranged between 49.88% and 50.82%. The results of cumulative methane and biogas production were assessed in relation to fresh mass, dry mass and dry organic matter. The use of the extrusion-cooking process as a pretreatment method of corn bran was predicted to be a source of biomass with a higher methane and biogas yield compared to that generated from pelletized bran and the control sample (unpretreated corn bran). The prediction was confirmed, as the results of cumulative biogas and cumulative methane generation were lower as fresh mass compared to the control sample for the pelletized samples only for corn bran processed through extrusion cooking at a 30% moisture level (Table 4). In the remaining samples, the values of cumulative methane and cumulative biogas generation were higher in relation to fresh, dry and organic matter.

The rotational speed of the extruder screw during the production of extruded samples had a significant impact on the subsequent volume of cumulative biogas and cumulative methane production. The lowest values of the above-mentioned indicators in relation to each comparative parameter (except for one case—that of 70 rpm—20%) were recorded for the samples processed at the lowest screw speed at 70 rpm, and the highest at the respectively higher speeds of 90 and 110 rpm. The level of moistening did not have a

significant effect on the production volume for both extrusion and pelletization. Overall, for fresh mass, the production of cumulative methane ranged from 95.32% (pel 30%) to 114.65% (extr 110 rpm 30%) in relation to the control sample, and for biogas from 95.28% (pel 30%) to 115.31% (extr 110 rpm; 30%). The increased methane productivity for dry matter ranged from 5.52% (extr 70 rpm 30%) to 10.14% (extr 110 rpm 30%) compared to the control sample, and in the case of biogas, it ranged from 5.26% (pel 35%) to 10.78% (extr 110 rpm 30%). Cumulative methane production for dry organic matter compared to the control sample ranged from 5.45% (extr 70 rpm 30%) to 10.20% (extr 110 rpm 35%), and in the case of biogas, from 5.26% (pel 35%) to 11.11% (extr 110 rpm 35%).

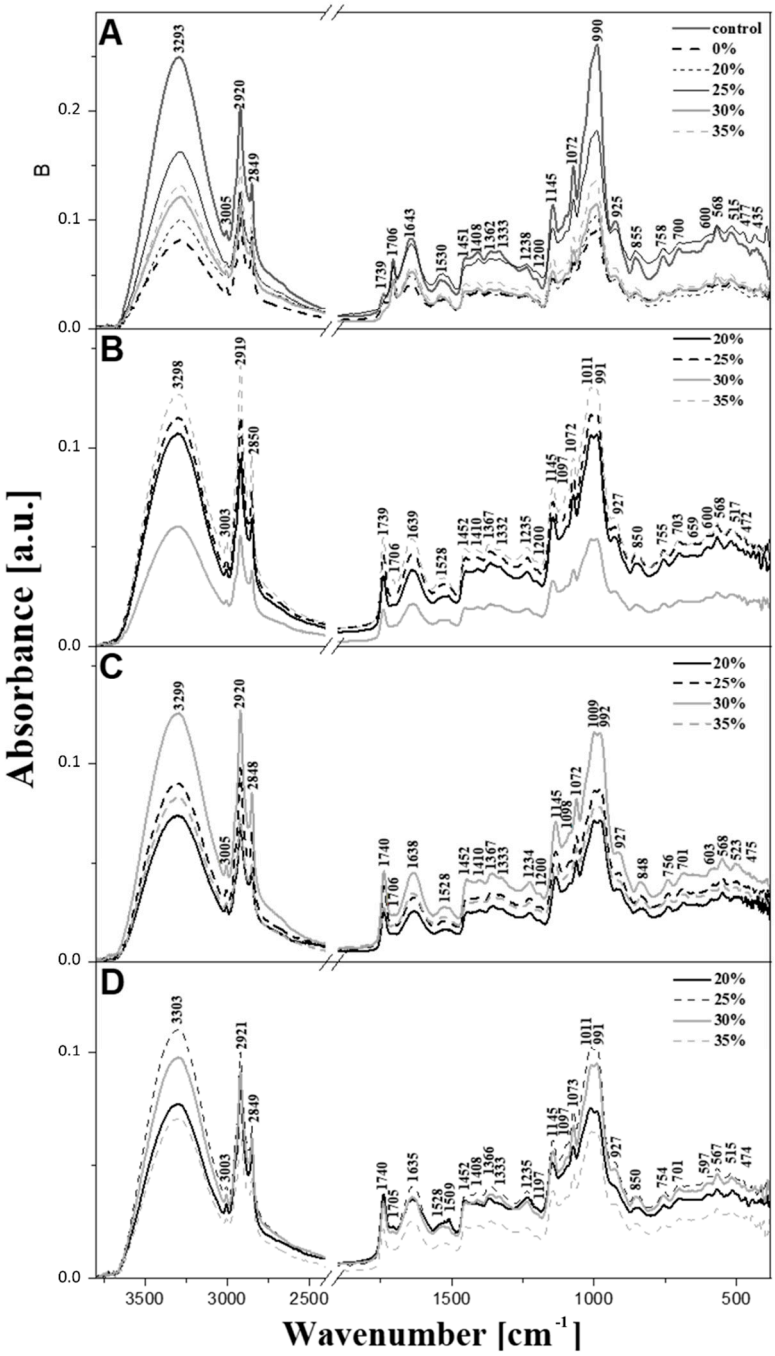

Figure 8. The *FTIR* infrared spectra for the samples selected for testing presented in the range from 400 to 3700 cm^{-1}. Panel (**A**): pelleted corn bran; Panel (**B**): extruded corn bran—70 rpm; Panel (**C**): extruded corn bran—90 rpm; Panel (**D**): extruded corn bran—110 rpm.

Table 4. Summary of methane fermentation measurements of processed corn bran.

Sample	Methane Content (%)	Cumulative Production in m^3 per Mg of Fresh Mass		Cumulative Production in m^3 per Mg of Dry Mass		Cumulative Production in m^3 per Mg of Dry Organic Matter	
		Biogas	Methane	Biogas	Methane	Biogas	Methane
control untreated	50.29	595.31	299.39	681.28	342.63	698.46	351.26
extr 70 rpm 20%	50.37	663.01	333.94	728.89	367.12	746.97	376.23
extr 70 rpm 25%	50.08	657.12	329.06	728.82	364.96	753.94	377.54
extr 70 rpm 30%	49.85	654.88	326.48	725.20	361.54	742.99	370.41
extr 70 rpm 35%	50.17	659.34	330.78	725.08	363.77	742.97	372.73
extr 90 rpm 20%	49.92	667.10	332.99	733.39	366.08	751.58	375.16
extr 90 rpm 25%	50.26	661.66	332.57	733.85	368.86	759.15	381.57
extr 90 rpm 30%	49.98	671.17	335.44	743.24	371.46	761.48	380.58
extr 90 rpm 35%	50.02	674.25	337.29	741.54	370.93	759.77	380.07
extr 110 rpm 20%	49.71	672.49	334.26	743.71	369.67	762.03	378.77
extr 110 rpm 25%	50.08	677.78	339.42	743.58	372.36	763.66	382.42
extr 110 rpm 30%	50.00	686.47	343.26	754.69	377.37	773.59	386.83
extr 110 rpm 35%	49.88	685.37	341.84	753.06	375.61	776.08	387.09
pel 20%	50.24	631.08	317.08	738.15	370.88	756.14	379.92
pel 25%	50.01	612.60	306.38	728.97	364.58	746.45	373.32
pel 30%	50.31	567.20	285.37	729.44	366.98	748.05	376.34
pel 35%	50.82	637.64	324.04	717.10	364.42	735.19	373.61

Corn bran enables a much higher yield of biogas and biomethane than the most popular maize silage in Europe. The content of methane in biogas from bran does not differ from the values from the literature [43], but despite a similar concentration of methane in biogas—at the level of 50–55%, the production of methane from silage per fresh mass is in the range of 170–220 m^3 per Mg [44–47]. This is much less than from corn bran (285–343 m^3 Mg^{-1}). Menardo et al. [48] and Pilarski et al. [49] showed an increase from 15.7% to 16.48% in their studies, respectively, for the production of biogas from corn straw after and before extrusion. However, these values are still lower than those obtained in the presented research for corn bran (and at the rotational speeds of the extruder screw, almost two times lower). Similarly, for other plants, e.g., common reed or Jerusalem artichoke, the methane production was approximately 66 m^3 Mg^{-1} and 108 m^3 Mg^{-1}, respectively [38].

The impact of the agglomeration by the extrusion-cooking process on the increase in biogas and methane productivity is specific for given types of substrates. Research on corn straw before and after extrusion showed a slight increase in concentration—by approx. 2%. In the case of methane efficiency, these was an increase of 8–15% for fresh mass, 9–11% for dry mass and 10–11% for dry organic matter [38]. Similar studies were carried out by another Polish team for extruded corn straw, which showed an increase in efficiency from 7.5% to 8.51% for biogas and methane production, respectively [50]. In individual studies, it is possible to find data for which, in the case of extrusion of, for example, Jerusalem artichoke, an almost 50% increase in methane yield can be obtained [51]. Similarly high—a several dozen percent increase in methane production was obtained for maize straw by Amith Abraham et al. [52] and Dell'Omo [53].

As indicated by the average values presented in the literature, in the case of agricultural substrates, one can expect an increase in biogas production from 8% to 70% through the use of appropriate treatment processes before fermentation, e.g., approx. 27% increase in methane productivity was obtained for ensiled and extruded maize straw [49]. However, the higher values may be found to the most frequently use combined methods, including biological, mechanical and thermal or chemical methods [54–56].

The increase by several percent of biogas yield in the presented study is therefore relatively large; however, it should be noted that the energy expenditure for the extrusion-cooking or pelleting process is significant. However, such processing can shorten the fermentation process by up to 8 days, which, in terms of waste material management, may be more important than energy requirements.

3.8. Results of the Energy Potential of Pretreated Substrates

When determining the suitability of corn bran for possible energy use, the technical and elemental analysis of the raw materials, including the ash content (A), volatile matter (V), bound carbon (BC), carbon content (C), hydrogen (H), nitrogen (N) and sulfur (S), as well as heat of combustion (HHV) and calorific value (LHV), must be undertaken. These analyses enable the comparison of the tested substrates with other types of biomass materials. However, attention should be paid to the fact that the tested biomass, being a plant material, is not a chemically homogeneous substance and even systematic analysis does not allow for a complete assessment of its technical usefulness.

The determined ash content in corn bran at the level of 2.92% is about 50% lower in the content of this residue after combustion than the average for all types of biomass materials, which is 6.8% [57]. The volatile matter content was 73.56% and is consistent with the average values in various types of by-products from the agri-food industry (74%), including agro-biomass and herbaceous biomass (75.2%) and in all types of biomass materials (75.4%) [57].

The content of carbon (47%), hydrogen (7.11%), nitrogen (1.61%) and sulfur (0.0557%) in the corn bran did not differ from the content of these elements in other types of biomass materials. The ranges of the content of individual elements in various types of by-products from the agri-food industry, namely agro-biomass and biomass of herbaceous plants and in all types of biomass materials are as follows: 49.9–51.3% for C, 6.2–6.3% for H, 1.2–1.4% for N and 0.15–0.19% for S [57]. The lower-than-average sulfur content is a good prognosis for corn bran, because the SO_2 load will be released into the environment during the combustion of this material.

The calorific values of the studied corn bran show that, for the control sample, the values of this parameter at the range of 15.77–16.5 MJ kg^{-1} are similar to the values obtained for the biomass of energy plants and agro-biomass (15.6–18.3 MJ kg^{-1}) [58,59], which indicates the potential of their use in producing thermal energy. Therefore, if the above-described parameters of corn bran have an ash content below 60%, content of organic parts above 40% and a moisture content below 50%, they will be able to burn autonomously [60,61]. It should also be mentioned that the higher the content of organic (flammable) substance and the lower the ash and moisture content, the higher the calorific value that is obtained. The average heat of combustion (*HHV*) obtained for a given material was 17.85 MJ kg^{-1}.

Therefore, the obtained results of the technical-elemental analysis and the calorific value allowed us to conclude that corn bran, when considered in terms of its suitability for combustion, is a suitable solid biofuel.

3.9. Analysis and Characterization of Samples Using FTIR Spectroscopy

Fourier transform infrared spectroscopy (*ATR/FTIR*) was used in the next research step for a more accurate and detailed characterization of the tested samples at the molecular level. In the research with the use of *FTIR*, marker bands were clearly observed, demonstrating the influence of the factors used, such as variable speed of the screw or the moisture level, and indicating that the selection of appropriate processing factors for the sample can significantly accelerate the decay rate of its main lignocellulosic structures. These changes are mainly due to the sample treatment process itself, such as pelletization or extrusion. On combining the obtained results from *FTIR* measurements with other measurements, it is clear that the extrusion factor should be used moderately, depending on the needs and, above all, the application of the material. For the convenience and clarity of the description,

as well as the interpretation of the obtained results, all spectra are presented in Figure 8, and all bands are additionally included in Table 3 (in the spectral range 3750–450 cm^{-1}). For all the spectra from each panel in Figure 8, the corresponding vibration bands are assigned in Table 5 to their characteristic functional groups as present in systems containing lignocellulosic structures. According to Rangel-Vázquez and Leal-García [62], the first and very characteristic area of vibrations in the described spectra is the range of vibrations with a maximum at ~3300 cm^{-1}. This corresponds to the stretching vibrations of the -OH groups present in the lignocellulose structure (Table 5 and Figure 8). As can be clearly seen (in particular) in Figure 8, the vibration intensity for this region is mainly amplified (essentially dependent) by a change in the moisture level of the samples. This band, according to well-known literature standards, may show noticeable shifts as the affinity of the components for the formation of intermolecular hydrogen bond structures increases, which is noticeably the case here. The next area, important from an analytical point of view and also a characteristic area, corresponds to the stretching vibrations of the C–H groups in the CH_2 and CH_3 groups in the lignocellulose structure [11,36]. The maximums of these vibrations are ~2920 and 2850 cm^{-1}. It is worth mentioning that this area is quite regular despite the processing factors used, which indicates that these samples are of quite good quality and that they are not significantly degraded at the molecular level. The very intensive absorption of the previously described broad vibrations of the hydroxyl groups underpins much weaker (Figure 8) stretching vibrations of the C–H groups in the tested samples. Usually, very wide bands of stretching -OH vibrations are often the result of the occurrence of hydrogen bonds resulting from interactions between structural units in the main building material of the lignocellulose samples [63]. Deformation vibrations of -OH groups occur in the form of bands with a maximum of ~1640 cm^{-1} (Figure 8) [64,65]. It should be noted, however, that this band may in this case come from the stretching vibrations of the C-C groups. Another very important area of vibration concerns the bands with a maximum of ~1740 cm^{-1}. This corresponds to the stretching vibration of the C=O carbonyl group (Figure 8) [38,66]. This area in the case of samples from the A panel is weaker, while in the B–D panels it is very distinct, for the tested samples. Moreover, it also differs significantly in intensity depending on the sample's moisture level and the rotational speed rpm during its production.

However, the main and, at the same time, very visible difference between these bands in the samples is most likely related to the treatment factor used, such as pelleting and extrusion-cooking processes. Most likely, the extrusion-cooking process caused degradation changes in lignocellulose bonds, which at the molecular level is visible as a significant increase in the band originating from the vibrations of the carbonyl group. This effect is visible in all B–D panels. A clear change in the intensity of vibrations from this area can therefore be a clear marker of the processes taking place and related to processing, such as pelleting or mainly the extrusion-cooking process. The different rotational speed of the screw during the production of the samples additionally enhances this effect. The changes in the sample moisture level may be of less importance in this case.

When analyzing the fingerprint region, we noticed that the spectra of all samples show very rich bands, which are quite important in their interpretation. In this case, the following vibrations should be described: deformation CH groups (~1370 cm^{-1}); deformation CH_2 (~1410 cm^{-1}); and deformation -OH groups mainly present in the structure of the main compounds of the tested samples, i.e., lignocelluloses [66–68]. It should be clearly emphasized that, despite the applied factors such as moisture change or rotational screw speed, these bands in relation to the spectrum of reference samples (Panel A in Figure 8) do not differ significantly in this spectra range from other samples from panels B–D. Vibrations with a maximum of ~1145 cm^{-1} are also very important. These mainly come from the stretching vibrations of the ring of the main material of the samples, as well as from stretching vibrations of the C-O groups. Successive vibrations with a maximum of ~1010 and ~990 cm^{-1} belong to the stretching vibrations of the C-O groups [11,66]. Changes in the shape of the bands within this range can be clearly observed,

with a maximum of 1010 cm^{-1} depending on the type of treatment (extrusion) for a given samples. The intensity of these bands is mainly due to stretching vibrations in the C-O-C system in the structure of lignocellulose. Changes in this maximum (especially at 1010 cm^{-1}) should be related to exactly the same factor as for vibrations with the maximum related to vibrations of the carbonyl group, as described earlier.

Table 5. The location of the maxima of absorption bands *ATR-FTIR* with arrangement of appropriate vibration for selected sampling made in terms of spectra 3750–400 cm^{-1}. The results were obtained at room temperature and humidity.

Position of Bands (cm^{-1})				Type and Origin of Vibrations
pel	**extr 70**	**extr 90**	**extr 110**	
3293	3298	3299	3303	ν (O-H) in H_2O and intramolecular hydrogen bonding
3003	3003	3005	3003	
2920	2919	2920	2921	ν (C-H) in CH_2 and CH_3 asymmetrical and symmetrical
2849	2850	2848	2849	
1739	1739	1740	1740	ν (C=O)
1706	1706	1706	1705	
1643	1639	1638	1635	ν (C=C) or/and δ (O-H) adsorbed H_2O
1530	1528	1528	1528	ν (C=C)
1451	1452	1452	1452	δ (-OH in plane), δ (CH_2), δ (C-H)
1408	1410	1410	1408	
1362	1367	1367	1366	
1333	1332	1333	1333	δ (C-H) and δ (O-H)
1238	1235	1234	1235	δ (C-H) and antisymmetrical bridge oxygen stretching –OH in-plane bending
1145	1145	1145	1145	antisymmetrical in phase ring stretching and ν (C-O-C)
1072	1072	1072	1073	
1110	1011	1009	1011	
990	991	992	991	ν (C-O) and ring stretching modes
925	927	927	927	CH_2 rocking *β*-linkage of cellulose ring breathing and antisymmetrical out of phase stretching -OH out-of-plane bending CH_2 rocking
858	850	848	850	
758	755	756	754	
700	703	701	701	
600	600	603	597	
568	568	568	567	
515	517	523	515	
477	472	475	474	

ν—stretching vibrations, *δ*—deformation vibrations, *s*—symmetric, *as*—asymmetric, *st*—strong.

Changes are also notable in the intensity of the obtained bands in the range from 950 to 450 cm^{-1}. These bands are related to vibrations in the bonds of sugar fractions that make up the lignocellulose structure, such as the *α*-1,6-glycosidic bond or the *α*-1,4-glycosidic bond. They show changes in intensity practically in the entire range, with a maximum of about 570 cm^{-1}; that is, in the area where deformation vibrations of the -OH groups occur, and are additionally related to the changing moisture level of the samples. These groups in this region correspond to the formation of hydrogen bonds between the cellulose units. To

summarize initially, it should be emphasized that the measurements by means of *FTIR* offer great interpretative possibilities in the context of further research on this type of material and structurally similar materials. We will perform this in the next stages of the research. The bands that are the most interesting in the assessment of degradation changes occurring in the analyzed samples (related to their processing) include the vibrations described in detail above, i.e., vibrations with a wavenumber of ~3300, 1520, 1370 and 1070 cm^{-1} and, above all, with a maximum at around 1740, 1706 and 1110 cm^{-1}.

It should be additionally emphasized that, by combining *FTIR* measurements with previous measurements of samples selected for testing, from the point of view of molecular tests, changes in the samples subjected to extrusion-cooking pretreatment are actually visible. These changes can lead to easier handling of these samples. However, as can be seen from other data, it is also worth considering which way to direct the process in this case depending on the needs. Often, pelletization alone can be sufficient in principle, as can be clearly seen in the combined interpretation of *FTIR* studies and other physical studies.

3.10. Microscopic Analysis of the Processed Materials

The analysis of microscopic pictures confirms the results on pelleted and extruded corn bran samples by *FTIR*. The microscopic analysis makes it possible to determine the degree of agglomeration, as well as the degree of changes taking place during the pressure and pressure-thermal treatment of corn bran. The agglomeration of corn bran is carried out in order to reduce the volume. Figures 9 and 10 show that both the untreated and pelleted material is not gelled, and there are still visible bran fractions resulting from the corn grain milling process.

In the case of unprocessed corn bran, the structure of the material is loose and has gaps. Similar deformations of the frontal surfaces were observed by Yanniotis et al. [69] in the case of extruded corn starch. According to these authors, this may be caused by exceeding the critical shear stress inside the matrix, which leads to incomplete starch gelatinization, and thus causes the formation of visible elements of raw material inside the structure.

Figure 10B–D shows parts of the casing and husks of corn grain. The bran is agglomerated; however, its durability is lower than in the case of extruded bran (Figure 7). The pictures show non-gelatinized fractions, remains of starch and husks (Figure 10). There are no honeycomb-like cells characteristic for extruded products. In the case of pelleted corn bran, there is a cross-linked, processed structure and visible solid pieces of material (Figure 10B–D). As with the control (untreated), a white coating can be observed sticking to the pelleted material, which results from the crystallization/ precipitation of the raw starch fractions.

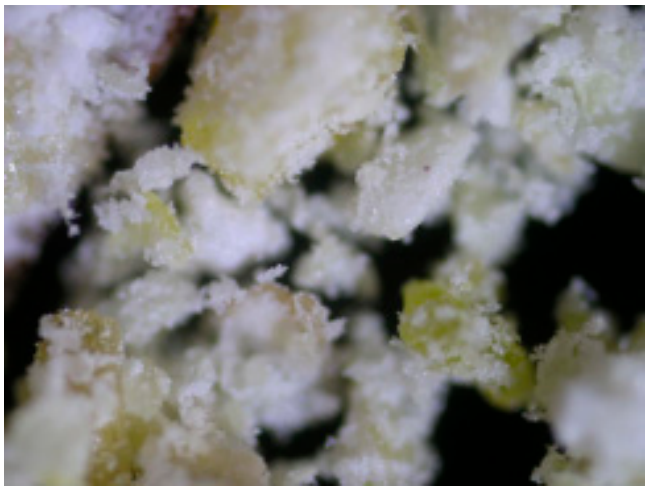

Figure 9. Structure of raw untreated corn bran.

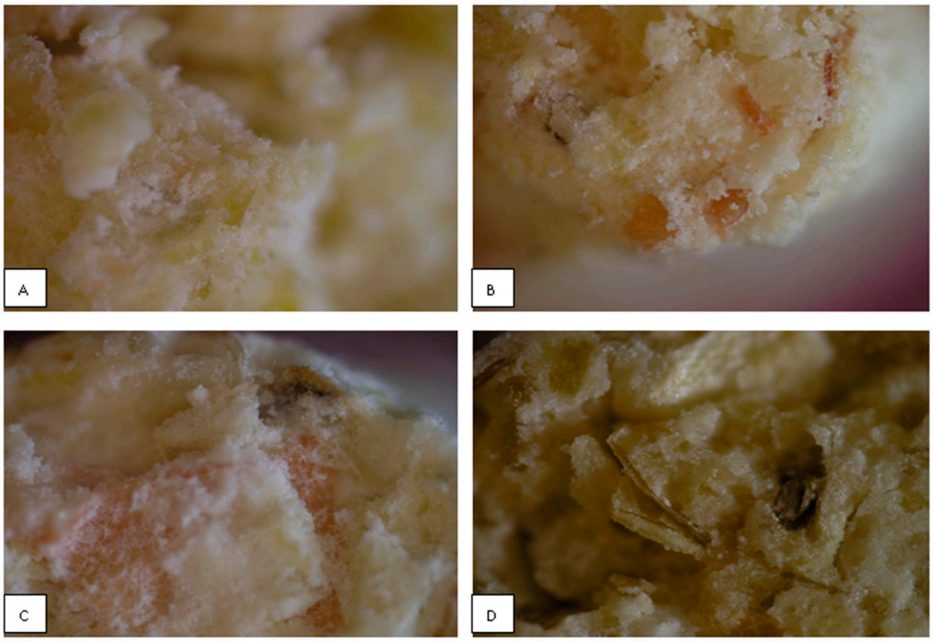

Figure 10. Microscopic pictures of pelleted corn bran: (**A**) 20% moisture level, (**B**) 25% moisture level, (**C**) 30% moisture level and (**D**) 35% moisture level.

The extrusion-cooking process of corn bran showed the effect of processed and compressed material through the process of gelatinization of the starch particles. These, unlike pelleted bran, are characterized by a crystalline, compact structure after processing. In the case of extruded corn bran, it can also be seen that, not only were the finely ground bran elements of the material transformed, but also parts of the kernel outside layer, i.e., the husks (Figure 11). In addition, air bubbles are visible, albeit only in the case of corn bran extruded at the screw speed of 70 rpm and at the highest level of moisture at 35% (Figure 11D). At higher rotational speeds of the extruder screw and a 35% level of moistening, such bubbles are not visible.

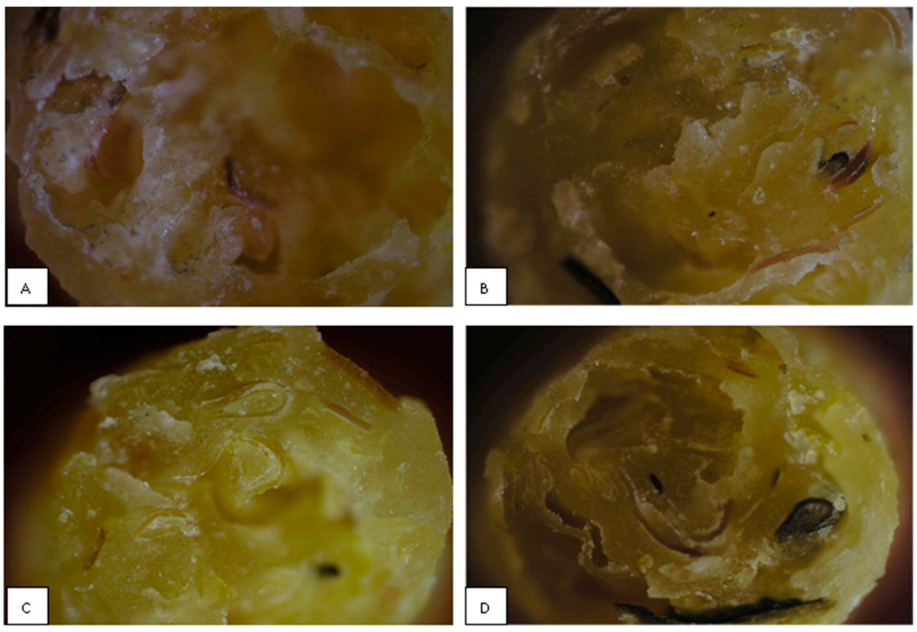

Figure 11. Microscopic pictures of extruded corn bran processed at 70 rpm extruder screw speed and at: (**A**) 20% moisture level, (**B**) 25% moisture level, (**C**) 30% moisture level and (**D**) 35% moisture level.

In the case of the extrusion of corn bran processed at the rotational speed of the extruder screw of 90 rpm (Figure 12), it can be observed that for each tested moisture level, raw material with a different degree of comminution was used (meal fraction, residues of corn kernel cover). Larger material particles are quite evident in Figure 12A,B,D. In the case of Figure 12C, the larger particles are corn parts, which, under the influence of high temperature and pressure, have been fused into the material, creating a uniform internal structure.

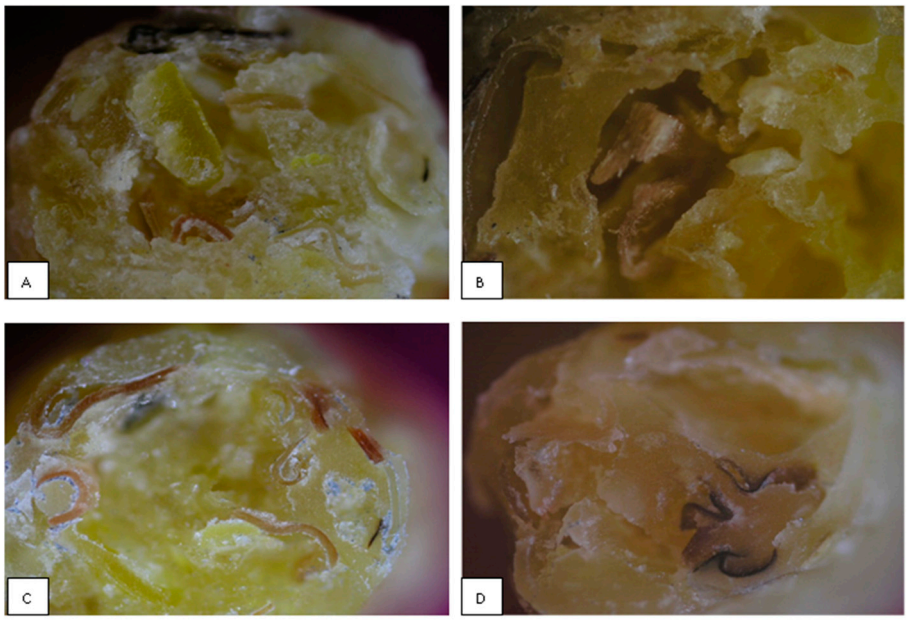

Figure 12. Microscopic pictures of extruded corn bran processed at 90 rpm extruder screw speed and at: (**A**) 20% moisture level, (**B**) 25% moisture level, (**C**) 30% moisture level and (**D**) 35% moisture level.

As it can be seen in Figure 13, the samples subjected to extrusion at lower moisture levels (Figure 13A,B) are characterized by the presence of bubbles. This effect indicates a high degree of expansion of the material as it leaves the extruder matrix at the highest screw speed applied during pretreatment. This is due to the fact that, in the case of mixtures with a lower moisture content, the influences of mechanical treatment, friction and shear forces in the extruder are greater. Samples presented in Figure 13C,D are characterized by a compact structure that connects the entire pretreated material, with the difference that, in the case of 30% of the moisture level, larger amounts of the white coatings surrounding the material can be observed, and in the case of the extrusion-cooking pretreatment at 35% of the raw material moisture level, only traces of such a coatings are observed. Similar observations were found by the authors of [70] upon comparing the surfaces of corn starch and thermoplastic starch—*TPS*. In both this work and ours, the morphology of the *TPS* showed that the starch granules were completely destroyed, indicating the efficiency of transformation of the plant material during treatment at elevated temperature and pressure. Overall observations confirmed that heat-treated corn bran forms a compact, homogeneous structure. In the case of pelletization, a white shell surrounding the material can be observed to a large extent, and in the case of extrusion, it is less visible because of higher shear forces, as well as the extrusion temperature and pressure. The samples subjected to extrusion at a lower level of moisture are characterized by the presence of visible bubbles, indicating the expansion of the material as a result of the rapid evaporation of water contained in the raw material mixture.

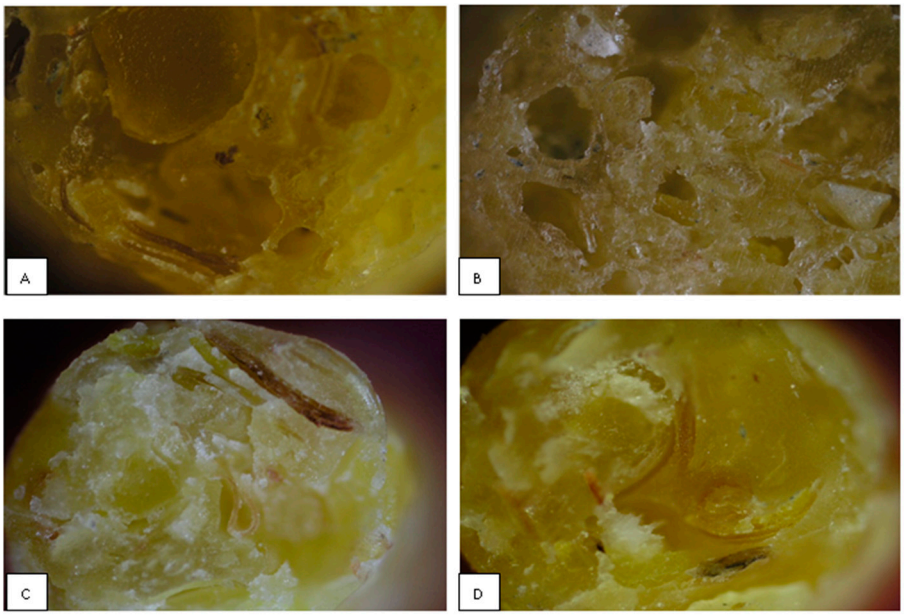

Figure 13. Microscopic photos of extruded corn bran processed at an extruder screw speed of 110 rpm and at: (**A**) 20% moisture level, (**B**) 25% moisture level, (**C**) 30% level of hydration and (**D**) 35% moisture level.

4. Conclusions

The article presents one of the examples of the possible application of corn bran as substrates for agricultural biogas plants. Two methods of pretreatment agglomeration were compared—pelleting and extrusion-cooking—as well as their influence on physicochemical properties and biogas efficiency. The comparison of these properties was aimed at selecting the optimal method for the agglomeration of corn bran, their transport, storage and the use of the obtained results in biogas production. The research shows that the extrusion-cooking process had a greater impact on the physical properties of the processed corn bran compared to the pelletization method. The methane fermentation efficiency of the processed material did not differ significantly with respect to the pretreatment method. Still, the higher biogas yield does not cover the additional energy expenditure related to the extrusion-cooking process.

Redesigning of extrusion-cooking device by changing the configuration system and the use of waste heat from the biogas plant (resulting from the use of cogeneration—the production of electricity and heat) to heat the device could be possible. The use of waste energy should be tested and calculated according to profitability of using the extrusion technique.

Several final conclusions can be formulated based on the presented research. The pelletization process, compared to the extrusion-cooking process, was characterized by a higher efficiency and much lower energy consumption. Extrusion-cooking pretreatment increased the water absorption of processed corn bran as compared to pelletization. Bulk density was much higher for agglomerated corn bran, and this effect can be beneficial during transportation and storage. The highest durability was obtained for pelleted samples due to the generation of a much higher pressure during the agglomerating of corn bran. The use of the extrusion process as a pretreatment of corn bran made it possible to obtain a higher yield of methane and biogas on comparison to pelletization. Moreover, the samples subjected to the extrusion pretreatment showed a higher biogas and methane productivity by approx. 10–15% compared to the control sample.

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