

Article

Sustainability Biogas Production from Ensiled Plants Consisting of the Transformation of the Digestate into a Valuable Organic-Mineral Granular Fertilizer

Hubert Prask ^{1,*}, Józef Szlachta ¹, Małgorzata Fugol ¹, Leszek Kordas ¹, Agnieszka Lejman ¹, Franciszek Tużnik ² and Filip Tużnik ³

- ¹ The Faculty of Life Sciences and Technology, Wroclaw University of Environmental and Life Sciences, 50-375 Wroclaw, Poland; jozef.szlachta@upwr.edu.pl (J.S.); malgorzata.fugol@upwr.edu.pl (M.F.); leszek.kordas@upwr.edu.pl (L.K.); agnieszka.lejman@upwr.edu.pl (A.L.)
- ² TUZAL Sp. z o.o., ul. Morsztyna 7, 05-075 Warsaw, Poland; tuznik@aol.com
- ³ The Faculty of Building Services, Hydro and Environmental Engineering, Warsaw University of Technology, 00-653 Warsaw, Poland; filiptuznik@yahoo.com
- * Correspondence: hubert.prask@upwr.edu.pl

Received: 15 December 2017; Accepted: 23 February 2018; Published: 26 February 2018

Abstract: The research concerned the elaborate of non-waste biogas production technology based on the development of digestate from anaerobic digestion. In the anaerobic digestion process, the substrates of plant origin in the form of silage were used. The digestate obtained after biogas production was processed using the ORTWED method into a valuable granulated organic-mineral fertilizer, which contains a solid fraction of digestate, calcium and biogenic elements. This method can be successfully applied in agriculture in the context of its sustainable development due to the growing problem of utilization of digestate forming in agricultural biogas plants.

Keywords: anaerobic digestion; biogas; digestate; ORTWED method; granular fertilizer

1. Introduction

With the development of the world and technologies surrounding us, agriculture is becoming more and more intensified too. The excessive use of chemicals in agriculture causes severe side effects to the environment. In addition to high costs of mineral fertilizers, their biogenic compounds are eluted in a significant percentage and rinsed to water reservoirs, instead of being absorbed by plants. Subsequently, that causes water eutrophication and endangers local ecosystems [1]. Therefore, there is a need for constant actions that would aim at sustainable fertilization and lower the negative impact on environment.

Since the global need for electricity and heating are constantly growing, the problem of harmful, hard-to-manage waste is also increasing. Agriculture biogas plants using anaerobic digestion process both reduces greenhouse gas emission and provides an interesting alternative for electricity and heat production that arises out of floral biomass, excrements, or agro-food industry waste [2–9]. Moreover, after the anaerobic digestion process is finished, there is still a large amount of digestate with fertilizing properties to be utilized [10]. Digestate contains mineral compounds (e.g., N, P, K), essential in floral vegetation process. Organic matter contained in digestate influences positively the physicochemical properties of fertilized soils, which upgrades its structure, water capacity and absorption characteristic. The hydration of the digestate is about 90–97% while its structure depends on the type and proportions of substrates used as an input to an agricultural biogas plant. Therefore, the utilization of the digestate on arable soils increases its reserves in biogenic elements and enhances fields in organic matter, which could consequently limit the use of mineral and natural fertilizers. Of course, there are immense



differences within the digestate composition, depending on substrate proportion. Nevertheless, the content of Nitrogen, Phosphorous and Potassium in the digestate could be settable for the mineral fertilizer equivalent. Unfortunately, it difficult to reclaim the digestate. There are problems with the lack of arable lands in the area surrounding the biogas plant and with social pushback to agricultural sludge treatment [11,12]. The classification of digestate is problematic too, since it can be classified as waste, by-product or sometimes fertilizer [13]. Taking the above into consideration, there occurs a real need for a waste-free technology to be used in agricultural biogas plants that would enable proper digestate management [14]. Digestate mass has some beneficial properties and its proper exploitation could bring some additional income to the biogas plant owner. One can apply the digestate directly on the arable fields, others can also separate it into solid fraction and effluent. The liquid fraction can be used for irrigating fields or can be simply returned to the chamber digestion to hydrate the batch [15,16]. In turn, the solid fraction can be directly applied to the field, composted, or be used to produce pellets for heating purposes, and incinerated. Moreover, the solid fraction could be used for organic and organic-mineral fertilizer production [17]. Many soils have acidic pH value so addition of calcium to granular fertilizer is necessary not only from the point of view of granulation process by ORTWED method but also from that of the need of liming soils. The main goal of the research was the elaboration of waste-free biogas production technology, which includes processing a by-product of anaerobic digestion of selected plants—digestate—which would be processed into full-featured organic-mineral granulated fertilizer. This solution could be applied to all agricultural biogas plants working on plant and animal origin substrates. It is the ORTWED method of utilizing the solid fraction into a granulated fertilizer with an addition of calcium and biogenic elements, such as: Nitrogen (N), Phosphorous (P), Potassium (K), Magnesium (Mg) and Sulfur (S), which was examined and validated in the research [18]. This is a method of granulating hydrated sludge. The method is implemented under the license agreements "KNOW-HOW". The ORTWED method describes the quick use of calcium for the treatment of sewage sludge as the best technology for the sludge utilization. Properly prepared thickened sludge is transported to a special granulator, in which, in accordance with suitably selected process parameters, both physical and chemical reactions take place between the water contained in the sludge, organic matter and calcium introduced into the granulator (thermo-chemical reaction). Because produced fertilizer contains over 90% of total solid content, it is hydrophobic and easy in practical use on the field. It can be easily stored, packed in any capacity bags, or containers, transported or stored in bulk. Granulate is environmentally friendly, safe for people and animals and due to the materials used (plant silages, natural mineral resources) it is also an excellent fertilizer to be used in ecological farming. Since the granulate is heavily hydrophobic, 95% of the granulate matter is being absorbed by plants throughout the whole vegetation period, and thus is harmless for environment [19]. The technology could be successfully utilized in agriculture, especially in the terms of sustainable utilization of agricultural biogas plant originated digestate, which is still important and an unsolved problem.

2. Research Methodology

2.1. Objective Purpose and Scope of Research

The main idea of the research was to find a solution for the digestate management problem at agricultural biogas plant in Poland. The solution would probably increase the attractiveness of biogas business and encourage investors to build such facilities more often throughout a country. The research was composed of the following tasks:

- 1. The diagnosis of fertility and method of silage selected annual and perennial plants for biogas production.
- 2. The evaluation of the usefulness of silage selected plants for anaerobic digestion and digestate to produce a granular fertilizer.

- 3. The development of technical documentation and installation methods of the manufacturing process granular fertilizer from digestate.
- 4. The production of granular fertilizer out of digestate, calcium and biogenic elements in terms of fertilizer.

2.2. Analytical Methods

The first task was to cultivate ten plant species (Elvira sugar beet, Cannavaro and Atletico maize, sucrosorgum, quitch, legume grasses, Bielik and Rubik topinambour, Progas and Palazzo rye) and to choose those of the most promising physicochemical specification, which would encourage yielding and biogas production.

The next task was to do anaerobic digestion process of single substrates and appropriate mixes (cosubstrates). Before biogas production the substrates were properly fragmented (the chop length was 10 mm). Subsequently, the substrates and the inoculum (digestate from an agricultural biogas plant using only plant batch) were subjected to the detailed physicochemical analyses to exclude abnormalities during the biogas production. The process of anaerobic digestion was carried out in accordance with VDI 4630 norm [20] in triplicate for each substrate. Research of batch process was conducted in thirty fermenters (eudiometers) with a capacity of 1 L at 38 °C.

In the next stage, the substrates with the biggest biogas yield were subjected to a continuous anaerobic digestion process to reflect the process conditions taking place in a real agricultural biogas plant. The research was done in full automatic continuous fermenters with a capacity of 10 L in conditions corresponding to the real agricultural biogas plant with constant loading of chamber digester (3.5 kg VS/m³/day—3.5 kg of volatile solid per cubic meter per day). The process temperature was 38 °C, mixing was done cyclically every 4 h for one minute at a speed of 60 rpm (rotations per minute). After anaerobic digestion process physicochemical analyses of arisen digestate was done. This is to determine the degree of fermentation of substrates with determination of the degree of retention of various compounds in the digested crop mass before using it as a fertilizer. The digestate was analyzed in three forms: liquid, immediately after anaerobic digestion (before the separator), formed after separation on the separator of the solid fraction (thicken on the separator) and liquid (derived from the dehydration of digestate on the separator—effluent).

The aim of the next step was to elaborate the innovative technology of converting the solid digestate into organic-mineral fertilizer granulate. The process included an addition of lime and biogenic elements, which would increase fertile value for selected plants. The research was realized in MLH 6 cyclic reactor, adapted to produce fertilizer granules. The reactor capacity is between 1.2 and 4.8 L, it has the maximum working time per cycle of 15 min and can handle stirrer rotation speed between 70 and 275 rpm. Granulation process is possible as a result of intense exothermic hydrolysis reaction between highly reactive lime and water contained in the digestate that takes place in the temperature of even 135–140 °C (the whole heat produced in the process comes from the lime hydrolysis reaction). The product—valuable organic-mineral granular fertilizer was supposed to have similar characteristic to fertilizer Polifoska Plus. The proportion used to evaluate quantities of respective biogenic components was as follows: N:P:K:Mg:S = 5:10:20:7:9. In the end, during the research, the proportions of nutrients in the granular were changed to: N:P:K = 5:9:11.

The last stage of the research will concern vase experiments of ten selected plants fertilized with various doses of organic-mineral granular fertilizer produced. These experiments will last for two growing seasons with constant humidity of the substrate in the vegetation hall. These studies are currently being carried out, and the results with economic analysis will be published in another article.

2.3. Statistical Analysis

The results of the study were subjected to statistical analysis based on the software Statistica 12 PL. The average values from measurements, measurement errors were determined. Multi-criteria package ANOVA analysis showed the importance of the effect of vs. and C/N on biogas yields. A multiple

regression model was used to show the dependence of the dependent variable Q_t on vs. and C/N. The accuracy of prediction was assessed by the coefficient of determination (\mathbb{R}^2), the root mean square error of prediction ($\mathbb{R}MSE$). In prediction models, higher values of \mathbb{R}^2 in combination with lower values of $\mathbb{R}MSE$ are indicators of well validation.

3. Results

3.1. Factors Determining the Production of Granular Fertilizer Using the ORTWED Method

The basic substrates for the production of fertilizer granules were sorghum and maize silage. Due to their lignocellulose structure, they were an excellent "scaffolding" to make organic-mineral granular fertilizer. The cost of acquire maize is very high, which is why sorghum was selected as a granule base. Based on the continuous anaerobic digestion process reflecting the work of the actual agricultural biogas plant, it was found that a mix of substrates was used to produce the granulate fertilizer, which included: sorghum, beet, rye, and grass in the following proportions: 20%:60%:10%:10%. These cosubstrates were stand-out the highest biogas and methane yield and also harvest of plant compared to the other five proposed mixes. Table 1 presents the basic parameters of substrate mixtures for which biogas yields are shown in Figure 1. Particularly the content of VS, C/N as well as content of P and K seem to be important for biogas yield. The multiple regression analysis (Table 2) confirmed the significant impact at the level of p < 0.0001 vs. content and C/N ratio on the biogas yield. These results explain biogas yields for six substrate mixtures tested. After anaerobic digestion on separator was pressed digestate upon process, obtained solid fraction was used for further research (Figure 2).

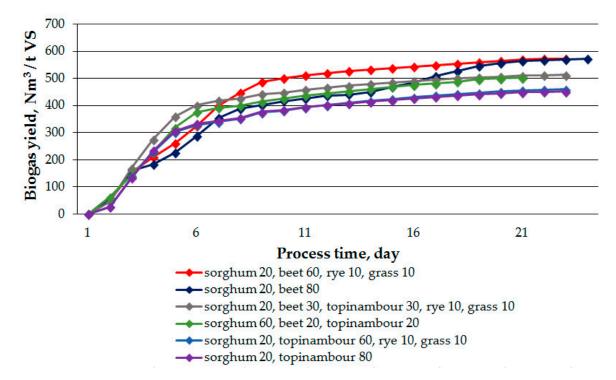


Figure 1. Biogas yield from cosubstrates on sorghum base.

| Mix of Substrates | Biogas Yield | VS | С | Ν | C/N | Р | K |
|--|---------------------|---------------|----------------|---------------|------|---------------|---------------|
| Sorghum 20% + topinambour 80% | 445.96 ± 35.3 | 74.41 ± 0.2 | 26.43 ± 0.12 | 9.68 ± 0.1 | 2.73 | 1.15 ± 0.1 | 5.11 ± 0.3 |
| Sorghum 20% + topinambour 60% + rye 10% + grass 10% | 453.60 ± 24.6 | 74.62 ± 0.2 | 26.47 ± 0.15 | 9.68 ± 0.12 | 2.73 | 1.16 ± 0.12 | 5.03 ± 0.2 |
| Sorghum 60% + beet 20% + topinambour 20% | 498.32 ± 26.9 | 74.57 ± 0.1 | 26.46 ± 0.09 | 9.67 ± 0.15 | 2.74 | 1.16 ± 0.21 | 4.72 ± 0.4 |
| Sorghum 20% + beet 30% + topinambour 30% + rye 10% + grass 10% | $506.53 \pm 21,3$ | 74.52 ± 0.1 | 26.41 ± 0.21 | 9.67 ± 0.09 | 2.73 | 1.15 ± 0.15 | 4.80 ± 0.12 |
| Sorghum 20% + beet 80% | 592.18 ± 35.7 | 74.63 ± 0.2 | 26.43 ± 0.16 | 9.66 ± 0.18 | 2.74 | 1.15 ± 0.12 | 4.56 ± 0.23 |
| Sorghum 20% + beet 60% + rye 10% + grass 10% | 593.00 ± 32.8 | 74.60 ± 0.1 | 26.41 ± 0.18 | 9.66 ± 0.20 | 2.73 | 1.15 ± 0.24 | 4.60 ± 0.17 |

Table 1. Biogas yield for analyzed mix of substrates, VS, C/N ratio and selected parameters.

Reference: own study.

| | | | Coef | ficient | | |
|----------------------|----------|-----------------------|----------|---------------------|----------|----------|
| Parameter/Statistics | b * | Stand. Error with b * | b | Stand. Error with b | t(15) | р |
| Free expression | | | 14.83894 | 5.219134 | 2.84318 | 0.012335 |
| VS | 1.84140 | 0.261594 | 2.46914 | 0.350773 | 7.03913 | 0.000004 |
| C/N | -1.43288 | 0.261594 | -1.97016 | 0.359684 | -5.47747 | 0.000064 |

Table 2. Multiple regression summary for dependent variable QB from vs. and C/N.

 $R^2 = 0.776527$, improved $R^2 = 0.746738$, F (2.15) = 26.061, p < 0.0001, Stand. error estimation: 15.724.

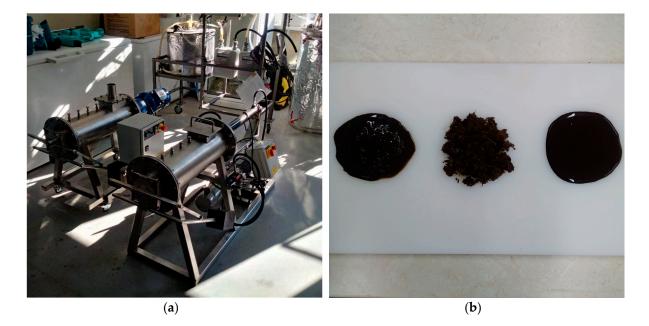


Figure 2. Two separators (a), and three forms of digestate: liquid digestate, solid fraction, effluent (b).

Solid fraction was fragmented to 3 mm and pre-dried to a total solid value of around 24% (Figure 3).



Figure 3. Solid fraction of digestate fragmented to 3 mm—granules component.

To describe the kinetics of the anaerobic digestion, the process of tested batches was used the kinetic Equation (1) of the first order Tabasarana model [21]:

$$G_t = G_0 \cdot (1 - \exp(-k \cdot t)), \text{ Nm}^3 / \text{t VS}$$
(1)

where G_t is the cumulative volume of biogas obtained by the end of the process, Nm³/t VS, G_0 kinetic biogas production from the unit of batch Nm³/t VS, *k*—rate constant, 1/day, and *t* is duration of anaerobic digestion, day.

Modeling was performed for each trial by iterating the start parameters. In order to check the degree of fit of the model to the results of the experiment, R² (Coefficient of determination of matching the model to the data) and RSME (Root Mean Squared Error) were determined, which was estimated based on the Formula (2):

$$RMS(S) = \sqrt{\frac{1}{n} \sum_{p=1}^{n} (t^{(p)} - y^{(p)})^2}$$
(2)

where $t_i^{(p)}$ and $y_i^{(p)}$ are measured and calculated values of the output vector and *n* is number of measurement. In addition, for the determined rate constants, based on the dependence (3):

$$T_{1/2} = \frac{\ln 2}{k}, d$$
 (3)

the degradation of half-lives of individual batches was calculated [22]. The parameters and Tabasarana model coefficients are given in Table 1.

Statistical analysis of the coefficient of determination R² and the root mean squared error RSME showed that the applied model describing the biogas production process is well suited to the experiment data for the analyzed batch (Table 3). The value of R^2 and RMSE determination coefficients for the selected batch amounted respectively: 0.985 and 20.96. The kinetic biogas production for the selected batch, determined from the first order equation, was the highest among all mix of cosubstrates and reached the value of $593 \text{ Nm}^3/\text{t VS}$. (normal cubic meters per ton of volatile solid). The least biogas was formed from a batch consisting of 20% sorghum and topinambour 80%-456 Nm³/t VS. The modeling of rate constant k was 0.175 and degradation half-lives $T_{1/2}$ —2.44 day. For individual substrates, the biggest biogas yield was formed from beet silage, and the least from sorghum silage and topinambour silage, respectively: 490 and 414 Nm^3 /t VS. The constant rate (k) values for the cosubstrates were between 0.130 and 0.257. For individual substrates, k values ranged from 0.124 to 0.223. However, the degradation half-lives and duration of process values for all cosubstrates and individual substrates were very similar. The remaining coefficients for individual substrates were similar to those for the selected batch. Only the RMSE coefficient for beet silage was much higher—40.96 and for sorghum silage, the lowest—11.55. The obtained process kinetics parameters for a batch based on sorghum are favorable. However, those parameters are lower values the an obtained for single substrates: maize silage and beet pulp [23]. Biogas production described by the Tabasarana model in this case for maize silage and beet pulp was higher and amounted to 677 and 649 Nm³/t VS. The rate constant of reaction was respectively: 0.173 and 0.318, degradation half-lives—2.449 and 1.840 and the coefficient of determination—0.990 and 0.994. On the other hand, the values of the RMSE coefficient were lower (18.09 and 12.5).

In addition to the biogas yield, the composition of the biogas production was also studied. After stabilization of the continuous anaerobic digestion process for the selected batch consisting of four substrates, the average methane content was: 54.2%; carbon dioxide: 45.0%. In addition, the content of trace compounds was also measured, the average oxygen in the biogas was: 0.6%; ammonia: 10.5 ppm; hydrogen sulfide: 46.5 ppm. Before the beginning of anaerobic digestion, physicochemical analyzes of four substrates, inoculum and batch were made (Table 4). These researches were designed to exclude the abnormalities during the anaerobic digestion process. The highest total solid (TS) was characterized

by: rye and sorghum, and the smallest: batch and inoculum, respectively: 38.4; 29.4; 6.0 and 5.5%. On the other hand, beet and sorghum had the highest volatile solid (95.7 and 94.9% TS). In this case, also the batch and the inoculum had the lowest parameter (76.2 and 74.2% TS). The pH was alkaline for rye, batch, and inoculum, for the remaining substrates the pH was acidic. The inoculum was characterized by the highest nitrogen content (9.84% TS), while the batch had the largest content of the remaining elements with ammoniacal nitrogen in comparison with other substrates and inoculum.

| Mix of Substrates | Efficiency of Biogas G ₀ , Nm ³ /t VS | Rate Constant <i>k</i> , 1/Day | Degradation Half-Lives T _{1/2,} Day | Coefficient of Determination R ² | Root Mean Squared Error, RMSE | Duration of Process <i>t</i> , Day |
|--|---|--------------------------------------|--|---|-------------------------------------|--|
| Sorghum 20% + Beet 60% + Rye 10% + Grass 10% | 593.00 | 0.175 | 2.44 | 0.985 | 20.96 | 23 |
| Sorghum 20% + Beet 80% | 592.18 | 0.130 | 2.73 | 0.986 | 18.96 | 22 |
| Sorghum 20% + Beet 30% + Topinambour 30% + Rye 10% + Grass 10% | 506.53 | 0.257 | 2.05 | 0.980 | 20.29 | 22 |
| Sorghum 20% + Topinambour 80% | 445.96 | 0.231 | 2.16 | 0.978 | 19.03 | 22 |
| Sorghum 20% + Topinambour 60% + Rye 10% + Grass 10% | 453.60 | 0.219 | 2.21 | 0.980 | 18.46 | 22 |
| Sorghum 60% + Beet 20% + Topinambour 20% | 498.32 | 0.224 | 2.19 | 0.985 | 17.82 | 20 |
| Beet silage | 744.51 | 0.223 | 2.19 | 0.965 | 40.96 | 22 |
| Rye silage | 582.14 | 0.124 | 2.78 | 0.994 | 13.04 | 27 |
| Grass silage | 517.08 | 0.179 | 2.41 | 0.973 | 25.13 | 24 |
| Sorghum silage | 489.99 | 0.197 | 2.32 | 0.992 | 11.55 | 28 |
| Topinambour silage | 414.48 | 0.214 | 2.24 | 0.979 | 17.02 | 24 |

Table 3. Kinetic parameters of biogas production from chosen batch in Tabasarana model.

Reference: own study.

Table 4. Physicochemical analysis of: batch, inoculum and selected substrates used in the anaerobic digestion process.

| Mark | Unit | Batch | Sorghum | Beet | Grass | Rye | Inoculum |
|---------------------|---------|--------------|---------------|---------------|---------------|---------------|--------------|
| TS | % | 6.0 ± 0.1 | 29.4 ± 0.1 | 23.3 ± 0.1 | 25.9 ± 0.2 | 38.4 ± 0.2 | 5.5 ± 0.2 |
| VS | % TS | 76.2 ± 0.1 | 94.9 ± 0.1 | 95.7 ± 0.2 | 85.9 ± 0.1 | 93.5 ± 0.1 | 74.2 ± 0.1 |
| Crude ash | % | 1.42 ± 0.1 | 1.50 ± 0.1 | 0.73 ± 0.1 | 3.57 ± 0.1 | 2.51 ± 0.1 | 1.41 ± 0.1 |
| pH | - | 8.4 ± 0.1 | 4.6 ± 0.1 | 4.7 ± 0.1 | 5.1 ± 0.1 | 7.6 ± 0.1 | 8.6 ± 0.1 |
| Ν | % TS | 8.6 ± 0.2 | 1.1 ± 0.3 | 0.70 ± 0.1 | 2.2 ± 0.1 | 1.0 ± 0.1 | 9.84 ± 0.2 |
| Р | g/kg TS | 10.0 ± 0.3 | 3.8 ± 0.2 | 1.0 ± 0.2 | 3.4 ± 0.2 | 1.2 ± 0.2 | 11.4 ± 0.2 |
| P-PO4 | g/kg TS | 3.5 ± 0.3 | 1.7 ± 0.3 | 0.60 ± 0.3 | 2.7 ± 0.6 | 0.40 ± 0.2 | 3.6 ± 0.4 |
| К | g/kg TS | 42.7 ± 0.4 | 8.9 ± 0.4 | 5.80 ± 0.1 | 23.9 ± 0.3 | 8.5 ± 0.2 | 45.2 ± 0.6 |
| Ca | g/kg TS | 28.4 ± 0.8 | 3.0 ± 0.2 | 1.30 ± 0.1 | 11.0 ± 0.5 | 3.2 ± 0.30 | 28.8 ± 0.2 |
| Na | g/kg TS | 9.1 ± 0.4 | 0.10 ± 0.05 | 0.30 ± 0.10 | 0.10 ± 0.05 | 0.10 ± 0.05 | 9.5 ± 0.1 |
| Ammoniacal nitrogen | g/kg TS | 44.6 ± 0.8 | 2.5 ± 0.2 | 0.20 ± 0.1 | 3.0 ± 0.1 | 1.8 ± 0.3 | 49.0 ± 0.7 |

Reference: own study.

After the anaerobic digestion process, further physicochemical analyzes of the digestate, solid fraction and effluent resulting from the separation of the digestate were carried out (Table 5). The granulation technology requires the fragmentation of the solid fraction to 3 mm and drying it so that the total mass was higher than 20%. The total solid and volatile solid content of solid fraction after grinding and drying were respectively: 20.7% and 91.7%. The liquid digestate had slightly higher values of total solid and volatile solid in relation to the effluent. The solid fraction before grinder and after fragmentation differed slightly from each other by individual parameters. The solid fraction after grinder and effluent contained the least nitrogen, phosphorus, and potassium in relation to the other tested forms of digestate. That is why it is necessary to increase the proportion of these elements to obtain the appropriate proportions of elements in the granular fertilizer.

| Mark | Unit | Digestate | Solid Fraction before Grinder | Solid Fraction after Grinder | Effluent | Solid Fraction after Grinder and Drying |
|--|------------------------|---------------|----------------------------------|---------------------------------|------------------------------------|--|
| TS | % | 5.9 ± 0.1 | 19.4 ± 0.1 | 18.0 ± 0.1 | 5.3 ± 0.1 | 20.7 ± 0.2 |
| VS | % TS | 76.9 ± 0.1 | 90.4 ± 0.1 | 90.8 ± 0.1 | 73.8 ± 0.1 | 91.7 ± 0.1 |
| Crude ash | % | 1.37 ± 0.10 | 1.86 ± 0.1 | 1.66 ± 0.1 | 1.37 ± 0.1 | 1.98 ± 0.1 |
| pH | - | 8.8 ± 0.1 | 9.1 ± 0.1 | 9.4 ± 0.1 | 8.7 ± 0.1 | 9.3 ± 0.1 |
| Ν | % TS | 7.84 ± 0.10 | 2.47 ± 0.10 | 2.39 ± 0.2 | 8.64 ± 0.13 | 2.12 ± 0.10 |
| Р | g/kg TS | 9.3 ± 0.1 | 4.8 ± 0.1 | 3.9 ± 0.1 | 9.3 ± 0.4 | 9.3 ± 0.5 |
| P-PO ₄ | g/kg TS | 1.8 ± 0.3 | 1.1 ± 0.2 | 1.2 ± 0.2 | 10.5 ± 0.2 | 4.3 ± 0.1 |
| K | g/kg TS | 94.6 ± 0.3 | 28.9 ± 0.2 | 32.1 ± 0.2 | 106.7 ± 0.4 | 22.8 ± 0.2 |
| Ca | g/kg TS | 93.6 ± 0.6 | 40.0 ± 0.7 | 39.6 ± 0.5 | 101.5 ± 0.5 | 9.3 ± 0.40 |
| Na | g/kg TS | 9.9 ± 0.1 | 3.0 ± 0.1 | 3.5 ± 0.1 | 11.2 ± 0.1 | 2.7 ± 0.2 |
| Ammoniacal nitrogen | g/kg TS | 40.4 ± 0.2 | 7.4 ± 0.1 | 6.8 ± 0.2 | 39.0 ± 0.2 | 6.8 ± 01 |
| Nitrate | g/L | | | | 1.02 ± 0.3 | |
| Nitrite | g/L | | | | 0.05 ± 0.01 | |
| Phosphates | g/L | 1.8 ± 0.4 | 1.1 ± 0.3 | 1.2 ± 0.3 | 2.5 ± 0.2 | 1.3 ± 0.3 |
| Chlorides | g/L | | | | 0.98 ± 0.22 | |
| Suspension | g/L | | | | 10.5 ± 1.8 | |
| Biomass degree of hydration | % | | 80.6 ± 0.2 | 82 ± 0.1 | | 79.3 ± 0.2 |
| Degree of separation TS from effluent | % | | 94.59 ± 0.20 | 94.17 ± 0.20 | | 94.93 ± 0.20 |
| Dehydration of digestate | minutes | | | | | |
| Total acidity | mmol/L | | | | | |
| Oxidisability | g/L O ₂ | | | | 16.4 ± 3.6 | |
| Turbidity | NTU | | | | $\textbf{22,700} \pm \textbf{850}$ | |
| Carbonic hardness | g CaCO ₃ /L | | | | 5.2 ± 0.8 | |
| Conductivity | mS/cm ² | | | | 31.6 ± 2.3 | |
| Color | - | | | | dark-brown | |
| Protein | % | | | | 54 ± 0.7 | |

Table 5. Physicochemical analyzes of: digestate, solid fraction and effluent.

Reference: own study.

The granule production research was phased. The parameters of granular fertilizer obtained for two sample (Table 6) were not satisfactory in terms of nutrient elements content and significantly differed from the assumed N:P:K:Mg:S—:2:4:1.4:1.8 ratio.

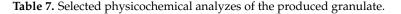
| Granulate | TS | Ν | Р | К | Mg | S | pН | Reactivity | | |
|-------------------|-----------------------|---------------|---------------|---------------|---------------|-----------------|--------------|------------|--|--|
| Giuntalate | % | | | % TS | | | - | % | | |
| Without nutrients | 67.1 ± 0.1 | 0.60 ± 0.03 | 0.20 ± 0.02 | 1.22 ± 0.06 | 0.68 ± 0.01 | 0.076 ± 0.002 | 12.2 ± 0.1 | 72 | | |
| With nutrients | 92.3 ± 0.1 | 4.10 ± 0.20 | 4.20 ± 0.13 | 11.0 ± 0.20 | 7.3 ± 0.11 | 0.013 ± 0.006 | 12.4 ± 0.1 | 84 | | |
| | Reference: own study. | | | | | | | | | |

Table 6. Selected physicochemical analyzes of the produced granulate.

In the current situation, it was necessary to make further attempts to produce further granulates with a satisfactory composition and effective impact on plants in fertilizing experiments. It has been found that the amount of added calcium during the granulation process cannot be significantly reduced due to a significant process temperature reduction and thus a deterioration in the durability of the granules. It is necessary to increase the amount of added mineral nutrients (mainly nitrogen) during granulation, which is against the original assumptions. Increased addition of mineral nutrients during the granulation process causes also a big problem, as there are large losses mainly of nitrogen. As a result, it causes difficulties in maintaining a stable level of content and composition of N:P:K:Mg:S in granular. Therefore, it is necessary to increase the content of nutrients in the granules so that in 1 ton of granular fertilizer there is a minimum of 50 kg N, 90 kg P and 120 kg K. These values are dictated by the standard requirement of plants for nutrients, however, the maximum nitrogen dose of

170 kg/ha can be achieved in several doses. Finally, it was shown that the only parameter that can control and change the properties of the granular is the mineral content of nutrients. As a source of nitrogen supplementing its possible absence in the solid fraction of digestate, urea (NH_2CONH_2) was used, in the absence of phosphorus, this element was supplemented with monoammonium phosphate ($NH_4H_2PO_4$). To supplement the lack of potassium, magnesium, and sulfur in the solid fraction, respectively: potassium hydrogen phosphate (KH_2PO_4), magnesium nitrate ($Mg(NO_3)_2$), sodium thiosulphate ($Na_2S_2O_3$) were used.

Granular fertilizer was produced with a content of: N 5% TS, P 9% TS, and K 12% TS so in 1 ton of fertilizer there would be 50 kg N, 90 kg P and 120 kg K. This means a significant increase in percentage of N, P, K, Mg, S in the fertilizer granulate, which differs from the original idea of a minimal nutrient addition to the granulate (Table 7). It was found that at the beginning of the fertilizing experiments plants will receive a starting dose of fertilizer in a mineral form. Organic-mineral granular also were produced which was immediately sown in vase experiments. These granular, according to assumptions, slowly release nutrients into the soil solution (Figure 4.).



| Granulate | TS | Ν | Р | К | Mg | S | pН | Reactivity |
|-----------|----------------|---------------|---------------|---------------|---------------|-----------------|--------------|------------|
| Gianulate | % | | | % TS | | | - | % |
| >6 mm | 87.9 ± 0.1 | 3.91 ± 0.02 | 8.68 ± 0.05 | 11.6 ± 0.25 | 11.4 ± 0.14 | 0.015 ± 0.001 | 12.6 ± 0.1 | 112 |
| <6 mm | 92.0 ± 0.2 | 3.93 ± 0.04 | 6.13 ± 0.05 | 11.5 ± 0.10 | 8.08 ± 0.21 | 0.017 ± 0.009 | 13.0 ± 0.1 | 109 |
| 6 mm | 88.6 ± 0.2 | 3.30 ± 0.06 | 6.43 ± 0.10 | 10.2 ± 0.10 | 8.32 ± 0.12 | 0.022 ± 0.011 | 13.0 ± 0.1 | 96 |



Reference: own study.

Figure 4. Granular fertilizer.

3.2. The Legitimacy of Processing of Digestate into Fertilizer Granules for 1 MW_{el} Biogas Plants

The calculations below present the legitimacy of processing digestate from a 1 MW biogas plant into granular fertilizer. This biogas plant uses a batch consisting of: sorghum, beet, rye, and grass in the percentage share used in the anaerobic digestion kinetics research. In addition, how much digestate is calculated per day and during the year is created in this example agricultural biogas plant. The basic parameters for calculations are included in Table 8. At these values, the capacity of the biogas plant is 1 MW, a total of 80.8 t/day of all four substrates should go to the chamber digestion per day. If 90% of the batch used to supply the biogas plant goes to the digestate chamber daily, the quantity of digestate is: 72.7 t/day. The annual production of digestate for this exemplary biogas plant is 26,550 t/year. If you want to use liquid digestate as a fertilizer, you must own hundreds of hectares of fields with this amount. It is often impossible, especially when the biogas plant is owned by a food industry company, which usually does not have its own arable land. That is why you should look for other ways to process the digestate, so that it can be applied more easily to the field and that it will be smaller amounts during the year. If the digestate contains 5% of TS, taking into account the reaction of water with calcium and assuming the addition of calcium equal to the amount of TS and using about 20% of additives containing N, P, K, Mg, S, you can produce 3613 t/year of fertilizer. The estimated production cost of one ton of granular fertilizer is PLN from 400 to 500, while the estimated price of fertilizer is about from 800 to 1000 PLN. The average annual profit for an example biogas power plant using the ORTWED method may amount to 1,625,850 PLN, while the cost of installing the ORTWED method in a biogas plant with a 1 MW of power is about 3,500,000–4,000,000 PLN.

| Substrate | Percentage | Amount of Substrate | Total Solid | Volatile Solid | Methane Yield |
|-----------|------------|---------------------|--------------------|----------------|-----------------------|
| Substrate | % | t/year | % | % TS | Nm ³ /t VS |
| Sorghum | 20 | 5900 | 29.9 | 94.1 | 320 |
| Beet | 60 | 17,700 | 16.2 | 93.7 | 462 |
| Rye | 10 | 2950 | 60.6 | 92.6 | 296 |
| Grass | 10 | 2950 | 20.2 | 76.1 | 298 |

Table 8. Basic parameters of substrates in an example agricultural biogas plant.

Reference: own study.

4. Summary and Conclusions

An excellent example of a suitable form of digestate is a valuable organic-mineral granular fertilizer made using the ORTWED method. By using digestate from a biogas plant and using its fertilizing properties, biogas production is waste-free and odor-free. In addition, the soil is enriched with the organic part of the solid fraction of the digestate contained in the granulate (improvement of soil conditions by reducing the humus deficit in the soil). The calcium contained in the granulate has a deacidifying effect on the soil, which improves the soil's properties by reducing the calcium deficit in the acidified soil. Another advantage of the use of granules is the enrichment of the soil with biogenic elements necessary for the vegetation of plants contained in the granulate (in the solid fraction of digestate + mineral additive) and there is a reduction in the use of mineral fertilizers. The resulting granulate is sterile and hydrophobic, thus reducing the problem of water eutrophication. In addition, the fertilizer can be 2 to 3 times cheaper for the farmer than the fertilizer produced industrially. However, there are also difficulties associated with the granulation process. The hydrophobic granulate showed low reactivity/solubility, due to which the nutrients were too slow to release from the granulate into the soil during fertilization experiments, which negatively influenced the growth of plants. Therefore, it was necessary to change the concept of fertilizer granulate into a less hydrophobic one, with a greater reactivity and availability for plants. It was necessary to increase the percentage of mineral supplements (biogenic elements) and to introduce the starting dose of nitrogen at the beginning of plant vegetation. The factor limiting the amount of fertilizer granulate per hectare is its high calcium content of about 50%, the permissible dose of calcium is 4 t \cdot ha⁻¹. During the production of fertilizer granules large losses of nitrogen in the form of oxidation of ammoniacal nitrogen were observed. In addition, at the beginning of the research in the granulation process, there was a problem with maintaining a constant repetitive level of biogenic elements N, P, K, Mg, S in subsequent replications.

Acknowledgments: The work was carried out as part of the NCBR PBS3/B8/23/2015 project—ID: 247127 entitled "Non-waste biogas production from plant substrates based on the transformation of digestate into a valuable organic-mineral granular fertilizer".

Author Contributions: Hubert Prask, Józef Szlachta and Małgorzata Fugol performed batch and continuous anaerobic digestion process of selected substrates. They prepared a digestate for the production of granulate. In addition, they developed research results and made statistics of test results. Leszek Kordas together with Agnieszka Lejman performed physicochemical analyzes of substrates, poferments and granulates. Franciszek Tużnik and Filip Tużnik produced a organic-mineral granular fertilizer for research.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Tambone, F.; Orzi, V.; D'Imporzano, G.; Adani, F. Solid and liquid fractionation of digestate: Mass balance, chemical characterization, and agronomic and environmental value. *Bioresour. Technol.* 2017, 243, 1251–1256. [CrossRef] [PubMed]
- 2. Alburquerque, J.A.; de la Fuente, C.; Campoy, M.; Carrasco, L.; Nájera, I.; Baixauli, C.; Caravaca, F.; Roldán, A.; Cegarra, J.; Bernal, M.P. Agricultural use of digestate for horticultural crop production and improvement of soil properties. *Eur. J. Agron.* **2012**, *43*, 119–128. [CrossRef]
- Nutiu, E. Anaerobic purification installation with production of biogas and liquid fertilizers. *Procedia Technol.* 2014, 12, 632–636. [CrossRef]
- 4. Fiorese, G.; Guariso, G. Energy from Agricultural and Animal Farming Residues: Potential at a Local Scale. *Energies* **2012**, *5*, 3198–3217. [CrossRef]
- 5. Lanzini, A.; Madi, H.; Chiodo, V.; Papurello, D.; Maisano, S.; Santarelli, M.; Van herle, J. Dealing with fuel contaminants in biogas-fed solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) plants: Degradation of catalytic and electro-catalytic active surfaces and related gas purification methods. *Prog. Energy Combust. Sci.* 2017, *61*, 150–188. [CrossRef]
- 6. Papurello, D.; Lanzini, A.; Tognana, L.; Silvestri, S.; Santarelli, M. Waste to energy: Exploitation of biogas from organic waste in a 500Wel solid oxide fuel cell (SOFC) stack. *Energy* **2015**, *85*, 145–158. [CrossRef]
- Papurello, D.; Tognana, L.; Lanzini, A.; Smeacetto, F.; Santarelli, M.; Belcari, I.; Silvestri, S.; Biasioli, F. Proton transfer reaction mass spectrometry technique for the monitoring of volatile sulfur compounds in a fuel cell quality clean-up system. *Fuel Process. Technol.* 2015, *130*, 136–146. [CrossRef]
- Papurello, D.; Schuhfried, E.; Lanzini, A.; Romano, A.; Cappellin, L.; Märk, T.; Silvestri, S.; Santarelli, M.; Biasioli, F. Proton transfer reaction-mass spectrometry as a rapid inline tool for filter efficiency of activated charcoal in support of the development of Solid Oxide Fuel Cells fueled with biogas. *Fuel Process. Technol.* 2015, 130, 78–86. [CrossRef]
- 9. Negri, M.; Bacenetti, J.; Fiala, M.; Bocchi, S. Evaluation of anaerobic degradation, biogas and digestate production of cereal silages using nylon-bags. *Bioresour. Technol.* **2016**, *209*, 40–49. [CrossRef] [PubMed]
- Blumenstein, B.; Siegmeier, T.; Bruckhaus, C.; Anspach, V.; Möller, D. Integrated Bioenergy and Food Production—A German Survey on Structure and Developments of Anaerobic Digestion in Organic Farming Systems. *Sustainability* 2015, 7, 10709–10732. [CrossRef]
- 11. Dahlin, J.; Herbes, C.; Nelles, M. Biogas digestate marketing: Qualitative insights into the supply side. *Resour. Conserv. Recycl.* **2015**, 104, 152–161. [CrossRef]
- 12. Calabrò, P.; Panzera, M. Anaerobic Digestion of Ensiled Orange Peel Waste: Preliminary Batch Results, Thermal Science and Engineering Progress. Available online: https://doi.org/10.1016/j.tsep.2017.12.011 (accessed on 22 February 2018).
- 13. Sigurnjak, I.; Vaneeckhaute, C.; Michels, E.; Ryckaert, B.; Ghekiere, G.; Tack, F.M.G.; Meers, E. Fertilizer performance of liquid fraction of digestate as synthetic nitrogen substitute in silage maize cultivation for three consecutive years. *Sci. Total Environ.* **2017**, *599–600*, 1885–1894. [CrossRef] [PubMed]
- 14. Kratzeisen, M.; Starcevic, N.; Martinov, M.; Maurer, C.; Müller, J. Applicability of biogas digestate as solid fuel. *Fuel* **2010**, *89*, 2544–2548. [CrossRef]
- 15. Koszel, M.; Lorencowicz, E. Agricultural use of biogas digestate as a replacement fertilizers. *Agric. Agric. Sci. Procedia* **2015**, *7*, 119–124. [CrossRef]
- 16. Al Seadi, T.; Drosg, B.; Fuchs, W.; Rutz, D.; Janssen, R. Biogas digestate quality and utilization. In *The Biogas Handbook*; Woodhead Publishing Limited: Sawston, UK, 2013; pp. 267–301. [CrossRef]
- 17. Santi, G.; Proietti, S.; Moscatello, S.; Stefanoni, W.; Battistelli, A. Anaerobic digestion of corn silage on a commercial scale: Differential utilization of its chemical constituents and characterization of the solid digestate. *Biomass Bioenergy* **2015**, *83*, 17–22. [CrossRef]
- Tużnik, F. Produkcja Zgranulowanych Nawozów Organiczno-Mineralnych z Osadu z Oczyszczalni Komunalnych. Promotional Materials. Available online: http://pl.tuzal.pl/upload/pliki/431940_ 1231879958.pdf (accessed on 22 February 2018).
- Mangwandi, C.; JiangTao, L.; Albadarin, A.; Allen, S.; Walker, G. The variability in nutrient composition of Anaerobic Digestate granules produced from high shear granulation. *Waste Manag.* 2013, 33, 33–42. [CrossRef] [PubMed]

- 20. Fermentation of Oganic Materials. *Characterisation of the Substrate, Sampling, Collection of Material Data, Fermentation Tests;* Verein Deutscher Ingenieure: Düsseldorf, Germany, 1 April 2006; VDI 4630.
- 21. Laval, A.A.; Dzivama, A.U.; Wasinda, M.K. Effect of inoculum to substrate ratio on biogas production of sheep paunch manure. *Res. Agric. Eng.* **2016**, *62*, 8–14.
- 22. Hoeks, J. Significance of biogas production in waste tips. Waste Manag. Res. 1983, 1, 323-335. [CrossRef]
- 23. Szlachta, J.; Fugol, M.; Prask, H. The impact of the raw material composition on fermentation kinetics and the yield of biogas and methane. *Przem. Chem.* **2016**, *95*, 1805–1810.



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).