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Physicochemical properties and agglomeration parameters of biogas digestate with addition of calcium carbonate

M. Dąbrowska*, A. Świętochowski and A. Lisowski

Warsaw University of Life Sciences, Department of Agricultural and Forestry Machinery, Faculty of Production Engineering, Nowoursynowska 166, PL02-787 Warsaw, Poland
*Correspondence: magdalena_dabrowska@sggw.pl

Abstract. The aim of the work was to determine the physical properties of digestate from biogas production - either with or without the addition of calcium carbonate and to determine the parameters of its compaction. The material for research was obtained from an agricultural biogas plant specialized in processing cattle manure, vegetable pomace, chicken manure and maize silage. The parameters of compaction of digestate were experimentally determined and its net calorific value was calculated based on the gross calorific value. Physical properties were determined according to standards. The moisture content of liquid digestate was 96%. Mechanical separation allowed to decrease the water content by 19% and addition of 20% of calcium carbonate by 30%. It was found that digestate with addition of calcium carbonate is not suitable to use for energy purposes, because of its low net calorific value (5.2–5.9 MJ kg^{-1}), however it can be used for fertilizer purposes in relation to its chemical composition. Without additives, the net calorific value was 14.9 MJ kg^{-1}, but due to the high moisture content of the raw material it is unprofitable to dry it and burn. On the other hand, it was proved that it is possible to obtain pellets of appropriate density out of the digestate using 40 mm of the die height and 0.3 g of single portion of the material.

Key words: digestate, binder, pellets, fertilizer, energy.

INTRODUCTION

The problem with the ever-increasing amount of wastes and pollution is one of the most serious problems in the world. After each production, side products are created, e.g. post-fermentation sludge in an agricultural biogas plant. In the Polish law, digestate is a waste (Czekała et al., 2012). Digestate arises from the decomposition of organic matter under anaerobic conditions caused by bacteria (Oyamoto & Kung, 1980; Pontus, 2014; Lalak et al., 2015). These are residues of the fermentation process, i.e. unfermented organic compounds, minerals and biomass of methane bacteria. The composition of post-fermentation sludge depends on the composition of the substrate to be decomposed (Alburquerque et al., 2012).

In the initial stage of fermentation, conversion to alcohols or lower organic acids takes place, followed by simple compounds such as methane and carbon dioxide. Transformation of substrates takes place in the biogas plant' digesters. This process consists of four stages, each of them takes place using a bacteria designated for it. All stages of fermentation take place in the same fermentation chamber, and include hydrolysis, acidic phase, acetogenesis and metagenesis (Gerardi, 2003; Ziemiński & Frąc, 2012).

The unfermented fractions of substrates, most often biomass, from fermentation chambers were considered to be a waste for a very long time. Along with the development of this sector, also digestates began to be used as a full-value fertilizer used in agriculture. However, due to the inhomogeneity of the material, high moisture content and odour nuisance, the sludge was not suitable for transport, which is why it was used only within 5 km from the biogas plant. Moreover, marketing barriers include transport costs and lingering negative perceptions (Dahlin et al., 2015). Yields after using digestates are comparable to those fertilized with mineral fertilizers, and better than those fertilized with liquid manure. Due to the mineral content in the forms directly available for plants, it is characterized by fast fertilizing action (Kowalczyk-Juśko & Szymańska, 2015). This was proved by investigating the effect of digestate on watermelon and cauliflower (Pontus, 2014). The size of watermelons was the same for all fertilizers, but the overall harvest was better for mineral fertilizers and digestate. After the first addition of digestate to the soil, it was noted that the concentration of nitrates and phosphorus in the soil increased rapidly. At the next doses there were no significant differences. The total organic carbon content in the soil did not increase because the supplied organic matter was degraded very quickly.

Due to the high moisture content, digestate treatment also belongs to problematic processes. This material requires dehydration and drying up to 15–20% of moisture content, because above this value processing is very difficult (Kratzeisen et al., 2010). However, there are several ways to reduce the moisture content. One of them is the drying up of the substrate under natural conditions to the moisture allowing further use (Lehtomäki, 2006). It is also possible to add a product that could absorb some of water from the material. Such a compound may be a calcium carbonate ($CaCO_3$) which has hygroscopic properties.

Calcium carbonate is used as a hardener and white dye, increases the yield of crops and restores the pH of the soil, which is why it is often used as a fertilizer (Ciesielska et al., 2011). However, in the production of pellets from biomass it significantly reduces moisture, but also causes decrease in calorific value (Lisowski et al., 2013; Dąbrowska et al., 2016). Chemical composition and physical properties of digestate fuel pellets depend on the blend of substrates used as feedstock for biogas production (Kratzeisen et al., 2010). Pellets made of digestate with the addition of calcium carbonate should be easier to process, transport and handling than digestate itself, due to their higher density and lower moisture content (Pedrazzi et al., 2015).

There are new technologies that have been introduced during the last years to treat biogas digestate for optimal transport and application conditions (Rehl & Muller, 2011), however there are not many studies on compaction parameters of digestate, which is an obstacle in using the material so full of potential. Therefore, tests were carried out to find out the properties of this raw material and to determine the parameters of its compaction, so that it would be possible to use the digestate as a fuel or valuable fertilizer in their best way. Thus, the aim of the work was to determine the physical properties of digestate from biogas production - either with or without the addition of calcium carbonate and to determine the parameters of its compaction. These information are crucial for large-scale technology in order to increase the efficiency of pellets production.

MATERIALS AND METHODS

Material

The material for research (Fig. 1) was obtained from an agricultural biogas plant, located in Poland, specialized in processing maize silage (40%), cattle manure (30%), vegetable pomace (10%), chicken manure (10%) and pig manure (10%). Liquid fraction was separated and a solid matters with and without addition of binder were investigated in WULS Analytical Centre according to standards to determine the main chemical compounds in the raw materials (Table 1).

Figure 1. Digestate as a raw material without binder (left) and with addition of calcium carbonate (right).

Moisture content

The moisture content of digestate was determined using drying-weighing method according to the PN-EN ISO 18134-3:2015-11 standard. Five samples of 30 g each were weighed on the scales RADWAG type WPS 600/C with an accuracy of 0.01 g. After that, samples were placed in the laboratory drier POL-EKO-APARATURA SP.J. type SLW 115 TOP+, at 105 °C for 24 hours. Dried samples were weighed once again and the moisture content was calculated using formula:

$$w = 100\frac{m_w - m_s}{m_w} \quad (1)$$

where w – moisture content of the material, %; m_w – mass of the wet material, g; m_s – mass of the dried material, g.

Calorific value

Net calorific value was calculated based on the gross calorific value, which was determined using the calorimeter Kl-10, Precyzja-BIT, Bydgoszcz, Poland according to standard PN-ISO 1928. For each material 5 repetitions were done.

$$Q_w = Q - 2454 \cdot (w + 9H) \quad (2)$$

where Q_w – net calorific value, MJ kg^{-1}; Q – gross calorific value, MJ kg^{-1}; w – moisture content, %; H – hydrogen content, %.

Agglomeration process

The parameters of digestate compaction were experimentally determined using a special designed device mounted on the universal testing machine TIRATEST (Fig. 2).

The stand was equipped with the piston and the die with heating bands on the external surface of the die. The process temperature was set using the ESM 3710i temperature controller. The die was an open cylindrical working chamber with an opening with 8 mm diameter. The changed parameters during the subsequent tests were: the dose of material and the thickness of the die, which was the height of the material layer after compaction. During test, the signals registered by the sensors of the testing machine were processed by the Matest program, which enabled monitoring of forces acting on the piston. Tests were carried out at various doses from 0.2 to 0.4 g, and the height of the forming die was varied from 30 to 50 mm. Each dose of material was weighed on the scales RADWAG WPA 40/160/C/1 with an accuracy of 0.0001 g.

Depending on the analyzed case, the tested material were: pure digestate or digestate with addition of 10 or 20% of calcium carbonate. Initially, the outlet opening was closed with a pellet, and then the die was heated to a set temperature of 140 °C for 1 hour. When the temperature was stabilized at the entire height of the die, the study could be started. Measured samples of digestate without and with the addition of binder were poured into the working chamber using a plastic container. The next step was to insert the piston into the die opening and compact the material using the Matest strength testing program. The end of the test was determined by the limit sensor at the set height and then the die returned to its initial position. One test, with previously determined parameters, involved carrying out 40 to 60 measurements.The only exception was when the selected compaction parameters did not allow the formation of durable pellets because the material did not compact well. Then the number of repetitions decreased. After measurements, the limit sensor was moved so that the piston completely pushed out the pellets. The obtained agglomerates were then arranged in order of their obtaining, to know which were obtained in the initial phase of the test and which were in stable conditions. The work of the pressure agglomeration was calculated using the formula:

Figure 2. Testing stand for agglomeration process.

$$L_c = \int F_{max}\, dl \tag{3}$$

where L_c – compaction work, J; F_{max} – maximum force, N; l – piston displacement, m.

Density

To determine the density of obtained pellets an electronic caliper with an accuracy of 0.01 mm and scales RADWAG type WPA 40/160/C/1 with an accuracy of 0.00001 g were used. Two diameters on perpendicular planes and two measurements of height were made and each pellet was weighed. Then, the density was calculated using a formula:

$$\rho = \frac{m}{V} \tag{4}$$

where: ρ – pelet density, kg m^{-3}; m – mass, kg; V – volume, m^3.

Elemental composition and statistical analysis

A chemical analysis included determination of dry matter and elemental composition of the material were determined in Analytical Centre of WULS. Dry matter was determined using weighing method, Ca, K_2O and P_2O_5 were determined using a spectrometry emission method (ICP-OES) and content of nitrogen N was determined using Kiejdahl method with a titration final mark.

Data analysis was carried out using Statistica v.12 computer program, with application of variance analysis procedure and Duncan test. Statistical inferences were made at the 0.05 level of probability.

RESULTS AND DISCUSSION

Received digestate was meeting the standards in the range of permissible contamination values in organic and mineral fertilizers as well as agents supporting cultivation of crops (Table 1). The main fertilizer compounds were slightly decreased after addition of calcium carbonate and the share of dry matter was significantly increased 20.3% to 64.8%. These results are also confirmed by moisture content results (Fig. 3).

Table 1. Chemical composition of digestates

Material	Dry matter, %	K_2O, %	P_2O_5, %	Ca, %	N, %
Digestate	20.3	1.01	1.08	-	2.26
Digestate with $CaCO_3$	64.8	0.53	0.99	27.5	< 1.00

The moisture content of liquid digestate was 96%. Mechanical separation allowed to decrease the water content by 19% and addition of 20% of calcium carbonate by 30%. To verify the results also a lower addition of binder was added to the raw material and the moisture content was above 65%.

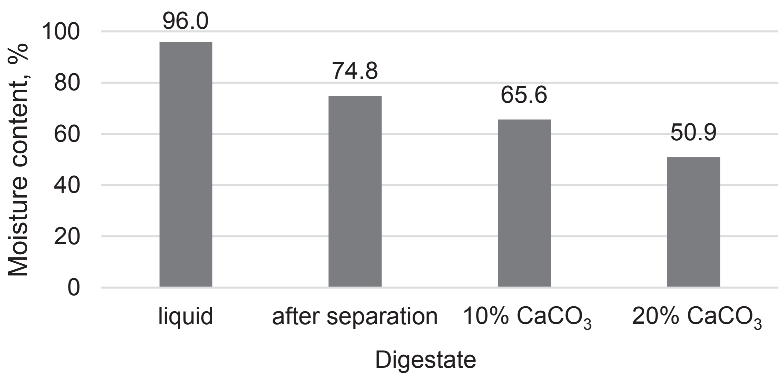

Figure 3. Moisture content for different types of digestate.

It was found that without additives, the net calorific value (Fig. 4) for tested material was 14.9 MJ kg^{-1}, but due to the high moisture content of the raw material it is unprofitable to dry it and burn. Similar results of net calorific value (15 MJ kg^{-1}) was obtained by Kratzeisen et al. (2010) however in another study (Kuligowski, 2011) this value was 11.3 MJ kg^{-1}. Differences in values of this parameter result from a different composition of digestate. High gross calorific value for pure digestate was 17.9 MJ kg^{-1}, which proves its usefulness for energy purposes. On the other hand, digestate with addition of calcium carbonate is not suitable to use for energy purposes because of its low net calorific values 5.2–5.9 MJ kg^{-1}. Addition of 10% of calcium carbonate caused decrease in calorific value by 60% to 5.9 MJ kg^{-1} and further addition of calcium carbonate to 20% caused smaller decrease in net calorific value nearly by 12%.

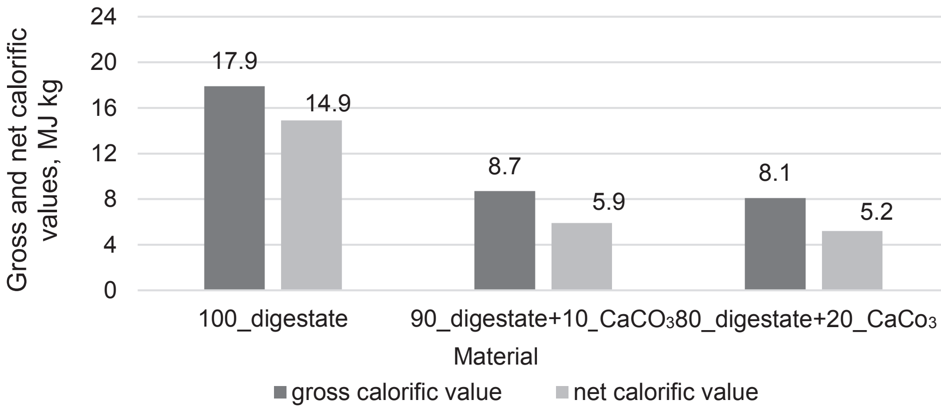

Figure 4. Gross and net calorific values of digestate with and without of binder.

Agglomeration research were carried out for various compaction parameters. Initially, for the same dose, the compaction height was changed per trial. Based on previous preliminary tests for other materials (Lisowski et al., 2017), the first trial was conducted at 40 mm and 0.3 g and durable pellets with high density (791 kg m^{-3}) were obtained (Fig. 5). Then, the die height was increased to 50 mm at the same single dose of raw material and durable pellets were also made, but with lower density (536 kg m^{-3}). When the die height was reduced to 30 mm at the same dose, no durable pellets were obtained, because the height was too low and the material fell out of the matrix. After determining the best height, the mass of a single dose of compacted material was changed. Both compaction tests for dose of digestate at 0.4 g and 0.2 g enabled the production of pellets with a stabilized compaction forces, but their durability was not satisfactory. Therefore it was decided, that pellets made of material with the addition of calcium carbonate should be produced for the parameters: 40 mm of the die height and 0.3 g of a single dose of compacted material as found as the best agglomeration parameters.

Figure 5. Pellets obtained at compaction parameters: 40 mm of the die height and 0.3 g of the single dose of digestate.

The obtained pellets (Figs 6, 7) were stable, with a lighter color than pellets without addition of calcium carbonate. Due to the use of calcium carbonate addition, not only the moisture of the digestate was reduced, but also the density of pellets was increased

(Table 4). Pellets created with such parameters had the smoothest surface and the most regular shape. Therefore, the quality of these pellets was the best. The displacement and compaction forces for these parameters were similar. The amount of calcium carbonate addition did not have a major impact on the pressure agglomeration process.

Figure 6. Pellets made of digestate with 10% of calcium carbonate.

Figure 7. Pellets made of digestate with 20% of calcium carbonate.

Pellets from digestate with the addition of 10% of calcium carbonate were characterized by the highest mean compaction work (1.81 J). The lowest compaction work was obtained for compaction the material without additives (Table 2).

Densities of pellets obtained under stable compaction conditions and the best parameters (40 mm and 0.3 g) were compared. The analysis of the variance of pellets density (Table 3) showed that the share of the additive statistically significantly affects the density of pellets made of digestate, which can be determined on the basis of F-Fisher-Snedecor test, where F was 13.7 for $p < 0.001$.

Table 2. The mean values of compaction work L_c, its standard deviations SD and 95% confidence intervals

Material	Binder, %	L_c, J	SD L_c, J	-95% L_c, J	+95% L_c, J
digestate	0	0.32	0.2	-0.08	0.72
	10	1.81	0.2	1.41	2.21
	20	0.68	0.18	0.31	1.04

Table 3. The variance analysis results of pellets density ρ

Source	Sum of squares	Degrees of freedom	Mean square	F-test	P-value
residual	10,497,656	1	10,497,656	8,316.3	< 0.0001
binder	34,549	2	17,275	13.7	< 0.001
error	15,147	12	1,262		

Table 4. The mean values of densities ρ of pellets made of digestate with and without the calcium carbonate, their standard deviations SD and 95% confidence intervals

Material	Binder, %	ρ, kg m^{-3}	SD ρ, kg m^{-3}	-95% ρ, kg m^{-3}	+95% ρ, kg m^{-3}	n
digestate	0	791.23	15.89	756.61	825.84	5
	10	815.50	15.89	780.88	850.12	5
	20	902.98	15.89	868.36	937.59	5

The density of pellets with the same compaction parameters was calculated for the last five pellets, which were produced under stable conditions of the compaction process (Table 4). The increase in the share of calcium carbonate added to the digestate caused the increase in pellets density. The highest density of pellets was obtained for agglomerates from digestate with 20% addition of calcium carbonate and it was 903 kg m^{-3} and the lowest for pellets without addition equal to 791 kg m^{-3}. These results were lower than those for pellets made of typical types of biomass, e.g. straw, hay and wood (Kaliyan & Morey, 2009; Larsson et al., 2008).

CONCLUSIONS

1. Digestate after separation is a difficult material to be used for energy purposes, because it is characterized by a high moisture content, reaching 75%.
2. Addition of calcium carbonate to the digestate decreased the net calorific value from14.9 MJ kg^{-1} to 5.9 MJ kg^{-1} (at 10% of binder) and to 5.2 MJ kg^{-1} (at 20% of binder).
3. The best quality of pellets were obtained at compaction parameters: die height of 40 mm and a dose of 0.3 g. With die height than 40 mm, the obtained agglomerates were of poor quality.
4. The share of calcium carbonate has contributed to the increase in compaction work.
5. Addition of 20% of calcium carbonate to the digestate reduced its moisture by almost 13%, which allowed to easier further processing.
6. Determination of agglomeration parameters for digestate are relevant information for practice in order to increase the efficiency of compaction in large-scale production.
7. Agglomerates made from the residue after the methane fermentation process should have high fertilizing properties, however, further research is needed to confirm this statement.

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