

The pyrolysis and gasification of digestate from agricultural biogas plant

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Keywords: anaerobic digestion, digestate, fertilizer, drying, pyrolysis, gasification.

Abstract: Anaerobic digestion residue represents a nutrient rich resource which, if applied back on land, can reduce the use of mineral fertilizers and improve soil fertility. However, dewatering and further thermal processing of digestate may be recommended in certain situations. Limited applicability of digestate as fertilizer may appear, especially in winter, during the vegetation period or in areas where advanced eutrophication of arable land and water bodies is developing. The use of digestate may be also governed by different laws depending on whether it is treated as fertilizer, sewage sludge or waste. The aim of this paper is to present the effects of thermal treatment of solid fraction of digestate by drying followed by pyrolysis and gasification. Pyrolysis was carried out at the temperature of about 500°C. During this process the composition of flammable gases was checked and their calorific value was assessed. Then, a comparative analysis of energy parameters of the digestate and the carbonizate was performed. Gasification of digestate was carried out at the temperature of about 850°C with use of CO₂ as the gasification agent. Gasification produced gas with higher calorific value than pyrolysis, but carbonizate from pyrolysis had good properties to be used as a solid fuel.

Introduction

Anaerobic digestion (AD) and biogas production are promising ways to achieve energy and environmental benefits at both the local and global level (Börjesson and Berglund 2006, Börjesson and Berglund 2007, Turkiewicz et al. 2013). Biogas plants can provide an alternative energy source for rural households and mitigate environmental emissions from agricultural activities (Chen and Chen 2012, Kogut et al. 2014, Prochnow et al. 2009). AD technology is unique because it can simultaneously be used for waste treatment, for production of renewable energy and for obtaining digestate, which can be used as organic fertilizer, replacing mineral fertilizers that require fossil energy.

However, some logistical problems can be identified. The increasing number of biogas plants especially larger ones generating more than 500 kW of electrical power results in larger transportation distances both on the input side (biomass feedstock) and on the output side (digestate). To solve the problem of digestate transportation there are several different ideas. One suggestion is that the most common way to utilize digestate from agricultural biogas plants is returning it with all containing nutrients directly to the agricultural environment. Anaerobic digestion residue represents a nutrient rich resource which, if applied back on land, can reduce the use

of mineral fertilizers and improve soil fertility. This solution is justified by the fact that digestate constituents produced during acidogenesis with particles of cellulose and lignin do not undergo complete biodegradation. Another reason is that the mineral components of digestate (nitrogen, phosphorus, micronutrients) generated during methanogenesis determine the fertilization value of digestate. Many reports point to the beneficial effect of digestate on soil and plant productivity (Badran 2001, Garg et al. 2005, Zaid et al. 2005). There are several problems concerning use of digestate as a soil fertilizer.

Firstly, an accumulation of biogas plants in certain regions might lead to an oversupply of digestate especially in regions with intensive livestock farming or fermentation of organic residues and bio-waste. If the agricultural area is too small for adequate use of the digestate, surplus material has to be transported to regions with nutrient deficits, or other solutions must be found (Rehl and Müller 2011). However, excessive nitrogen content in digestate can be a problem due to European Union standards. Limited applicability of digestate as fertilizer may appear, especially in winter, during the vegetation period or when there is advanced eutrophication of arable land and adjacent waters (rivers, lakes). For optimal deployment of fermentation residue as fertilizer, the application limit for nitrogenous fertilizer of 170 kg nitrogen per hectare has been determined (Commission of the European Communities 1991).

Another, environmental, problem with digestate utilization for soil improvement can be found, especially during land application of a raw digestate. NH_3 and odors emission mainly happens after field application of fermentation residues (Amon et al. 2006). After field applications, over 70% of nitrogen can be lost (Bauer et al. 2009). In comparison to untreated liquid manure, fermentation residues are characterized by a much lower content of dry matter. A high risk for increased ammonia losses can be expected as a result of the high pH-value (around 8.0 units) in fermentation residues, which influences the NH_3 volatilization (Pötsch et al. 2004).

Moreover, another odor problems appear when conventional digestate management based on its storage in open tanks, chambers and field application is implemented (Sandars et al. 2003, Voca et al. 2005).

Unfortunately, the high water content of the residue somewhat reduces the value as large volumes have to be stored, transported and land applied. Finally, the post-production residue – digestate is considered to be hardly manageable waste, although it can also be perceived as valuable material whose potential for further conversion has not been revealed yet.

To reduce water and nitrogen content several procedures have been implemented, mostly based on digestate drying with the use of: belt dryers, drum dryers, solar dryers (greenhouses), evaporators, and thermal dryers (Rehl and Müller 2011). For the mentioned methods the following issues were investigated: quality of digestate (presence or absence of toxic compounds), ecological requirements (safe application), development of new products, low energy consumption and high economic efficiency of a biogas plant (minimizing operations costs).

The digestate drying overcomes logistical and environmental problems appearing when conventional techniques of digestate management are used. Additionally, digestate drying brings several new approaches to utilize the digestate for energy production, second generation solid fuel production, and biochar production for soil improvement,

which are under investigation. Among numerous examples of such studies, some novel approaches are distinguishable, i.e. use of dehydrated digestate to produce biochar through torrefaction process (Wiśniewski et al. 2012) or other thermal treatment processes: pyrolysis and gasification (Wiśniewski and Gołaszewski 2013).

Accordingly, in order to allow better comparison of these methods we asked which thermal treatment method, namely pyrolysis or gasification, has a greater potential for dewatered digestate energy production. Therefore, the purpose of this study has been to determine the energy generation potential of digestate from an agricultural biogas plant, in which the main substrates are cattle manure and maize silage, subjected to pyrolysis and gasification.

Materials and methods

Digestate from a pilot biorefinery located at the Experimental Station in Baldy, Poland (N53° 36' 1.8073", E20° 36' 8.5295") was used in this research. The technological parameters of fermentation were as follows:

- feedstock moisture 90%;
- the total batch fed to a digester 1.2 m³;
- the total load of organic compounds 2.3 kg VS/m³;
- the set temperature during the fermentation process 35–40°C;
- residence time in the pre-fermentation tank 3 days;
- residence time in the fermentation chamber 20 days;
- residence time in the post-fermentation tank 20 days.

A sample of 30 dm³ of the dry digestate (10% moisture content) was collected from the biogas plant. Drying was done in thermal evaporator associated to biogas plant.

The pyrolysis and gasification of dried digestate processes were performed in a batch reactor (Fig. 1).

The batch reactor consisted of a sealed chamber with an electrically heated bottom and a gaseous products cooler. As a cooling medium, circulating water was used. The reactor was equipped with a process temperature control system within

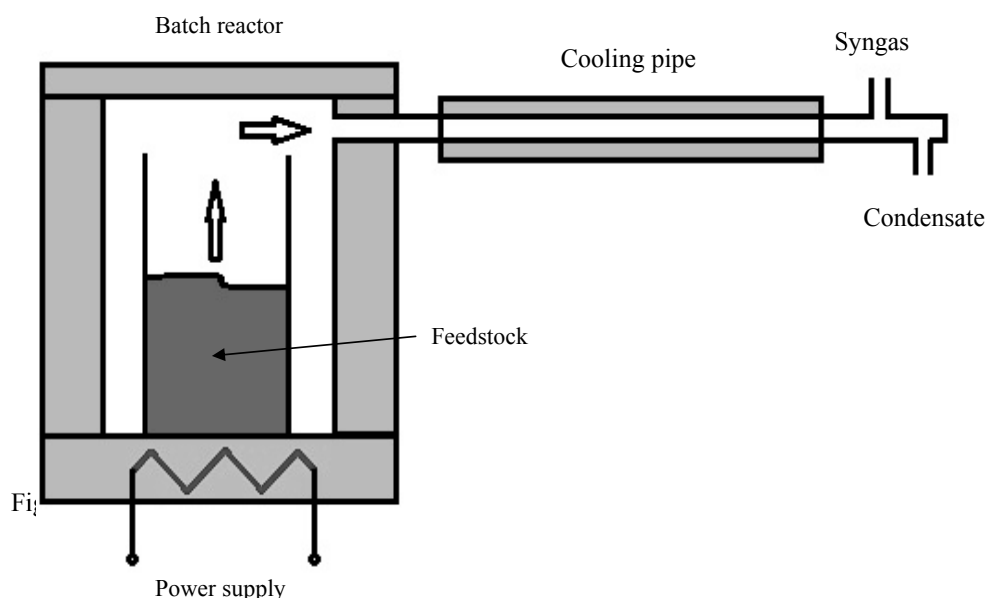


Fig. 1. The construction of pyrolysis/gasification batch reactor

the range of about 1000°C. Dried digestate was fed into the reactor through the top cover and then thermally processed in the heating chamber. Two thermal treatment methods: pyrolysis, and gasification were applied. The gaseous products of processes were then cooled and condensed in a pipe cooler. The process parameters in the reactor were measured and recorded in real time. Gaseous products of pyrolysis and gasification composition was determined [% v/v] in range of: carbon oxide (CO), carbon dioxide (CO₂), methane (CH₄), hydrogen (H₂), and oxygen (O₂). Changes of calorific value [kJ/Nm³] of gaseous products were monitored.

Pyrolysis was carried out at 500°C. Gasification of digestate was carried out at 850°C with use of CO₂ as the gasification agent. Pyrolysis was carried for 2000 s, but the duration of gasification was 1500 s. Before feeding digestate, the reactor was pre-heated to 850°C. Once a sample of digestate was inside and the process of gasification started, the chosen gasification agent CO₂ was fed into the reactor with the volumetric flow 0.004 m³/h.

The comparative analysis of energy parameters of the digestate and the pyrolysis product – carbonizate was performed. Digestate, and carbonizate samples were taken and analyzed in the same range of parameters. The following parameters of solid materials were determined: moisture/dry mass (DM), content of nitrogen, carbon, hydrogen, and sulphur, as well as lower and upper heating values, combined carbon, gaseous particles and ash.

Moisture was determined gravimetrically at 105±2°C in a Binder dryer. Dry samples were ground in laboratory mills IKA MF 10 to a size below 0.25 mm. In that form the samples were analyzed for determination of analytical moisture, ash content, and loss on ignition by TGA ELTRA THERMOSTEP thermogravimetric analyzer. The high heating value was determined with IKA Werke GmbH C2000 calorimeter. The low heating value was calculated according to the moisture and hydrogen content using following equation:

$$H_l = H_h - 24.42 \cdot (8.94 \cdot H - W)$$

Where:

H_h – high calorific value determined analytically (kJ/kg),
H – measured hydrogen content in the solid sample (%),
W – measured moisture content in the solid sample (%),
24.42 – water vaporization heat in standard condition related to 1 % of water generated during sample combustion (kJ/kg),
8.94 – coefficient of hydrogen content calculation on water.

Dry solids (DM), lower heating values (LHV) and upper heating values (UHV) were expressed also as dry, ash free basis (daf): LHV(daf), UHV(daf), respectively.

For determination of nitrogen content, Kjeldahl method was used. Carbon, hydrogen, and sulfur in the samples were determined using CHS500 ELTRA elemental analyzer. Metals: Ca, K, Na, Fe, Mn, Cu, Zn were analyzed in Zeeman Atomic Absorption Spectrometer AA280Z coupled with GTA-120 Graphite Tube Atomizer Varian GTA-120. H/C ratio of digestate and carbonizate was determined.

The elements of mass and energy efficiency validation were estimated. Mass yield of pyrolysis Y_M , was calculated by considering weight loss during pyrolysis, also expressed as dry, ash free basis. The mass yield is defined by equations (Kim et al. 2012):

$$Y_M = \frac{100 \cdot DM_c}{DM_d}$$

$$Y_{M(daf)} = \frac{100 \cdot DM_{c(daf)}}{DM_{d(daf)}}$$

where:

Y_M – mass yield [%]

$Y_{M(daf)}$ – mass, dry, ash free basis yield [%]

DM_c – dry mass of carbonizate [g],

DM_d – dry mass of digestate [g],

$DM_{c(daf)}$ – dry, ash free basis mass of carbonizate [g],

$DM_{d(daf)}$ – dry, ash free basis mass of digestate [g].

Energy yield (Y_E) per dry raw material indicates the total energy preserved in the carbonizate. The energy yield, on dry, ash free basis (daf), indicates the energy content of raw digestate retained in the carbonized solid (Kim et al. 2012). This was calculated using the following equation:

$$Y_E = \frac{Y_{M(daf)} \cdot UHV(daf)_c}{UHV(daf)_d}$$

where:

Y_E – energy yield [%]

$Y_{M(daf)}$ – mass, dry, ash free basis yield [%]

$UHV(daf)_c$ – upper heating value of dry, ash free basis carbonizate [MJ/kg DM(daf)]

$UHV(daf)_d$ – upper heating value of dry, ash free basis digestate [MJ/kg DM(daf)]

Results and discussion

Prior to placing digestate, the reactor was preheated to about 580°C, which corresponds to the range of conventional pyrolysis (Yaman 2004). During the pyrolytic process at 500°C, changes in concentrations of particular gases were monitored as well as changes in the calorific value of pyrolytic gas in time (Fig. 2, 3). The proper pyrolytic processing started at the time point of $t=500$ s, when quantities of flammable gases such as carbon oxide (CO), methane (CH₄) and, to a lesser extent, hydrogen (H₂) increased significantly. After 1500 s, when gas composition became relatively constant (24% of CO₂, 10% of CO, 8 % of CH₄, and 2 % of H₂) (Fig. 2), the plateau of gas calorific value about 3700 kJ/Nm³ was achieved (Fig. 3).

Dried digestate and produced carbonizate were analyzed in terms of their chemical composition and calorific value. The experimental results showed the considerable accumulation of ash, from 26.62% in digestate to 49.55% in carbonizate, and combined carbon from 14.7% in digestate to 30.27% in carbonizate (Tab. 1). This phenomenon may be the consequence of the fact that large amounts of carbon found in the biodegradable fraction of organic matter are bound during methane fermentation, so consequently hardly degradable carbon compounds (e.g. lignin) remain in digestate. During pyrolysis, reduction of residual moisture occurs, volatile fractions are evaporated and carbon is converted into molecules of higher molecular weight. Carbonizate was characterized by lower heat of combustion and calorific value than digestate (16.6% and 11.9% lower, respectively). It could be caused

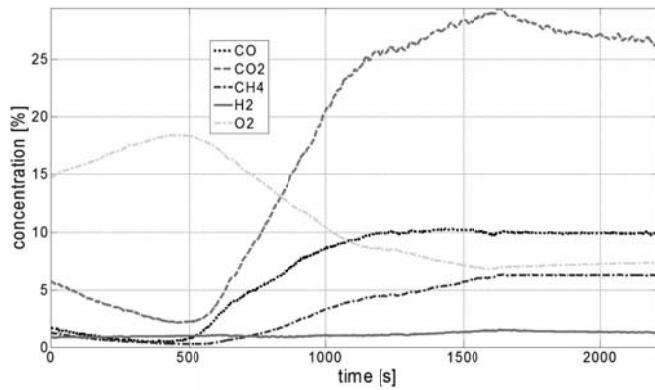


Fig. 2. Changes in concentrations of gaseous products generated during pyrolysis of dried digestate

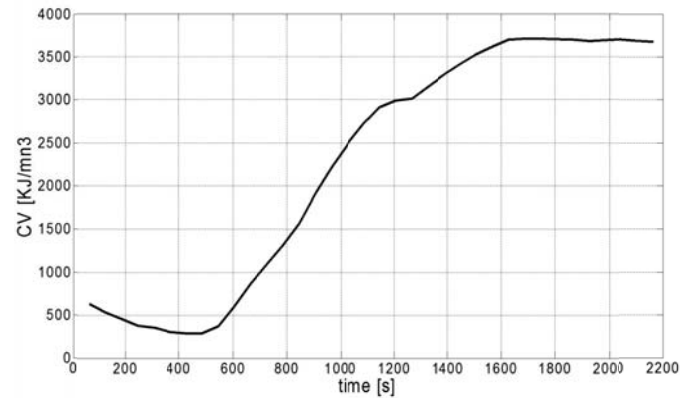


Fig. 3. Changes in calorific value (CV) [kJ/Nm³] of pyrolytic gas

by water, volatile compounds and CO releasing (Prins et al. 2006). When considering the content of ash in dry matter, the energy value of carbonizate was higher about 21–28% than in digestate (Tab. 1). In turn, the content of sulphur, nitrogen and chloride was decreased significantly during pyrolysis (46%, 28.2% and 27.9%, respectively). The mass yield and energy yield of digestate pyrolysis were 43.3, and 52.5%, respectively (Tab. 1). Additionally, about 59% decrease of H/C ratio from 1.41 to 0.58 was observed. Usually, for biomass containing lignin H/C ratio is higher than 0.9 (Kim et al. 2012, Rousset et al. 2012, Wannapeera and Worasuwanarak 2012).

In the case of experiment on dried digestate gasification, the proper process began after 600 seconds, when reactions typical for gasification commenced (degasification

of the fed batch in the sphere of pyrolysis). From that moment, carbon dioxide was supplied to the reactor, and the concentration of flammable gases, especially CO and H₂ and, to a lesser extent, CH₄ started to rise (Fig. 4). At the same time, the concentration of oxygen decreased distinctly. The process of gasification terminated at t=1000 s. The high concentration of CO₂ which persisted until that moment was due to the fact that the gasification agent, i.e. CO₂, continued to be supplied. This gas reduced CO₂ in the reduction zone to CO. The highest calorific value of the generate gas coincided in time with the maximum concentration of all flammable gases: CO, H₂, and CH₄ (34 % in total), which took place at t=900 s (Fig. 4). The calorific value recorded then was 5 kJ/Nm³ (Fig. 5), and was higher than in the case of pyrolysis.

Table 1. Calorific and chemical parameters of digestate and carbonizate after pyrolysis

Specification	Unit	Digestate		Carbonizate		Change in %
		Mean	Standard deviation	Mean	Standard deviation	
Moisture	%	7.85	0.087	3.27	0.021	-58.3
UHV	GJ/Mg DM	16.86	0.038	14.06	0.027	-16.6
UHV(daf)	GJ/Mg DM (daf)	22.97	0.041	27.87	0.036	+21.3
LHV	GJ/Mg DM	15.34	0.049	13.52	0.027	-11.9
LHV(daf)	GJ/Mg DM (daf)	20.90	0.045	26.80	0.029	+28.2
Combined carbon	% DM	14.7	0.070	30.27	0.066	+105.9
Volatile ingredients	% DM	58.67	0.273	20.18	0.125	-65.6
Ash	% DM	26.62	0.336	49.55	0.085	+86.1
C	% DM	39.68	0.078	35.93	0.573	-9.5
H	% DM	4.65	0.029	1.75	0.047	-62.4
S	% DM	0.87	0.006	0.47	0.010	-46.0
N	% DM	3.76	0.040	2.7	0.020	-28.2
Cl	% DM	0.43	0.010	0.31	0.012	-27.9
O	% DM	23.98	0.278	9.29	0.662	-61.3
H/C	–	1.41	0.06	0.58	0.04	-58.9
Y _M	%	–	–	63.0	3.2	–
Y _M (daf)	%	–	–	43.3	2.7	–
Y _E	%	–	–	52.5	4.1	–

DM – dry matter

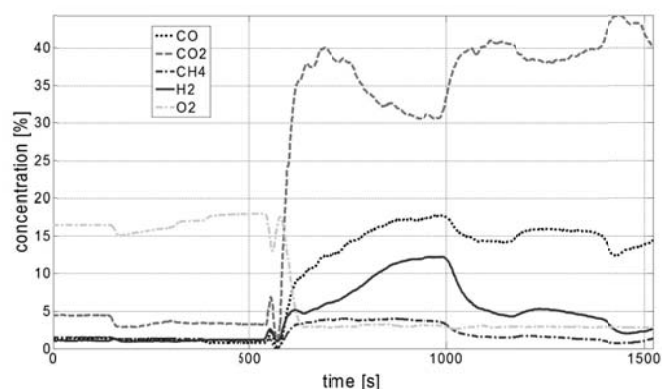


Fig. 4. Changes in concentrations of gaseous products generated during gasification of dried digestate

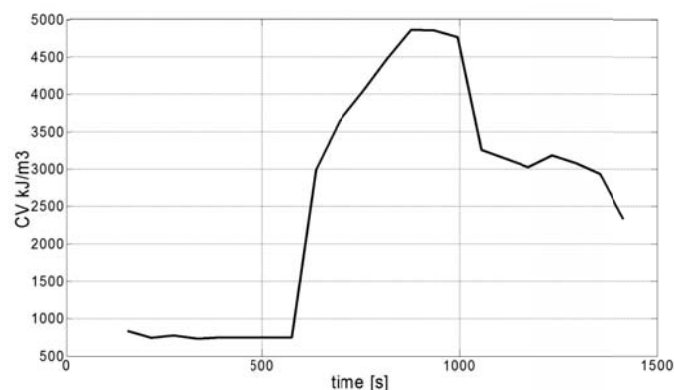


Fig. 5. Changes in calorific value (CV) [kJ.Nm³] of gas generated during gasification of dried digestate

Summary

Fractionation of digestate and use of its solid phase for generation of energy is one of the alternative uses of this anaerobic digestion byproduct. This solution creates a certain potential for using digestate in production of the 2nd generation biofuels from pyrolysis: carbonizate and pyrolytic gas. Carbonizate may be reused either as a fuel or fertilizer in form of biochar. Pyrolytic gas is usually recycled and used for heating the pyrolytic reactor. Gasification leads to generation of more calorific gas and ash which can be used as soil amendments or fertilizer. The high ash content in dried digestate may cause problems with slag often vitrifying during gasification, but this problem requires further investigation.

Acknowledgments

The paper has been written under the strategic program of the National (Polish) Centre for Research and Development (NCBiR): “Advanced Technologies for Energy Generation. Task 4: Elaboration of Integrated Technologies for the Production of Fuels and Energy from Biomass, Agricultural Waste and other Waste Materials.”

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Piroliza i gazyfikacja pofermentu z biogazowni rolniczych

Streszczenie: Pozostałości z biogazowni rolniczych stanowią bogaty w substancje nawozowe surowiec, w przypadku którego, jego rolnicze wykorzystanie, może zmniejszyć stosowanie nawozów mineralnych i poprawić właściwości gleby. Jednakże poferment powinien być wcześniej odwodniony i przetworzony termicznie. Ograniczona stosowalność w środowisku przyrodniczym pofermentu może szczególnie wystąpić w okresie zimowym oraz na terenach zagrożonych eutrofizacją. Wykorzystanie pofermentu podlega także ograniczeniom prawnym w zależności od tego czy jest traktowany jako nawóz, osad lub odpad. Celem artykułu jest przedstawienie efektów zastosowania termicznego przetwarzania odwodnionego pofermentu w procesach pirolizy i zgazowania. Proces pirolizy pofermentu prowadzono w temperaturze 500°C. Monitorowano skład i kaloryczność gazu pirolitycznego. Wykonano porównawcze analizy kaloryczności odwodnionego pofermentu i uzyskanego w wyniku pirolizy karbonizatu. Gazyfikację prowadzono w temperaturze 850°C w atmosferze CO₂. Wykazano, iż uzyskany w procesie gazyfikacji gaz syntezowy posiadał wyższą kaloryczność, jednak dodatkowy produkt procesu pirolizy – karbonizat posiadał dobre właściwości do wykorzystania jako paliwo stałe.