Investigation on Thermal Decomposition of Biogas Digestate to Producer Gas

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Abstract. The main objective of this research was to find optimal time and temperature of thermochemical decomposition of biogas digestate. Hence, the article presents results of both experimental research and theoretical analysis of high temperature thermal decomposition of biogas digestate in a screw conveyor reactor. Experimental investigation was focused on pyrolysis and gasification of the digestate with particular interest of obtaining highly-calorific producer gas (commonly called syngas). Moreover, the proximate and ultimate analysis as well as thermogravimetric analysis with mass spectrometry (TGA-MS) were carried out. Based on the results obtained from the experiments, calculations using the CHEMKIN-PRO software were conducted in the scope of the chemical compositions of pyrolysis and gasification gaseous products. The experimental and numerical results show that the biogas digestate can be managed as attractive fuel in terms of combustion as well as gasification and pyrolysis.

1. Introduction

Nowadays green energy production through the anaerobic digestion of agricultural feedstock has been increasing and becoming a common practice world-wide. This technology is particularly promising as an energy source for both highly industrialized and developing countries [1]. Activity of agricultural biomass-to-biogas plants, although focused on the acquisition of biogas, is always connected with the formation of biogas digestate, which is a waste requiring disposal. The main direction of biogas digestate utilization (about 36%) is its use as a fertilizer [2]. However, such application requires several permits and fulfilments of quality standards to ensure both safety issues and quality of this product. The use of digestate as a fertilizer is not always possible because of risk of heavy metals, organic pollutants, microbial contaminants and antibiotics, which contents are under international limits [3]. Meanwhile, after dewatering and thermal utilisation, it can also be managed as valuable fuel. It should be emphasized, that in addition to the traditional combustion methods, the biogas digestate may also be subjected to conversion by other thermochemical means, i.e. pyrolysis and gasification, which are promising alternatives and arouse increasing interest [4-6].

The pyrolysis is one of the stage of gasification and can be defined as thermal decomposition of biomass into gases, liquids, and solids. The main products of pyrolysis are the following: bio-oil, bio-char and pyrolysis gas. This process usually takes place in a relatively low temperature ranging between 250-700°C and in the total absence of oxygen (except cases, in which partial combustion is
allowed to provide the thermal energy needed for this process).Due to different operating conditions the pyrolysis process can be divided into three major stages. The first one is the torrefaction, in which the biomass is heated up to 230÷300°C without contact to oxygen [7]. The second and the third one are “slow” and “fast” pyrolysis. The “slow pyrolysis” is operated at lower temperature around 400÷500°C with a heating rate of approximately 0.1 to 1°C/s at a residence time (RT) ranging between 5 and 30 min. The “fast pyrolysis” is performed at temperature range between 850÷1250°C, with a heating rate of 10÷200°C/s for a short span of time varying between 1 and 10 s [8].

As known, gasification is the thermochemical conversion of an organic material into useful gaseous fuels or chemical feedstock. This process occurs at temperature range between 500°C up to 1300°C and in the presence of a partial gasifying agent (air, oxygen, steam, carbon dioxide, hydrogen, or mixtures) with the total oxygen content remaining significantly below stoichiometric conditions. The gaseous product, such as syngas, can be used for power generation or biofuel production [9]. Generally, the syngas is a mixture mainly composed of hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂) and nitrogen (N₂), as well as minor components such as: light hydrocarbons: methane (CH₄), ethane (C₂H₆) and propane (C₃H₈), and heavier hydrocarbons [5]. The syngas can also include undesirable gases, such as hydrogen sulfide (H₂S) and hydrogen chloride (HCl), which both at moisture presence can form acids, as well as inert gases, mainly nitrogen. The composition of syngas depends on the type of feedstock and operating conditions of the gasification process. Impact of various parameters such as biomass type, moisture content, temperature, oxygen concentration, equivalence ratio was analyzed in both experimental and theoretical investigations. The quality of the syngas depends on the concentration of combustible components contained therein. Thus, during analysing the thermochemical conversion, it is important to properly evaluate composition of the syngas.

The major objective of the investigation presented in this manuscript is to show possibilities of the biogas digestate use for energy purposes by thermochemical conversion through pyrolysis and gasification processes. This work is focused on characterizing physical and chemical properties of biogas digestate using experimental and calculation methods using CHEMKIN-PRO software particularly concentrating on gaseous content formation. Application of numerical calculations during this study allows for better identification of the formation pathways of the vast majority of compounds produced by the pyrolysis and gasification of biomass. Furthermore, it provides useful information on optimal process conditions which in turn enables to increase the efficiency of biomass conversion and to obtain a high quality gaseous fuel.

2. Material and methods
Material considered in this study is a biogas digestate obtained from a typical agricultural biogas power plant. Its composition is as follows: 65% - maize silage (leaf stems), 28% - silage of other plants, such as lupine, grass mowed as well as rotten potatoes and beets and 7% - cattle slurry.

The biogas digestate was investigated in the scope of: ultimate, proximate and thermo-gravimetric analyses with mass spectrometry (TGA-MS). Furthermore, computer simulations with the use of Chemkin solver program were performed. All the experimental analyses were conducted to calibrate and verify model built in Chemkin program. The properly worked out model for thermal processing for digestate should be considered as useful tool in design and construction of pyrolysis and gasification systems.

2.1. Description of the screw conveyor reactor
The experiment was conducted at an atmospheric pressure with the use of a screw conveyor reactor with an internal diameter of 0.08 m and length of 0.67 m. The reactor was surrounded by a co-axial insulated shell made of mineral wool and aluminium layer. A screw type reactor was a continuous reactor, consisting of one screw that transport the material through the reactor. The reactor was placed horizontally and it was heated using two electric heaters with a power of 1.5 kW (each) located outside the screw. The temperature prevailing in the reactor was monitored and controlled by two temperature
regulators connected with J-type thermocouples located on the outer surface of the heaters of the screw-conveyor tube. Retention time of biomass in the auger depends on rotational speed of the auger screw. The detailed elements of the reactor are illustrated in Figure 1.

**Figure 1.** Set-up of thermal decomposition of various biomass, where: 1 – drive for the auger screw (motor and snail gear box), 2 – hermetic bin filled with biomass, 3 – auger screw, 4 – electric heaters of 3 x 1.5 kWe, 5 – snail screw core, 6 – connectors for electric wire, 7 – outlet of pyrolysis gas, 8 – ash or carbonized digestate (charcoal), 9, 10 – thermocouples type J, 11 – hydraulic cylinder, 12 – press plunger, 13 – compressed ash or carbonized briquette.

2.2. **Ultimate, proximate and thermal analysis**

The ultimate analysis (carbon, hydrogen and nitrogen content) was measured by Elemental Analyzer TrueSpec CHN Leco. The LECO CHN628 is a combustion elemental C, H, and N instrument that utilizes only pure oxygen in a furnace, ensuring complete combustion and superior recovery of the elements (the Dumas method of combustion).

The proximate analyses of the digestate were done according to the European standard methods as follows: moisture − PN-EN ISO 18134, ash − EN ISO 18122, calorific value − PN-EN 14918. Table 1 contains results of the analysis.

Thermal analysis was carried out using the TG–DSC techniques (Thermogravimetry and Differential Scanning Calorimetry). Netzsch STA 449 F3 Jupiter apparatus was used to conduct the experiments. For the thermogravimetric analysis (TG/DSC), the samples were placed in an alumina crucible. The thermogravimetric investigations of pyrolysis and gasification of biogas digestate included the following stages which play crucial role in both the gasification and the pyrolysis zone:

1) Dry biogas digestate was heated from an ambient temperature up to 900°C at a constant heating rate 10°C/min, in 40 ml/min flow of air atmosphere to study combustion process during typical air assisted gasification process. Thus, ambient air was used as the main oxidizer carrier.

2) Dry biogas digestate was heated from an ambient temperature up to 900°C at a constant heating rate 10°C/min, in 40 ml/min flow of argon atmosphere to study high temperature pyrolysis process.

3) Dry biogas digestate, the first was heated from an ambient temperature up to 500°C at a constant heating rate 20°C/min, in 40 ml/min flow of argon atmosphere, and next isothermally heated through 2 hours, to study low temperature pyrolysis process.

4) Dry sewage sludge, the first was heated from an ambient temperature up to 900°C at a constant heating rate 20°C/min, in 40 ml/min flow of argon atmosphere, and next isothermally heated through 2 hours, to study high temperature pyrolysis process.
2.3. Numerical simulations

The main aim of the numerical simulation was to evaluate the chemical composition of the gaseous products of thermal decomposition of digestate/residue from biogas plants in terms of energy purposes. The next target was to validate chemistry mechanisms for modelling digestate thermal decomposition at selected, elevated temperatures and finally, if successful, to calibrate a model worked out for those purposes. As reviewed, there is hardly possible to find a chemical kinetics mechanism, which could satisfactorily simulate thermal decomposition of biogas digestate. Among others, the mechanism developed by CRECK Modelling Group containing “Biomasses mechanism” (Version 1412, December 2014) was selected as the most appropriate for this purpose. It was successfully tested by Corbetta et al. [10] and Wilk et al. [11] for pyrolysis of wooden biomass. Hence, this mechanism was applied for numerical modelling. The mechanism includes 137 compounds, 4533 chemical reactions, and thermochemical and transport data. The input file of kinetics data contains elements and compounds as well as a set of reactions enabling calculation of the rate constant of reactions given by the Arrhenius equation. The numerical simulations of syngas composition from pyrolysis and gasification of biogas digestate were carried out with use of the CHEMKIN-PRO software. The mechanism by CRECK contains 137 compounds and 4533 chemical reactions. In the modeling procedure it was assumed that both the gasification and pyrolysis takes place in a Perfectly Stirred Reactor (PSR). Residence time was varied from 1 to 120 min, fixed RT of 10 min was taken to formulate initial conditions. The average mass loss of the fuel during time period was equal to 0.00135 g/s÷0.0027 g/s. The temperature of reactor was between 500°C and 900°C and the pressure was equal 1 bar. The atmosphere was as follows: air with a composition of 21% O\textsubscript{2} and 79% N\textsubscript{2} (case 1) and 100% of Ar (case 2). Flowrates of argon and air in the reactor were constant and they equalled to 40 cm\textsuperscript{3}/min, 0.67e-6 m\textsuperscript{3}/s.

3. Results and Discussion

3.1. Proximate and ultimate analysis

The results of the proximate and ultimate analysis of biogas digestate was presented in Table 1. The analysis findings show that tested digestate in the oven-dry state has a high content of combustible compounds, i.e. carbon and hydrogen. The biogas digestate has LHV equal to 16.786 MJ/kg with water content up to 4.94%. However, in the case of analyzed samples, the LHV relates to a biogas digestate in the oven-dry state. The digestate was characterized by a very high water content equal to 70.8%. Only after dehydration and drying the digestate may be used as a valuable fuel [11].

| Table 1. Results of proximate and ultimate analyses of analytical biogas digestate. |
| --- |
| Ash, % | Moisture, % | LHV, MJ/kg | C, % | H, % | O, % | N, % |
| Biogas digestate | 8.0 | 4.9 | 16.8 | 51.59 | 5.94 | 34.14 | 3.33 |

3.2. Thermal analysis

The TG curves presents the weight loss via temperature and DSC the heat flow via temperature, too. The evolved gaseous products from decomposition were identified on-line using mass spectrometry (QMS Netzsch). The following ions, which are characteristic of the molecules of interest, were monitored: 16, 18, 28, 44, 64 and 80 for CH\textsubscript{4}, H\textsubscript{2}O, CO, CO\textsubscript{2}, SO\textsubscript{2} and SO\textsubscript{3}, respectively. TG, DSC and MS curves for the studied biogas digestate were obtained as outputs (Figures. 2, 3). These curves were used in order to assess the thermal characteristics of the investigated samples. Figure 2a shows the TG, DSC curves and gaseous products profiles for dry biogas digestate under air atmosphere. Dry sample does not have moisture, what is confirmed on TG, DSC and H\textsubscript{2}O profiles. On raising the temperature, thermal processing of dry biogas digestate goes as combustion and mainly takes place with an associated mass loss in the temperature range 220÷560°C. The mass loss is 85%. The DSC profiles additionally confirm this thermal decomposition is combustion process. There are
wide peaks with four maxima in the temperature range 200÷550°C. The effects obtained on DSC curve correspond with the emission of CO₂. The main H₂O release takes place up to 400°C. The mass loss after the main stage is c.a. 85%. Above 560°C there is no significant mass change observed. Similar trends were obtained in the works [12,13] where the TGA studies were also performed.

Figure 2b presents the TG, DSC curves and gaseous products profiles for dry biogas digestate under argon atmosphere corresponding to the pyrolysis process. Comparing to combustion (Figure 2a), in the pyrolysis process the character of TG and DSC curves is quite different, but it can be divided on three stages, too. The most important differences are observed in the second stage, where one very wide exothermic peak (DSC) is observed. There were detected H₂O, CO, CO₂ and SO₂ gases. The main mass loss of dry biogas digestate pyrolysis takes place in the temperature range 200÷500°C with the maximum gas emissions at 330°C. Above 700°C a slight decay of dry biogas digestate is observed. The final solid residue at 900°C is 40%. Huang et al. [14] made a similar division of the TA–MS curves on stages. The experiments were performed at the heating rate of 5°C/min from an ambient temperature to about 900°C in the helium atmosphere. They noticed that the overall temperature range can be divided into four stages, namely: below 150°C, 150÷250°C, 250÷500°C, and above 500°C. Furthermore, most of the gas products were primarily formed at the same temperature range of 250÷500°C, what may suggest the pyrolysis of biomass feedstocks mainly occurred at this stage.

Figure 2. TG, DSC curves, H₂O and CO₂ (m/z =18, m/z = 44) evaluation profiles of dry biogas digestate under air (left) and argon (right) atmosphere at heating rate of 10°C/min.

Figure 3 presents isothermally heating of biogas digestate at 500°C (Figure 3a) and 900°C (Figure 3b). Not evident effects are observed on TG and DSC, because, as it was mentioned earlier, the thermal process of biogas digestate takes place above 600°C. Hence, only marginal weight loss (c.a. 1%) and small amount of gaseous products are observed.

Figure 3. TG, DSC curves, and CH₄, CO, CO₂ (m/z =16, 128 and 44) evaluation profiles of dry biogas digestate under argon atmosphere isothermally heating at 500°C (left) and 900°C (right) through 2 h.

3.3. Numerical simulations

Figure 4 presents the numerical calculation results of the pyrolysis and gasification products composition of biogas digestate at temperature 900°C under argon atmosphere (a) and air atmosphere (b) vs. RT. As found from modelling, trends in all the curves showing main components of gaseous
products for both argon and air environment are similar to each other. Slightly higher concentrations can be observed in the case of gasification process performed under air atmosphere. Concentrations of CO and H$_2$ are almost identical to each other. During the first 10 minutes their contents rapidly decrease and then gradually increase. For these two compounds, the longer the process time, the higher concentrations are achieved. Taking into account the methane concentration, it can be noticed that the highest increase in CH$_4$ occurs within the first 10 minutes, reaching 12% and 14% for argon and air, respectively. After that time a slight decrease is observed. In the case of carbon dioxide concentration, its reduction can be obtained by performing pyrolysis in a longer residence time.

Figure 4. Comparison of the composition of syngas from biogas digestate pyrolysis under argon atmosphere and gasification under air (a) atmosphere at temperature of 900°C (b).

In turn, in Figure 5 the correlations between the products of pyrolysis and RT at temperature 500°C was presented. The concentration of methane intensely grows in the first 10 minutes of the process reaching a value of 9%. Further increase in residence time do not significantly affect its content in the fuel gas. The opposite trend is observed in the case of hydrogen where its concentration drastically decreases from 20% to 8% in the range of the first 10 minutes. Further, increase in RT contributes to gentler decrease in the concentration of H$_2$.

Figure 5. The composition of syngas from biogas digestate pyrolysis under argon atmosphere at temperature of 500°C.

Based on the numerical calculation results, it was observed that the pyrolysis of biogas digestate mainly occurred in the range of RT up to the first 10 minutes. Thus during the further analysis the residence time equal 10 minutes was assumed.

Figure 6 shows results from calculations of the pyrolysis products composition of biogas digestate at temperature range of 400–900°C in the atmosphere of argon (Figure 6a) and air (Figure 6b). Making a general comparison of results for the atmosphere of argon, and air as a function of temperature, it can be seen that the trends of most of the compounds in both cases are very similar. Slightly higher values are observed in the case of gasification in the atmosphere of air. The concentration of carbon monoxide slightly decreases with the temperature growth until 800°C and then it increases. Similar relation can be seen in the case of hydrogen but it reaches the lowest values.
at temperature from 600 °C to 700°C. The temperature increase has a positive effect on the methane concentration. The optimum temperature for the highest concentration of CH₄, that equal to 15% and 17% under argon and air atmosphere respectively, is between 650°C and 800°C. Similar trends were observed by Peng Fu et al. [15] that investigated the effects of pyrolysis temperature on the gas composition during the pyrolysis at temperatures ranging from 600 to 1000°C. The research show that as the temperature increased, the CO content in the product gases significantly grows up from about 45.4% at 600°C to 60.6 % at 1000°C and the CH₄ content increased from 15.0% at 600°C to 19.7% at 1000°C, while the CO₂ content exhibited the opposite trend. In turn Pacioni et al. [6] during the research of the pyrolysis in the nitrogen atmosphere at a heating rate of 200°C/min and RT of 5 min at temperatures from 650°C to 850°C observed that the concentration of CH₄ was minor and almost not influenced either by the biochar type or by the gasifying conditions.

Figure 6. Comparison of the composition of syngas from biogas digestate pyrolysis under argon atmosphere (a) and gasification under air atmosphere (b).

On the basis on the numerical simulations results, i.e. the concentration values of combustible compositions of the gaseous products obtained during pyrolysis and gasification the LHV were calculated and presented in Figure 7 vs. temperature. Profiles of the both LHV curves are similar to each other. Higher LHV was observed in the case of gasification in the atmosphere of air and it was ranging between 10.7 MJ/m³ and 12.6 MJ/m³. The heating value of the fuel gas obtained during pyrolysis was from 9.5 MJ/m³ at 400°C to 10.2 MJ/m³ at 900°C with the maximum value of 11 MJ/m³ at 700°C. The increase in the heating value occurs at the temperature range from 400 to 700°C. Further growth of temperature contributes to a drop in the LHV. As determined, the most advantageous range of temperature in both cases is between 650°C and 750°C.

Figure 7. Comparison of the LHV of syngas produced during pyrolysis under argon atmosphere and syngas during gasification under air atmosphere.

4. Conclusions
The research performed in the scope of this paper shows that the biogas digestate can constitute an attractive fuel not only in terms of combustion but also the gasification and pyrolysis. The heating value (LHV) of digestate was high and comparable to the value of other residues investigated in the
literature. However, the raw biogas residue has a very high content of moisture, thus it can be applied for energy use only after dehydration and drying.

Computer simulations have provided data on the chemical composition of pyrolysis and gasification products for different conditions of the thermal conversion of digestate from the biogas plant. As found, the model based on the kinetic mechanism by CRECK was validated correctly, hence, the results provided credible conclusions. Results from modelling show that the most favourable option in terms of use for energy production is the gasification at the atmosphere of air at temperature range 650÷750°C (up to 800°C) at a residence time equal 10 minutes. This is associated with a high content of combustible components in the gas, including CO, CH₄ and H₂.

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