Analysis of the combustion products of biogas produced from organic municipal waste

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Abstract
Urban areas produce large amounts of organic waste, among others at eateries and residential locations. Methane fermentation can be used to turn these wastes into a valuable substrate for biogas production. Malopolska region (Poland), in 2010, produced 547,796 Mg of biodegradable waste. The estimated volume of biogas from this amount of waste is 62,449,000 m$^3$. The composition of biogas produced from the fermentation of the municipal waste is about 45 vol% CH$_4$, 35 vol% CO$_2$ and other gases (H$_2$O, O$_2$, N$_2$). This paper presents the results of modeling the kinetics of the biogas combustion process. For this purpose the program Chemked II was used, implementing the combustion mechanism created by the Gas Research Institute called the GRI-Mech version 3.0. The software enables thorough analysis of 325 reactions. Concentrations of CO, CO$_2$, NO, N$_2$ and O$_2$ in flue gases were calculated.

Keywords: Biogas, Fermentation of the municipal waste, Combustion of biogas

1. Introduction

Biodegradable materials can be fermented to produce biogas, and the residue after fermentation (digestate) is a valuable fertilizer. Biogas consists mainly of methane (45...75 vol%) and carbon dioxide (25...50 vol%), but also contains several impurities (H$_2$S, NH$_3$, water vapour, N$_2$, siloxanes and dust) [1]. The fermentation process must be conducted in conditions suitable for methane bacteria (such as temperature, pH, content of C:N). In Poland, like in the whole of Europe, this mostly involves mesophilic fermentation (temperature 32...42°C) [2]. Anaerobic methane fermentation requires a pH of 6.8...7.4. A favorable load composition is one in which the proportion of C:N is from 10:1 to 25:1. If the C:N ratio is greater than 25:1, the methanogenic bacteria will quickly consume the nitrogen to create proteins, and it will not be available for some carbon contained in the raw material, which will reduce the production of biogas. In contrast, if the C:N ratio is too small (<10:1), the ammonia produced raises the pH above 8.5 [3]. Biogas is formed during anaerobic fermentation of organic wastes from agricultural, industrial and municipal waste. Substrates of agricultural origin are mainly waste from crop production, horticultural and vegetable waste from livestock production (manure, liquid manure) and energy crops. Wastes of industrial origin are classified as: food, meat, milk, sugar, paper, pharmaceutical or fatty. Substrates of urban origin are mainly sediments, sewage treatment plant products, wet organic fraction of municipal waste, grass clippings and plants and catering waste [4].

Biogas in Poland is a relatively new field. Fig. 1 shows the number of biogas plants in Poland and their annual performance in 2011...2013. In mid-2014 51 biogas plants were operational, with a total capacity of 228.9 million m$^3$ of biogas/year [5]. The vast majority of existing biogas plants in Poland are mainly installations using agricultural waste. In all biogas plants the end product is used for
Figure 1: Number of biogas plants in Poland and annual production of biogas in the period 2011–2013 [5]

Table 1: Quantities of selected organic waste generated in the Malopolska region [own elaboration]

<table>
<thead>
<tr>
<th>Type and code</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodegradable kitchen waste, code 20 01 08</td>
<td>1162</td>
<td>1456</td>
<td>1974</td>
</tr>
<tr>
<td>Biodegradable waste, code 20 02 01</td>
<td>14,194</td>
<td>17,712</td>
<td>19,069</td>
</tr>
<tr>
<td>Waste from markets, code: 20 03 02</td>
<td>2,854</td>
<td>2,927</td>
<td>1,543</td>
</tr>
<tr>
<td>Sum</td>
<td>17,885</td>
<td>21,688</td>
<td>22,033</td>
</tr>
</tbody>
</table>

Table 2: Estimated theoretical yield of methane from selected organic waste in Malopolska [own elaboration]

<table>
<thead>
<tr>
<th>Methane from waste, 10² m³</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodegradable kitchen waste, code 20 01 08</td>
<td>836</td>
<td>1,048</td>
<td>1,421</td>
</tr>
<tr>
<td>Biodegradable waste, code 20 02 01</td>
<td>14,194</td>
<td>17,712</td>
<td>19,069</td>
</tr>
<tr>
<td>Waste from markets, code: 20 03 02</td>
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</tbody>
</table>

the purposes of electricity production and heat cogeneration systems. However, after reprocessing to natural gas quality biogas can be compressed to CBG (Compressed Bio Gas) and liquefied to LBG (Liquid Bio Gas). The products have the same properties as CNG (Compressed Natural Gas) and LBG (Liquid Natural Gas). These are ideal fuels for cars, buses and trucks, especially in district areas, because they produce virtually no particulate matter or NOx emissions. Use of CBG is growing rapidly in Scandinavia.

The use of waste fermentation lowers the acquisition cost of the substrate and reduces waste management problems. It is worth noting that, for example, 1 Mg of organic municipal waste (dry weight) can produce approximately 397 m³ of biogas, which is higher than can be obtained from animal wastes, such as pig slurry (301 m³) and cattle slurry (222 m³) [6]. In accordance with the Act on maintaining cleanliness and order in municipalities, the local authority is responsible for municipal waste management. In Poland, annually about 10 million Mg of municipal waste are produced, of which about 30...50 wt% is organic waste (biodegradable). Assuming that the organic fraction of municipal waste produced per inhabitant in Poland is around 100 kg/year (including dining-waste, from eating and from stores) and Poland has 38.5 million inhabitants and that in the initial phase the system is able to selectively collect 10 wt% of this amount (Sweden now collects 17 wt%), we obtain 385000 Mg per year high quality feedstock for biogas plants [7]. The table below shows the amount of organic waste produced in the Malopolska region (Table 1) and the theoretical yield of methane from this quantity (Table 2). According to the report for Malopolska region, on a yearly basis approximately 20,000 Mg of waste is produced which could act as a substrate for biogas and this amount of waste could produce an average of 2 million m³ of methane annually (Table 2).

Vegetable and animal wastes still constitute a significant percentage of the total municipal waste deposited in landfills. In accordance with the Council Directive 1999/31/EC of 26 April 1999 and the Act of 27 April 2001 on waste (Journal of Laws of 2007 No. 39, item. 251) Poland is committed to reducing the weight of landfilled biodegradable municipal waste, ranging from 75 wt% in 2010 to 50 wt% in 2013 to reach the level of 35 wt% in 2020 relative to the weight of the waste generated in 1995. One method of utilization is to produce biogas through the fermentation of wastes. Suitable for this purpose are wastes with high water content, such as leftovers and out of date products, and non-municipal wastes [8, 9]. The prevalence of biogas production based on municipal waste requires that they be treated as valuable and low-cost substrates, and involves making a number of changes in the
collection of organic municipal waste and increasing the level of awareness in terms of waste segregation. Above all, it must be separately collected at source. In the European Union the leading countries in biogas energy are: Germany, Denmark, Austria and Sweden. 95% of German biogas fuelled power plants use waste from crop and livestock farms such as slurry, manure and dedicated energy crops. Germany relies mainly on farms for its raw materials. The Polish agricultural bioenergy sector has the potential to generate 10...25% of the total energy supply in 2030, which is even higher than that projected for Germany [10]. Despite the considerable increase in the number of biogas plants recently, little use is made of this energy source in Poland [11]. With its low emissions of harmful substances compressed biogas (CB), much like natural gas, is well-suited for powering urban transport vehicles such as city buses. Due to impurities biogas cleaning is usually required [12]. The aim of this study is to analyze the quality and quantity of biogas obtained from the fermentation of municipal waste and 3 selected groups of agricultural waste. Biogas combustion modeling was also carried out for 4 variants (methylene content: 45, 50, 55 and 60 vol%).

2. Experiments

2.1. Fermentation of organic waste

The fermentation process used four types of substrates and a control sample. Fermented substrates were: undersize fraction of municipal waste from the sorting drum, silage corn, bagasse 25 wt% and 75 wt% maize silage and cake 50 wt% and 50 wt% corn silage. Batch 1, accepted as control material, was proved and introduced to the digester. Batch 1 was placed in the digester (2) in which by means of sondes (5) fermentation parameters, such as temperature, redox and pH are checked. These parameters are automatically saved with time interval on the hard disc of a computer of the measuring system. In the digester, the batch was mixed with a mechanical mixer (4) to avoid delamination. The mixer may be smoothly regulated within the range 0 to 400 rot./min. and is equipped with three blades of regulated spacing, which enables it to change the intensity of mixing zones in the fermenter.

The digester of the fermenter is equipped with a water jacket (3) where three cartridge heaters are placed (1), which are responsible for heating liquid. The measuring system equipped with a thermometer (6) PT100 is responsible for controlling the process temperature. The biogas produced is collected over the surface of the batch in the fermenter and in the container (7) of variable volume, from which it is drawn in by the biogas composition measuring meter. This meter analyzes the following parameters: moisture, temperature, pressure, methane CH_4, oxygen O_2 and carbon dioxide CO_2. The biogas composition parameters which are measured are automatically saved on the computer disc of the measuring system. Determination of the intensity of biogas production in the remaining batches was carried out according to standard DIN 38414. Batch mixes were fermented in static conditions consisting in a single introduction of fraction to digesters and conducting the process to the end of fermentation. Fermentation devices were installed in a container with regulated temperature forming a part of the test stand, which was additionally composed of a switch panel and the measuring system. A schematic representation of the test stand is shown in Fig. 3. Devices for maintaining a constant temperature environment were mounted on a rack (1) located next to the container (2). Controlling took place by means of an ESCO ES-20 electronic thermostat (unit switch 16 A) with precision up to ±0.2°C resulting from hysteresis of a sensor. Temperature decreases by a value exceeding 0.1°C triggered a heater of 1,500 W (3) power and a simultaneous start-up of a Hanng DPO 25-205 water pump (4) in order to ensure a uniform distribution of temperature in the whole chamber. After heating water to the temperature exceeding the set temperature by 0.1°C the heater switches off and with a 30 seconds delay so does the pump.

Separators combined in a row along with cut-off valves (6) and a manometer (7) which measures pressure in particular measuring branches constituted a switch board (5). With this system servicing all the fermenters, one measuring system sufficed. The system of measuring volume (8) was composed of two columns filled with water with drain valves and a container for filling up the liquid level in columns (9). The measuring system was combined with a switchboard and a biogas composition meter by means of a conduit (10), which is presented in Fig. 2. The dry mass of fraction and reaction were determined. For each researched batch, fermentation was carried out simultaneously. The amount of gas produced was read out twice daily at the same time.

2.2. Biogas combustion

Description of the reaction occurring in the combustion process is very difficult and depends on many factors such as temperature, pressure, type of burner, the composition of the mixture of fuel and combustion oxidizing hydrocarbons, etc. The mechanism consists of a plural-
Figure 2: A schematic representation of the test stand with a 20 liter fermenter
Figure 3: A schematic representation of the test stand with a 2 liter fermenter
Table 3: Content of CH\textsubscript{4} in biogas of fermented wastes and yield of biogas

<table>
<thead>
<tr>
<th>Batch</th>
<th>Content of CH\textsubscript{4} in biogas, % vol.</th>
<th>The total yield of biogas, dm\textsuperscript{3}/kg DM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch A</td>
<td>45</td>
<td>151</td>
</tr>
<tr>
<td>Batch B</td>
<td>52</td>
<td>178</td>
</tr>
<tr>
<td>Batch C</td>
<td>58</td>
<td>214</td>
</tr>
<tr>
<td>Batch D</td>
<td>53</td>
<td>169</td>
</tr>
</tbody>
</table>

where (wt%):

Batch A: Municipal organic waste 100%
Batch B: Maize silage 100%
Batch C: Bagasse 25%, Maize silage 75%
Batch D: Oil-cake 50%, Maize silage 50%

ity of successive and overlapping reactions of various elementary reaction speeds. The literature features dozens of detailed models dedicated to the combustion of solid, liquid and gas fuels. The most commonly used mechanisms for the combustion of biogas are: GRI-Mech [13] and AAUmech [14]. GRI-mech 3.0 developed by the Gas Research Institute contains 325 elementary reactions, taking into account 53 chemical compounds, is optimized for combustion including methane in the temperature range from 1,000 to 2,500 K at a pressure range of $1.3\cdot10^{-3}...1$ MPa. In this paper, modeling of the combustion of biogas was done with the Chemked II version 3.5.2 [15] using the thermodynamic database thermo30.dat [14] and combustion mechanism GRI-mech 3.0 [14]. Calculations assume perfect mixing of the reactants in the kinetic combustion burner. Calculations were performed in flame temperature of 1,600 K at a constant pressure $P = 0.1$ MPa. Substrate temperature was 300 K. The residence time of the reactants in the reactor was 1 second.

### 3. Results and discussion

The fermentation process yielded data on the content of methane in the biogas and the total yield of biogas from different groups of substrates (Table 3).

The CO\textsubscript{2} and O\textsubscript{2} in the biogas were also analyzed. During the tests the changes in concentration of components in the biogas (Fig. 4) and biogas production (Fig. 5) during the fermentation of organic municipal wastes (Batch A) were recorded. It can be seen that methane begins to emerge after about 5 days and its production continues to approximately the 30 day mark. For fermented agricultural wastes (Batch B, C, D) the methane content increases significantly up to 52...58 vol%. The yield of biogas is also high (Table 3). Therefore, the best solution seems to be to operate the co-fermentation process of municipal waste and agricultural waste.

For the calculation of biogas combustion four concentrations of the components of biogas variants were used (Table 4). The results from the fermentation of organic municipal wastes and theoretical variants (forecast 1...3) were used. Content of N\textsubscript{2} is as a complement to 100% of biogas composition.

As a result of modeling biogas combustion with methane content of 45 vol%, 50 vol%, 55 vol% and 60 vol% it was observed that the concentration of CO (in the dry flue gas)
increases as the CH$_4$ concentration decreases in the biogas (Fig. 3). This is due to the CO$_2$ content in biogas. Larger amounts of CO$_2$ in the combustion chamber make difficult to combust the methane. In this respect, there is an increase in the concentration of CO from 29 to 37 ppm in the exhaust gas. The increase in the mole fraction of NO in the exhaust gas (Fig. 3) corresponds to the combustion chamber introducing a larger amount of air (i.e. adequate to CH$_4$ in the biogas compactness while maintaining $\lambda$).

The CO$_2$ content in the flue gas is below 18% and is practically constant. Despite the increase in the methane content in biogas, CO$_2$ concentrations do not rise. This is due to the fact that an increase in the methane content in the biogas is associated with a lower CO$_2$ content in the biogas. The increase in exhaust gas N$_2$ concentration (with an increase in the methane content of the biogas) corresponds to the combustion chamber introducing a larger amount of air required for oxidation of CH$_4$, and maintaining constant the designated $\lambda$. The O$_2$ content in the exhaust gas is maintained at a constant level of about 1.3 vol%.

Combustion of the biogas in real conditions will be associated with higher concentrations of CO and NO because the combustible mixture will not be perfectly mixed, and the temperature during combustion is higher. Due to its content, municipal waste is a demanding substrate (large morphological diversity, unpredictability composition, seasonal differences) and therefore, in order to stabilize the fermentation process, co-fermentation with other substrates should be applied. To obtain a higher efficiency of biogas production a mixture of organic substances matched to the bio-fermentation of the individual groups can be added, to increase the degree of degradation in the process of co-digestion of agricultural waste. It also makes for a better use of the capacity of fermentation tanks and a better use of waste which does not provide a good substrate for biogas production. For example, the yield of biogas from kitchen waste from households and catering is in the range 85...120 m$^3$/Mg, and from sewage sludge it is 20...30 m$^3$/Mg. Municipal waste receives additions mainly in the form of food industry waste, animal manure or sewage sludge. A characteristic feature of a biogas plant of this type is its extensive system of collection and pre-treatment of substrates (grinding, hygienization, homogenization). This translates into the increased use of energy for their own installation and higher investment costs for pretreatment module substrates.

4. Conclusions

Biodegradable municipal waste such as kitchen waste from households, catering and restaurant wastes from the agro-food, food past its sell-by date—all these and other organic waste fractions are valuable sources of energy and are a potential feedstock for biogas plants. It would be desirable to conduct the process of co-digestion of organic municipal waste with agricultural waste, as it increases the content of methane in the biogas from 45 vol% to
The increase in the concentration of methane in the biogas simultaneously causes a decrease in the concentration of CO\textsubscript{2} in the biogas. Therefore, the combustion of the biogas with higher concentrations of methane does not increase the concentration of CO\textsubscript{2} in the exhaust gas. The biogas plants that started functioning in recent years in Poland co-generate thermal and electric power. Electrical energy and heat generation from biogas are a source of green, environmentally-friendly energy. At the same time, there is a reduction in methane emission from the decomposition of unmanaged biomass (especially animal droppings) [16]. The development of the biogas sector in Poland is in its initial stage and there are still only small numbers of specialist companies, qualified specialists, construction businesses and engineers specializing in design, construction and operation of agricultural biogas plants [16]. Poland is perhaps better suited for biogas energy than all other renewable energy sources. Unexplored feedstocks for sustainable biogas production in Poland include energy crops, grasses and organic wastes [12].

**Acknowledgements**

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**References**