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Full Length Research Paper

Experimental biogas research by anaerobic digestion of waste of animal origin and biodegradable garden waste

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Currently, one of the most efficient and prospective methods of biodegradable waste management is anaerobic digestion in a bio-reactor. The use of this method for managing biodegradable waste generating in agriculture and elsewhere would result in the recovery of biogas that could be used as an alternative to natural gas. The article presents the results of the experimental tests of biogas production through biological degradation of waste in a bio-reactor by using a mixture of pig manure (PM) and garden waste (GW) in a ratio of 90:10%, a mixture of hen manure (HM) and GW in a ratio of 90:10%. A higher concentration of methane was recorded during the treatment of a pig manure and garden waste mixture in a ratio of 90:10%. The maximum concentration of methane reached 68.0%. Since the methane concentration in this mixture was from 1.5 times higher than in the other mixture. The mixture of pig manure and garden waste was better suitable for biogas and methane production. The biggest amount of bio-gas was registered in 22 days which amounted to 0.650 m^3/m^3d. The methane concentration in biogas was largest (65%) and this mixture of organic wastes was the best for energy production. Anaerobic digestion of other mixtures showed the following biogas amounts and methane concentrations: 0.311 m^3/m^3d and 52% (in the case of a PM and GW mixture), respectively; and 0.39 m^3/m^3d and 26.7% (a mixture of HM and GW), respectively.

Key words: Bio-reactor, biogas, methane, anaerobic digestion, garden waste.

INTRODUCTION

The development of energy production from local and renewable sources of energy is one of the major goals of the energy policy of countries of the world. The development of biogas production and the construction of biogas plants is one of the areas of implementation of this commitment. As stated in programmes and forecast documents on electricity development, the share of electricity produced in biogas plants may be increased from the current 0.5 up to 4% of the total electricity consumption. Where renewable energy sources, such as biodegradable wastes generating in agriculture, the food industry, wastewater treatment plants, household and elsewhere, are used for biogas production (Weiland, 2003; Taherzadeh and Karimi, 2008), energy production is enhanced and attention is drawn to ecological problems (Baltrėnas and Kvasauskas, 2008; Zuokaitė and Zigmontienė, 2010). A focus on ecological problems resulted from increasingly stringent environmental protection requirements. Anaerobic treatment of liquid organic waste reduces its adverse effects on the environment by up to 40 to 60%, which results in: a decreased risk of pollution of surface and ground waters, and a considerable reduction of an adverse effect on the atmosphere (Savickas, 2010).

The biogas production technology differs from other technologies using renewable sources of energy for energy production because of two advantages. First,

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Abbreviations: PM, Pig manure; **GM,** garden waste; **HM,** hen manure.

biogas is a relatively clean fuel with a high content of methane which can be used for the generation of electricity and/or heat energy. Second, a fertiliser that could be applied on soils is obtained from the anaerobic digestion of organic waste (Taleghani and Kia, 2005; Kvasauskas and Baltrėnas, 2009; Holm-Nielsen et al., 2009).

In addition to the three advantages, that is, ecological, economic and agricultural, the development of biogas energy is distinguished by another no less important advantage, that is, social one. Social efficiency is achieved when additional jobs are created.

As mentioned before, during industrial and other activities the main flows of biodegradable waste are generated in agriculture, food industry enterprises and wastewater treatment plants. It should be noted that biodegradable waste from agriculture accounts for ~80% of the total biodegradable waste of the country. Therefore, considering these indicators, biodegradable waste from agriculture was selected for the experiments.

In other countries of the world, huge amounts of such waste are generated also, therefore the problem of waste utilization arises. Scientists from various countries investigate the potential of the use of this waste for production of biogas. The results of biogas production investigation, anaerobically treating pig manure, mixtures of pig manure and other mixtures of biodegradable organic waste are explicitly described in the scientific papers of Yu and Schanbacher (2010), Lansing et al. (2010), Masse et al. (2007), Uzodima et al. (2007), Chae et al. (2008), Chae et al. (2002), Kvasauskas (2008) and Kaparaju and Rintala (2005). The results of the research of hen manure and its mixtures are presented in the works of Ghafoori and Flynn (2007), Abouelenien et al. (2009), Kvasauskas (2009) and Callaghan et al. (2002).

Thus, anaerobic processing of the waste generated in cattle farms in a bioreactor is not just an efficient way for reasonable use of biodegradable waste, but it is also useful in economic sense. Huge potential for making biodegradable waste, generated in farms, into biogas is available not only in Lithuania or in the other countries and the world as large. Taking into consideration the studies on investigation of biogas production made by other scientists, it is possible to state that this problem and its solution are efficient and useful. Each scientist is looking for optimal mixtures of biodegradable waste, which, used in a bioreactor, would result in the maximum yield of biogas, at the same time as high methane concentration as possible.

Based on the researches performed by scientists, it has been established that the yield of biogas depends on the composition of the substrate. One of the key factors determining the yield of biogas is the ratio between total carbon and nitrogen (C/N). This factor has to be considered when selecting mixtures. The recommended C/N of the mixtures should be 25:1 (Lindorfer et al.2008). Production of biogas is a complex process when organic, substances are affected by different types of bacteria.

Under the impact of anaerobic bacteria, the transformation of organic materials into biogas occurs in three steps: hydrolysis, acetogenesis and methanogenesis. Each step is related to particular group of micro-organisms having different functions and properties (Bailey, 1991).

During hydrolysis bacteria destroy complex compounds into fine molecular – sugar, carbon dioxide and acetates (Jørgensen et al., 2007). In the step of metanogenesis the bacteria producing methane may use hydrogen, carbon dioxide and acetates as substrates for obtaining methane in the process of metabolism. About 70% methane is produced from acetates and 30% from hydrogen and carbon dioxide (Ghose, 2003).

In the course of biological degradation process in a bioreactor all groups of micro-organisms combine their activity so that interim products discharged by one group are used by another groups of micro-organisms. The micro-organisms which produce biogas require specific medium to maintain their vitality. Methanogenic bacteria are very sensitive anaerobes, therefore when the amount of oxygen or nitrogen (ammonia) increases in the media, their activity, and at the same time discharge of biogas, is disarrayed. Temperature, acidity and alkalinity, oxidation reduction potential and other medium factors therefore conform to their needs. The activeness of materials circulation and the activeness of methane production depend on the following factors: Composition of the substrate under processing, the maintained temperature and its fluctuations, sustention duration, acidity and suppressing factors (Nagel et al., 2001; Anonymous, 2004).

The objective of this study was to analyse, in terms of quantity and quality, the release of biogas and methane from animal waste and biodegradable garden waste and to determine which mixture of organic waste is better suitable for the production of biogas and methane.

MATERIALS AND METHODS

Tests were carried out in bio-reactor of continuous operation (Figure 1) whose volume amounts to 30 L, respectively. Bio-reactor was filled with mixtures of organic biodegradable waste and operated in the mesophilic mode. The temperatures of 35±1°C (in 30 L bio-reactor) were maintained. Throughout the experiment, the amount of released biogas and the concentrations of methane, hydrogen sulphide and oxygen were recorded on a daily basis.

Methods for determining the chemical composition of substrate

Total nitrogen, total phosphorus, total carbon, pH and heavy metals were analysed in the substrate before biogas production to evaluate the impact of methanogenesis on the substrate's chemical composition. Five samples of substrate were taken in each experiment to ensure accurate evaluation of parameter values. Total nitrogen was determined by the method using oxidative digestion with peroxodisulfate (ISO 11905- 1:1997). The analysis employed a photometer and wavelength of 540 nm. The

Table 1. Characteristics of treated waste.

Mixture	Ratio of waste mixture (%)	pH of waste prior to treatment	Dry matter content in bioreactor (cow manure, g)	Dry matter content in bioreactor (grassy waste, g)	Waste moisture (%)	Garden, vegetable, fruit waste fraction (mm)
PMGW	90:10	6.5	2700	300	Pig manure (75.2)	10
HMGW	90:10	6.35	2700	300	Hen manure (42.6)	

PMGW, Pig manure and garden waste; HMGW, hen manure and garden waste.

standard error of total nitrogen in laboratory measurement is ±6%. Total phosphorus was determined using the ammonium molybdate spectrometric method (BS EN 13137:2001). The standard error of the total phosphorus in laboratory measurement was ±0.01%. Total carbon was analysed using the total carbon (TC) analyser of SSM-5000A type. The standard error of total carbon in laboratory measurement is ±3%.

Heavy metals were analysed using the Atomic absorption spectroscopy (AAS) method. The standard error in laboratory measurement is ±5%. The substrate's pH was determined using a pH-meter. Five samples of 50 ml each were analysed before the biogas production experiment. Characteristics of treated waste is shown in Table 1.

Biomass is supplied to the bio-reactor via a biomass funnel and biomass supply pipe with a valve which is opened upon filling the funnel and closed after biomass has been supplied to bio-reactor. Biomass is discharged through a biomass outlet pipe with a valve which is opened during biomass discharge and closed after the required amount of it has been discharged. Biomass is discharged to a biomass storage tank (Figure 1).

Biomass in a bio-reactor is heated up to 35°C (in 30 L bio-reactor). To know the existing temperature the bio-reactor is fitted up with a temperature sensor. Should temperature fall or rise, which depends on the ambient air temperature, it will be automatically increased or decreased to the required value.

A biomass mixer consists of a bar and two paddles. The biomass mixer is rotated by the biomass mixer motor which is mounted on the top to bio-reactor. Mixing duration and frequency are regulated automatically. Biomass is measured every day 1 min every 10 minutes. To measure a gas amount, a gas accumulation vessel [polyvinyl chloride (PVC pipe)], a ballast for keeping the vessel in the water, a vessel with water, branch pipes for hose fixing, hoses and a ruler were equipped (Figure 1).

The pH was determined using the pH-meter HI 98127 which measures solution's pH (measurement range varies from 0 to 14 ± 0.1) and temperature (measurement range varies from -5 to 6 0°C ± 0.5°C). The substrate's pH indicator is determined before and after the experiment.

The composition of biogas was recorded with the biogas analyser INCA 4000 showing the concentrations of methane (%), carbon dioxide (%), oxygen (%) and hydrogen sulphide (ppm). The device's measurement range: oxygen, 0 to 25% (error – ±1 %), hydrogen sulphide, 0 to 100 ppm (error: ±5%), methane, 0 to 100% (error, ±1%), carbon dioxide, 0 to 100 (error: ±1 %). The device's working conditions was: ambient air temperature, 5°C to +40°C and relative humidity ~ 95%.

RESULTS AND DISCUSSION

One of the key indicators showing the efficiency of the anaerobic treatment of biodegradable waste is the evolved amount of biogas. The larger the biogas yield at a stable amount of methane, the higher is the benefit (more energy) obtained during anaerobic digestion of organic waste. Data on the chemical composition of the waste are presented in Figures 2 and 3.

The experimental results of anaerobic digestion of hen manure and garden waste mixture ratio (90:10%)

During biological degradation of hen manure (HM) and garden waste (GW) (in a ratio of 90:10), the amount of released biogas increased suddenly, while upon reaching the maximum value it was gradually falling until the end of the experiment. At the beginning of the experiment the amount of biogas was at 0.105 m^3/m^3d and increased to 1.097 m^3/m^3d until the 3rd day of the experiment. Subsequently, the amount of evolved gas started decreasing and reduced to 0.035 m^3/m^3d at the end of the experiment (Figure 4). 1 m^3 of such substrate was able to produce 9.75 m^3 of biogas within the entire period. Theoretically, 1 m^3 of hen manure could produce around 48 m^3 of biogas (Al Seadi, 2001).

The results obtained from our experiments differ by 5.2 times from the theory; such a difference could have been predetermined by several reasons:

First, the use of GW as admixture reduced the amount of proteins but increased the amount of carbohydrates in a biomass. In the meantime, a smaller amount of biogas is obtained from the anaerobic digestion of carbohydrates than from that of proteins. The second reason of no less importance is the composition of HM (the content of carbohydrates, proteins and fats). The composition of hen manure depends on the composition of the feed hens are fed on. Thirdly, the presence of admixtures in a biomass, such as GW containing cellulose, results in a slower decomposition of this waste, which can have an influence on biogas production. Tunisian scientists carried out research on biogas and methane

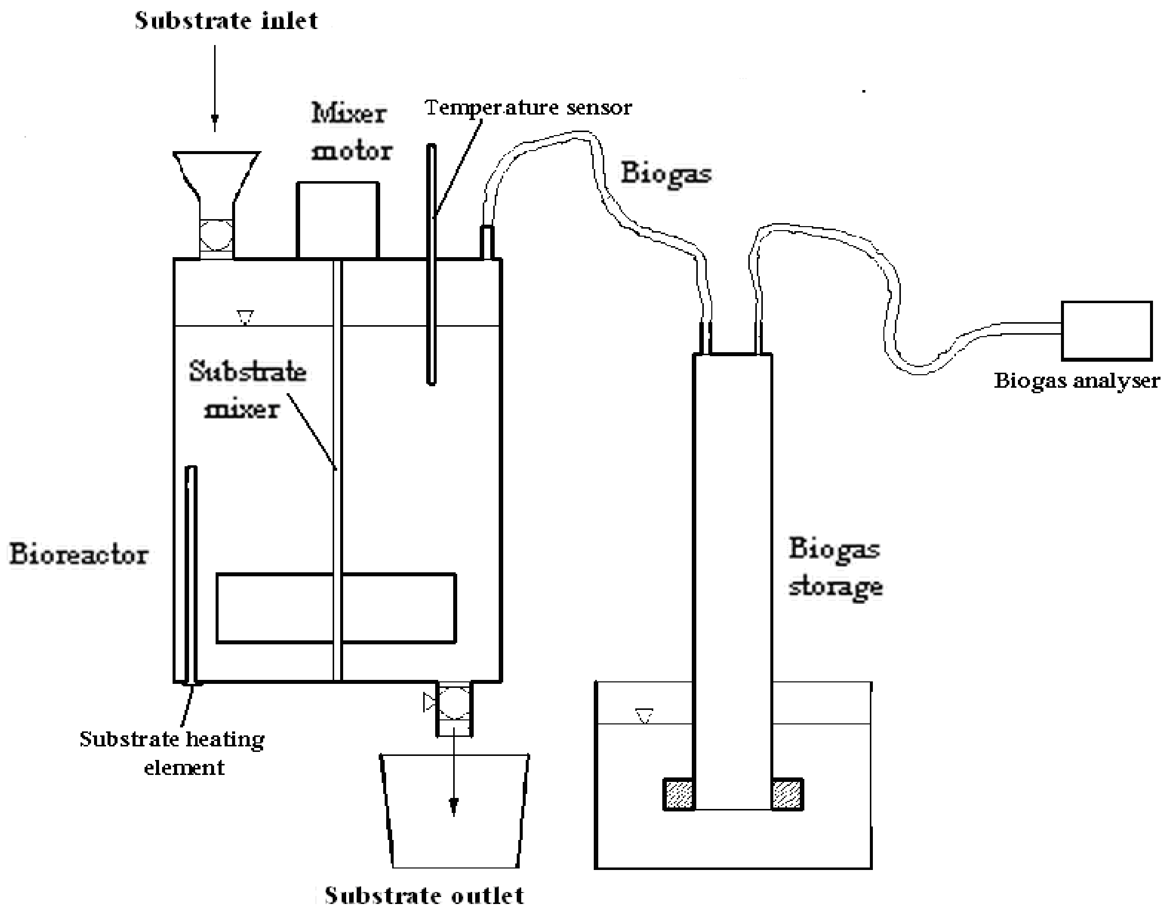

Figure 1. Charts of laboratory bio-reactor stand.

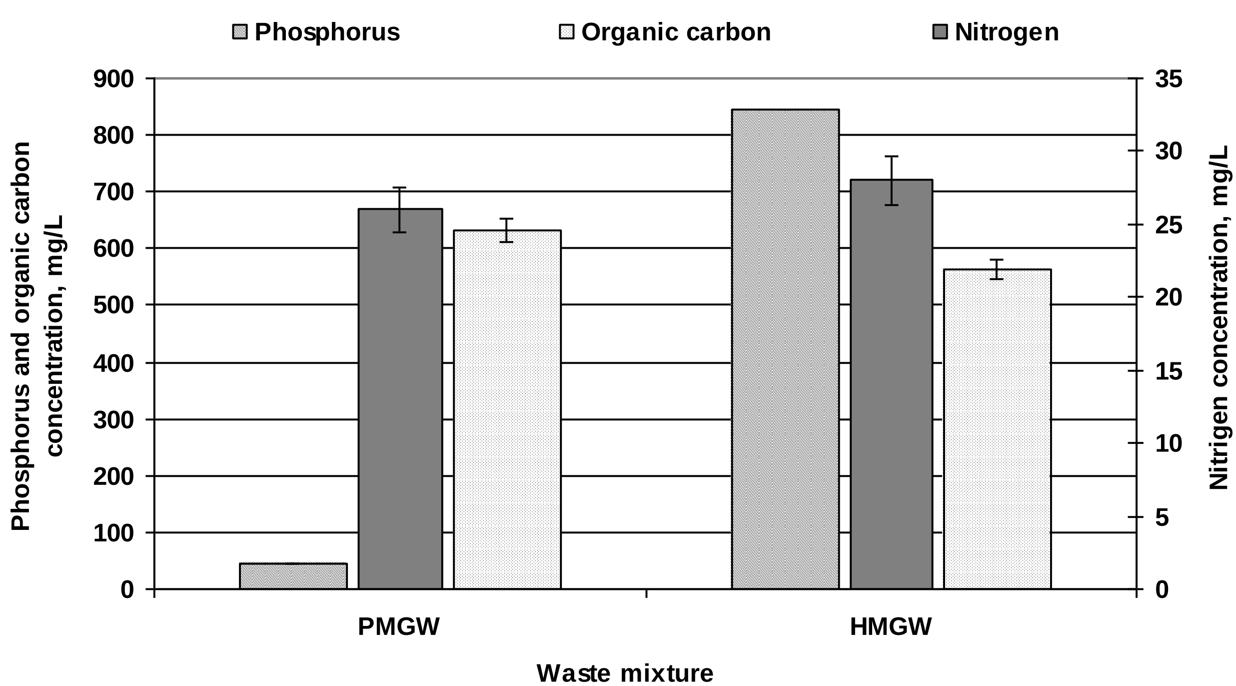

Figure 2. Phosphorus, organic carbon and nitrogen concentrations of the studied substrates.

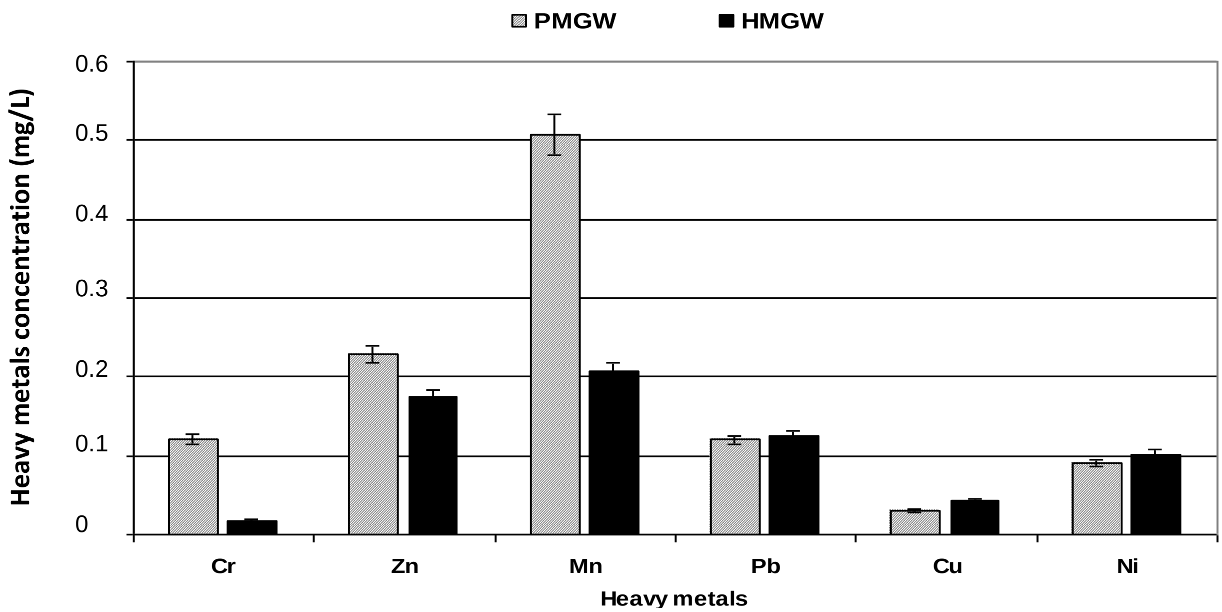

Figure 3. Heavy metals concentrations of the studied substrates.

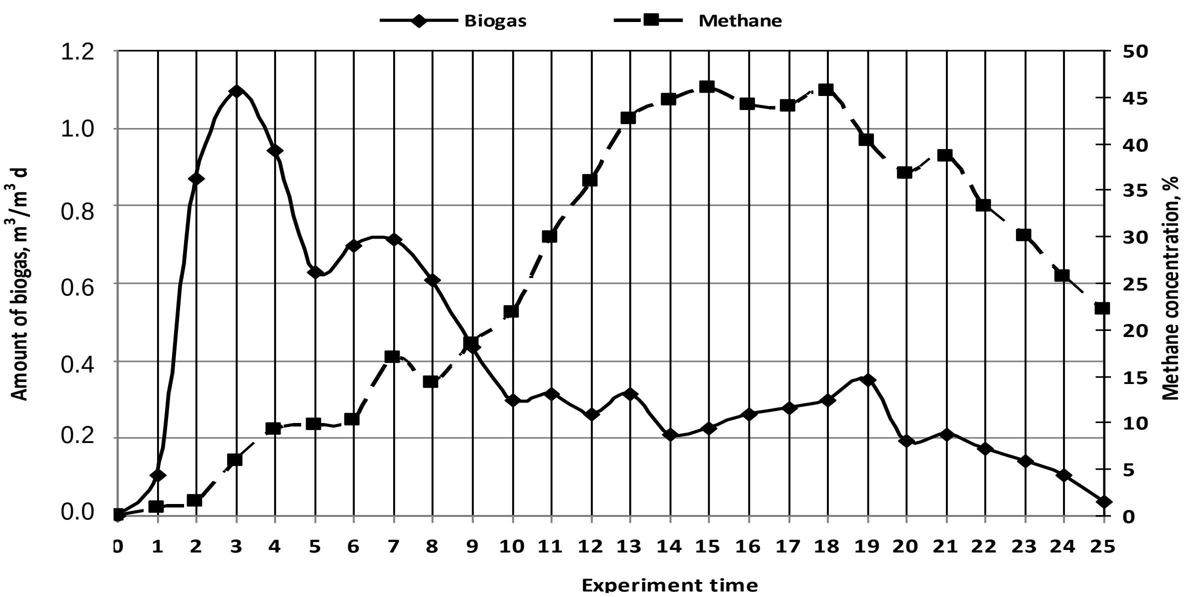

Figure 4. Amount of biogas (m^3/m^3 d) and methane concentration (%) during anaerobic degradation of hen manure and garden waste in a bio-reactor under mesophilic conditions.

production by using GW. As maintained by them, the recovery of biogas from this waste is inefficient as garden waste decomposition results in a rapid production of volatile fatty acids which suppress the activity of the methanogenesis bacteria (Bouallagui et al., 2005).

From the beginning of the experiment until its 15th day, the concentration of methane was rising. On the same day the methane concentration reached 45.9% (Figure 4). An increase in the concentration of methane until the 15th day shows that the process of methanogenesis was sufficiently balanced, but subsequently a low concentration of methane was predetermined by the lack of nutrients, a small content of fats in this waste and the decreased amount of proteins with high energy potential in the biomass.

Kvasauskas (2009) investigated the same mixture of waste, only with different ratios (hen manure and fruit, vegetables waste 3:1, 1:1 and 1:3) maintaining

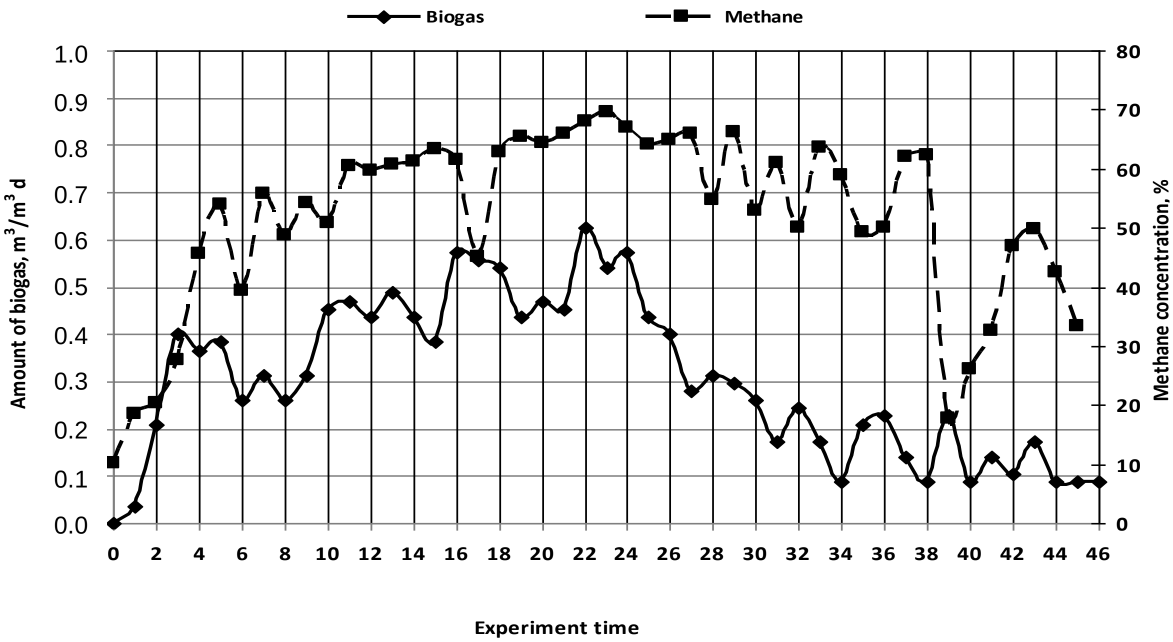

Figure 5. Amount of biogas (m^3/m^3 d) and methane concentration (%) during anaerobic digestion of pig manure and garden waste in a bio-reactor under mesophilic conditions.

psychophilic temperature in the bioreactor. During the research it has been established that increasing the amount of fruit, vegetable waste in the mixture, the amount of biogas and the methane concentration went down. Therefore it is possible to ascertain when selecting mixtures for biogas production, depending on the C/N ratio, the most of the mixture being the hen manure.

The concentration of hydrogen sulphide in gas gradually decreased from 105 ppm at the beginning of the experiment to 28 ppm at the end of the experiment. The concentration of oxygen in the evolved biogas was decreasing within the entire experiment from 1.7% at the beginning to 0.1% at the end of the experiment, which ensured anaerobic conditions in the bio-reactor.

At the beginning of the experiment, a pH indicator remained at 6.35, while it ended at 6.72. In the presence of such pH the bio-reactor was dominated by a weakly acid medium. Microbiological activities in biogas reactors is the most favourable in the presence of a neutral or weakly alkaline medium ($6.5 < pH < 8.5$) (Schön, 2009). Such pH indicator could have resulted from inefficient neutralisation of the excess of fatty acids due to non-intensive activities of bacteria.

The experimental results of anaerobic digestion of pig manure and garden waste mixture ratio (90%:10%)

In the course of treatment of this waste mixture (90% of pig manure and 10% of garden waste), an increase in biogas amount was recorded until the experiment's 22nd day totaling 0.627 m^3/m^3d. Later, a biogas amount started decreasing and reached 0.087 m^3/m^3d at the end of the experiment (Figure 5). Such a decrease in biogas amount relates to the lack of new nutrients. Anaerobic microorganisms treat the existing substrate containing proteins, fats and carbohydrates and when the amount of these substances start decreasing the process of biogas production also slows down. At that point, 1 m^3 of biomass can produce around 14.30 m^3 of biogas.

Kaparaju and Rintala (2005) investigated production of biogas anaerobically processing pig manure and potato waste (pig manure made the most in the mixture). During the investigation methane concentration appropriate for energy obtaining, rather high, amounting up to 60 to 63% was established. Pig manure is fit for biogas production, but when mixed with fruit, vegetables waste it may result in higher yield of biogas and methane, because if processing only pig manure the obtained methane concentration if by some 10% lower. (Xie et al., 2011).

As presented, Figure 6 shows that the content of methane progressively grows from the beginning of the experiment which is the same in our experiments. The content of methane in biogas increased from 10.1% at the beginning of the experiment to 69.7% until its 23th day. The content of methane decreased gradually until the 39th day. Variations occur in a range of 50 to 67% (Figure 5).

A more sudden increase was recorded only after the 39th day. As also observed by Xie et al. (2011), when treating pig manure and grass silage mixtures (in 3:1, 1:1 and 1:3 ratios) in a bio-reactor of continuous operation, the highest concentration of methane, varying in a range

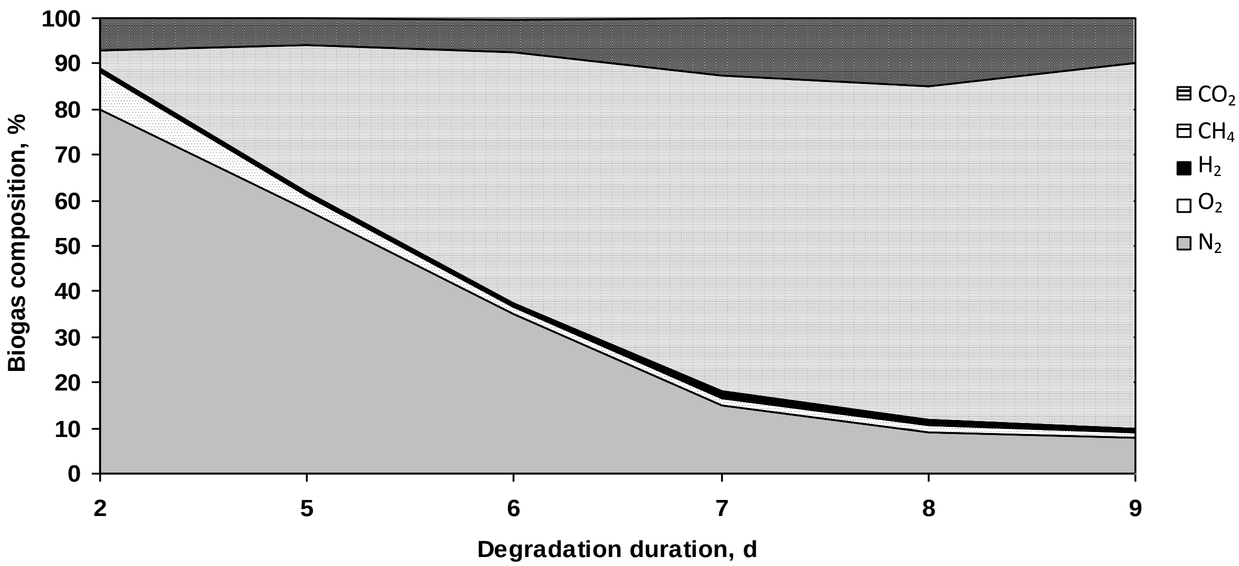

Figure 6. Variation in biogas composition during substrate degradation (Cecchi et al., 1992).

from 60 to 70%, was obtained on the 20th day of the experiment, while later, the methane concentration decreased and, on the average, remained stable, ~60%, until the end of the experiment. A decrease in methane content proportionally relates to a variation in biogas amount. With biogas amount decreasing the content of methane also decreases as methane is the major component of biogas.

Having performed additional tests, Xie et al. (2012) noted that substrate's pH has a major influence on the release of methane. After having performed experimental tests with pig manure and grass silage mixtures in three different ratios (80:20, 70:30 and 60:40%) in a bio-reactor of continuous operation, it was maintained that methane production was poor until the 24th day of the experiment when bio-reactors were not additionally filled and substrate's pH reduced from 7.45 to 6.42. The content of methane in biogas varied from nine to 23%. However, upon additional filling, the pH rose and at the same time methane production increased. During our experiments, at the beginning pH remained at 6.5, while at the end of the experiment increased to 7.05. The pH recorded during the experiments allows an assumption that pH was increasing during the experiment which resulted in the efficient production of methane.

A hydrogen sulphide variation tendency is similar to that observed during the treatment of a hen manure and garden waste mixture in a ratio of 90:10%. The highest H_2S amount was recorded at the beginning of the experiment, that is, on its 9th day and reached 99 ppm. Afterward, the amount of hydrogen sulphide in biogas reduced until the end of the experiment when its concentration was 1 ppm.

The largest O_2 concentration in biogas, 4.6%, was recorded at the beginning of the experiment. A decrease in oxygen concentration was observed until the 25th day of experiment (which was recorded as 0%). From the 26th day until the end of the experiment, the content of oxygen in biogas varied from 0.2 to 0.8%. Therefore, the obtained research results allow a conclusion that anaerobic conditions were ensured.

Conclusions

1. The largest amount of biogas evolved from the degradation of a hen manure and garden waste mixture in a ratio of 90:10%. While processing this mixture the yield of biogas was equal to 1.105 m^3/m^3d and was 1.7 times higher than the yield of biogas obtained processing a pig manure and garden waste mixture in a ratio of 90:10%.
2. A higher concentration of methane was recorded during the treatment of a pig manure and garden waste mixture in a ratio of 90:10%. The maximum concentration of methane reached 68.0%. Since the methane concentration in this mixture was ~1.5 times higher than in the other mixture.
3. The mixture of pig manure and garden waste in a ratio of 90 to 10% was better suitable for biogas and methane production. The biggest amount of bio-gas was registered in 22 days and amounted to 0.650 m^3/m^3d. The methane concentration in biogas was the biggest of 65% and this mixture of organic wastes is the best for energy production.
4. After the performance of the investigations, it has been established that all investigated mixtures may be used for the production of biogas. Aiming at better energetic and environment protection effect, biogas produced from anaerobically processed organic waste could be mixed with natural gas.

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