DETERMINATION OF THE BIOMETHANE POTENTIAL OF DIFFERENT TYPES OF MANURE FROM EXTENSIVE ANIMAL FARMING

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
Livestock production is a potential environmental pollutan because of the high concentartions of animals on the small area. Production of biogas with anaerobic degradation from organic waste is one of the pledge alternative energetic solutions, especially from organic manure made from animal farming and other residuals of agricultural production. The aim of this paper was to determine posibillity of using manure different origin from extensive animal breeding for production of biogas in labaratory conditions. The results obtained will be based on posibillity of use waste streams from extensive animal husbandry as basic substrate for anaerobic digestion. In this regard, cosubstrates were formed as mixture 1 chicken excrement; mixture 2 sheep manure; mixture 3 cow manure; all three basic substrates were in mixture with the sludge from the wastewater treatment plant. The results showed production of 71,5 ml CH_4/gVS for mixture 1, 68,65 ml CH_4/gVS for mixture 2 and 48,68 ml CH_4/gVS for mixture 3.

KEYWORDS: extensive breeding, manure, anaerobic digestion, biogas, biomethane potentional

INTRODUCTION

One of the main environmental protection problems of modern society is the continuous increase in the generation of organic waste. In many countries, sustainable waste management, which includes preventing its creation and reducing new quantities, has become a major political priority and an important part of joint efforts to reduce environmental pollution and greenhouse gas emissions in order to mitigate global climate change.

Biodegradable organic waste, due to its specificity and continuous flow of production from industrial and agricultural production as well as households and wastewater treatment plants, represents a potential danger to human health and environmental protection. In addition to the fact that the legal regulation prescribes a reduction in the amount of disposed biodegradable organic waste, a smaller amount of waste in landfills directly reduces the emission of methane, which is created by the spontaneous anaerobic decomposition of waste in landfills [1].

It has long been known that animal husbandry generates large amounts of nutrient-rich organic waste that is used to condition agricultural land. Manure treatment would improve the physico-chemical characteristics of the waste and thereby reduce its toxicity [2].

It is considered that the production of biogas by anaerobic digestion is the optimal process for treating animal excrement, as well as a wide range of organic waste, since it transforms these substrates into a renewable energy source and, often, an environmentally friendly fertilizer in agriculture [3]. Biogas is a cheap and CO_2-neutral renewable energy source, which provides the possibility of processing and recycling various agricultural residues and by-products in a sustainable and environmentally friendly way. At the same time, biogas entails numerous socio-economic benefits for society as a whole, but also for actors involved in its production and exploitation [4].

MATERIAL AND METHODS

For research purposes, glass eudiometric tubes "Šurlan-Medulin" were used, placed on glass bottles with a volume of 500 ml. Achieving anaerobic conditions was done by blowing nitrogen, which squeezes air out of the reactor, while due to the required constant temperature of the reactor system, heating was done in a water bath with water circulation. At the top there is a shelf with bottles to level the level and catch excess liquid.

Using eudiometric tubes, biogas production is easily read, because the produced gas moves the liquid level, and the liquid returns to the receiving bottles, as shown in Figure 1. A 22% NaCl solution was used as the liquid, because the constituents of biogas are difficult to dissolve in to the solution prepared in this way, with the addition of three drops of concentrated sulfuric acid and methyl orange indicator so that the solution takes on a color and is more noticeable.

The pressure and temperature of the surrounding air were measured using a baro-thermohygrometer placed next to the eudiometric tubes, and these values were used to recalculate the volume of the obtained biogas to normal conditions. Mixing was done mechanically using magnetic stirrers.

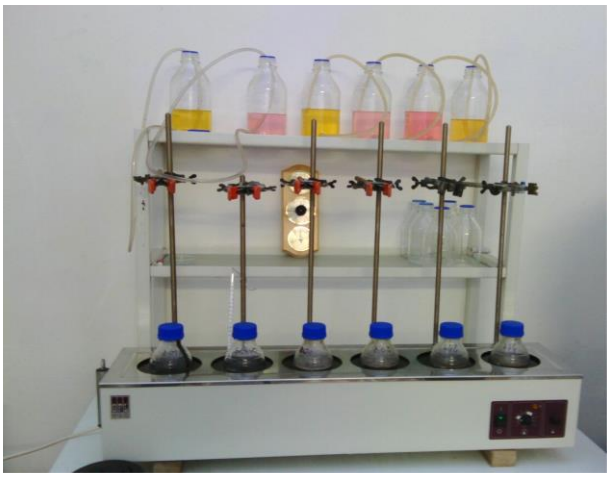

Figure 1. Reactor system

Gas sampling was done using a glass aspirator, with valves on both sides of the cylinder. At one end, the aspirator is connected with a rubber hose to a level bottle containing a 22% NaCl solution.

Gas composition analysis was performed on a Clarus 500 gas chromatograph (Perkin-Elmer, India), equipped with a thermal conductivity detector (TCD-R) and a gas analyzer model 4016 Arnel TotalChrom Work-station software. Helium was used as carrier gas (flow rate 34 ml/min).

A gas mixture consisting of CO, CO_2, CH_4 and O_2 (Messer, Germany) was used to calibrate the device.
By connecting the free part of the aspirator to the inlet of the chromatograph and raising the level of the bottle, the flow through the chromatograph column is enabled, which is necessary for determining the biogas composition.

After a twelve-minute analysis, the display shows the composition of the analyzed gas sample in volume percentages.

Three types of manure from extensive farming were used as the basic substrate, chicken (sample 1), sheep (sample 2) and cow (sample 3), and in order to achieve biogas production, sludge from the municipal wastewater treatment plant in Živinice town was used as inoculum.

In order to obtain the necessary parameters, it was necessary to characterize the materials used in the experiment, by determining:

- dry matter content,
- content of volatile organic matter,
- nitrogen content according to Kjeldahl,
- total phosphorus content,
- chemical oxygen demand.

The dry residue means the proportion of dry matter in the sample obtained after the determined drying procedure. It is expressed as a percentage or in grams per kilogram. Determination of dry matter content was performed according to Method 2540-Solid B. Standard Methods for the Examination of Water and Wastewater 21st edition. APHA, Washington, DC (2005). All the analyzed samples were dried in an oven at a temperature of 105 °C to a constant mass. To calculate the dry residue, the difference between the mass before and after the drying process is taken.

Volatile-volatile substances (VS) are those substances that are lost when the sample is heated 550 °C. Volatile organic matter content was analyzed according to Method 2540-Solid E. Standard Methods for the Examination of Water and Wastewater 21st edition. APHA, Washington, DC (2005). The ash content was determined in an incineration furnace for six hours at a temperature of 550 °C. Volatile organic matter content was determined as the difference between dry matter content and ash content in the samples.

The electrometric measurement of the pH value was carried out by direct measurement of the value on a METTLER TOLEDO FE 20/EL 20 pH meter. Before each measurement, the internal control of the device was carried out with certified reference materials with a pH value of 4.01; 7.01; 10.01.

The Kjeldahl nitrogen content was determined according to Method 4500-NorgB. Standard Methods for the Examination of Water and Wastewater 20th edition. APHA, Washington, DC (1998). The method consists of three stages: digestion at a temperature of 340 °C (boiling temperature of H_2SO_4) in the presence of concentrated sulfuric acid and Kjeldahl catalyst with selenium; distillation in the presence of NaOH where the distillate is accepted in a solution of boric acid and titration with 0.1 M HCl in the presence of the bromine cresol green indicator. The determination was made on a Gerhardt Kjeldahl apparatus, which consists of three blocks: a cleaning block, a digestion block and a distillation block.

When determining the content of total phosphorus in the substrates, the sample was prepared for analysis by weighing a sample mass of about 1 g, transferring it to a beaker with distilled water, and then digesting it in the presence of $K_2S_2O_8$ and 4.5 M sulfuric acid heated on a stove. After digestion, the samples were transferred to a measuring flask of 1 l, supplemented with distilled water, and then filtered. A certain amount of the filtrate was used as a test sample to determine the total phosphorus in the substrate. According to the instructions for the formation of the base diagram, the samples are also treated, and the concentration of total phosphorus is determined through the absorbance, which was read on a Shimadzu UV 1800 spectrophotometer at a wavelength of 880 nm.

A modified method according to BAS ISO 6060:2000 was used to determine COD. A mass sample of 0.03g was diluted with distilled water to 10 ml in an Erlenmayer flask with a ground neck. After that, 20 ml of concentrated sulfuric acid with $AgSO_4$ and 10 ml of $K_2Cr_2O_7$ were added to the sample. After connecting the neck of the flask to the return cooler, reflux is ensured, as the sample is boiled for two hours at a temperature of 148 °C. After cooling, the sample was titrated with a standard ferroammonium sulfate solution with the FEROIN indicator. In parallel with the sample, a blank test was done in an identical manner, as well as one sample without cooking for the purpose of determining the ferroammonium sulfate factor.

Based on the results of the physico-chemical characterization of the substrate, mixtures with an optimal content of dry matter were formed for carrying out the anaerobic digestion process. For all mixtures that were formed and subjected to the process of anaerobic decomposition, two tests were performed and the results were expressed as mean values.

RESULTS AND DISCUSSION

Anaerobic digestion experiments were carried out in mesophilic conditions of different types of manure from extensive animal husbandry with the addition of waste sludge from municipal wastewater treatment plants.

Before the formation of the mixtures, it was necessary to carry out a physical and chemical characterization of the substrates used in the process of anaerobic digestion in order to optimize the parameters in the mixtures.

The results of the analysis of physical and chemical parameters of different types of manure are shown in table 1.

Table 1. Results of physico-chemical parameters of used manures

Parameters	Unit	1	2	3
TS	%	27.0	24.8	17.5
VS	%	15.9	21.2	14.8
VS/TS	-	0.59	0.85	0.84
TP	g/kg	4.45	2.22	0.31
COD	g/kg	144.83	154.56	86.4
TKN	g/kg	10.73	7.63	3.27

TS – total solid; VS – volatile solids; COD – chemical oxigen demand; TKN – total Kjeldahl nitrogen

As can be seen from the table, all the substrates that were analyzed are potential raw materials for biogas production due to the favorable content of VS (volatile matter VS) and COD, which represent the amount of organic matter that is transformed into biogas/methane during anaerobic processes.

In addition, the favorable ratio of COD : TKN (from 13.5:1 to 26:1) in potential raw materials corresponds to the ratios recommended in the literature for substrates undergoing anaerobic decomposition [5],[6],[7],[8].

Generally, it is known that sludge is a carrier of anaerobic microorganisms, but it was also used for to optimize the content of dry and organic matter, i.e. to achieve optimal conditions related to the TS content of less than 20% for the so-called "wet" process of anaerobic digestion [9].

Based on the content of dry matter in the raw materials, which were the subject of research, manure and waste sludge, mixtures were formed through which the biomethane potential was determined.

The composition of the formed mixtures based on the optimal proportion of dry matter is shown in Table 2, while Table 3 shows the most important physical and chemical parameters of the formed co-substrates.

Table 2. Composition of formed cosubstrates expressed in mass percentages

Mixture	Manure mass %	Sewage sluds %	H_2O %
1	26.0	74.0	0
2	35.1	19.29	45.61
3	44.12	16.18	39.70

Table 3. Physical and chemical characteristics of the co-substrates formed

Parameters	Unit	1	2	3
TS	%	5.24	11.92	9.14
VS	%	4.47	10.18	8.10
VS/TS	-	0.85	0.85	0.88

Mixture 1 has a significantly lower content of TS (dry matter) compared to the other two mixes due to the structure of chicken excrement. For easier control and handling of the process (primarily mixing), the mixture was formed with a lower TS content. A smaller share of TS leads to a smaller share of VS in mixture 1 because the parameters are mutually dependent.

Excluding the first mixture, the dry matter content is in the optimal range because it was the parameter on the basis of which the co-substrates were formed. The ratio of organic and dry matter in all three mixtures is in the ideal ratio, which according to literature data ranges from 70-90% [10].

The diagrams (Figure 2 and Figure 3) show the production of biogas per day and the cumulative yield of biogas for all three mixtures that were used in the research.

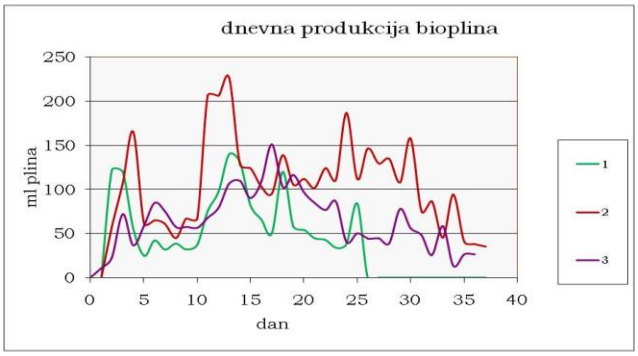

Figure 2. Diagram of daily biogas production

It can be seen from the diagram that in mixture number 2 (sheep manure with sludge) the largest amount of biogas was produced on a daily basis, and on the twelfth day the maximum production of biogas was recorded when it reached a value of 226.8 ml.

After the twenty-sixth day, biogas production was completed in mixture 1, while the process of anaerobic digestion continued until the thirty-sixth day in the remaining two mixtures.

The diagram of cumulative biogas yield (Figure 3) confirms the stages of adaptation and the beginning of hydrolysis in the first days of the process. A significantly higher production of biogas is clearly visible in mixture number 2 compared to mixtures number 1 and 3.

Figure 3. Diagram of cumulative biogas production

In addition, the aforementioned confirmation that the process in mixture number 1 was completed on the twenty-sixth day was confirmed.

The process in mixtures number 2 and 3 lasted ten days longer, and therefore the cumulative production of biogas in those mixtures was slightly higher.

Comparing the obtained results of this research with the results obtained in previously conducted research under the same or similar conditions, it can be concluded that the production of biogas on a daily basis in mixtures 1 and 3 (62.42 ml/day and 65.65 ml/day) is significantly higher compared to the results obtained in the research [11] who obtained a biogas yield of 33.20 ml/day and 23.80 ml/day, respectively, for 40 days of experimental research.

Based on the share of methane in the produced biogas, the composition of the formed co-substrates and the production of biogas, the daily, cumulative and specific production of methane was calculated (Figure 4, Figure 5 and Figure 6) for all three mixtures.

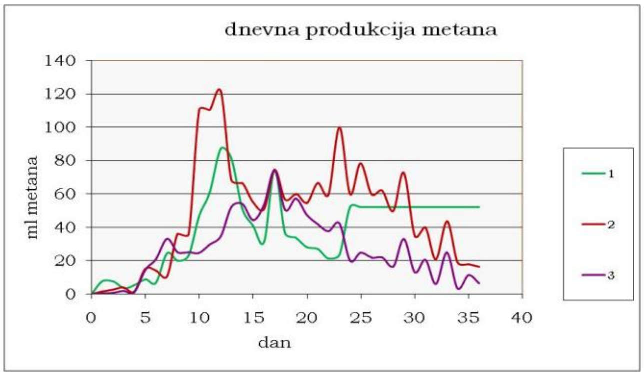

Figure 4. Diagram of daily methane production

The diagram of daily methane production shows discontinuous methane production in all mixtures. The diagram of daily methane production indicates the fact that the production from the second mixture had the highest daily methane yields, and the maximum daily methane production was achieved on the twelfth day in mixture 2 and was 121.38 ml of methane.

The results of daily methane production are largely consistent with the results of daily biogas production.

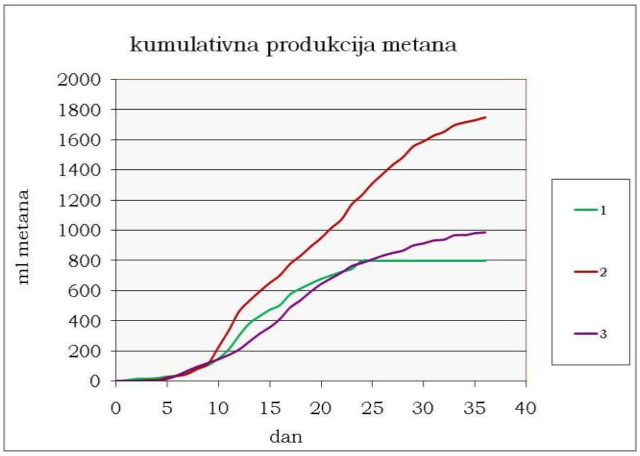

Figure 5. Diagram of cumulative methane production

Identical as in the case of cumulative biogas production, the production of methane from mixture 2 is significantly higher compared to the production of methane in mixtures 1 and 3. Thus, the cumulative production of methane from mixture 2 was almost 1800 ml, the production from mixture 3 was approximately 1000 ml, while methane production from mixture 1 was the smallest and amounted to 800 ml.

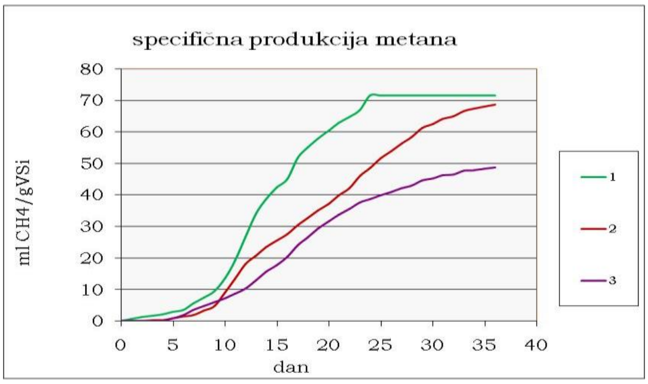

Figure 6. Diagram of specific methane production

On the diagram of specific methane production, it is clear that the biogas potential of chicken manure is the highest, because in the shortest time it has the highest specific yield of methane [mlCH_4/g VSi] compared to the other tested samples. It should be emphasized here that the first mixture (chicken excrement with waste sludge) had a significantly lower content of dry and organic matter compared to the remaining two mixtures, which directly affected the result of specific methane production.

This research result provides a very good basis for further research aimed at optimizing the content of dry and organic matter in different mixtures of raw materials, which especially applies to mixtures containing animal manure.

Comparing the obtained results of specific methane production in relation to the input content of organic matter from mixture 1 (71.5 mlCH_4/gVSi) of this research with the results obtained from the research [12] who conducted an experimental study of dry anaerobic decomposition of chicken manure in mesophilic conditions.

The research results, expressed as specific methane production, amount to 31 mlCH_4/gVSi, and indicate that the production of methane obtained by anaerobic digestion from mixture 1 of this research is significantly higher compared to the previously mentioned research.

Due to the fact that after the anaerobic (co)digestion process is completed, the digestate is left behind, in table 4 the characteristics of the digested residue (digestate) representing the UXO product, as well as the final results of the production of biogas and methane are given.

If the content of dry and volatile organic matter is compared before (table 3) and after (table 4) the process, it is easy to conclude that a certain part of the matter was transformed into gas products.

Table 4. Final results of batch anaerobic digestion after the implementation experiment

Parameters	Unit	1	2	3
TS	%	2.83	9.65	7.95
VS	%	1.86	7.22	5.8
pH	-	7.62	6.64	6.33
V_{biogas}	ml	1623	3869.98	2363.54
$V_{methane}$	ml	800	1747.16	985.8
$W_{methane}$	%	0.49	0.45	0.41
spec.methane yield	mlCH_4/gVS_i	71.5	68.65	48.68

The greatest reduction of TS and VS was recorded in mixture 1, while mixture 2 had an approximate value of reduction of TS and VS. Mixture 3 recorded the lowest reduction of dry matter and organic matter compared to the first two.

Regardless of the slightly lower content of organic matter in the digestate compared to manure and mixtures, the digestate has a useful value in agriculture for the needs of soil conditioning, and the higher water content favors easier handling when applying it to the soil.

After the anaerobic digestion process, the mixtures had different pH values. The pH value of the obtained digestate from mixture 1 was in a slightly basic environment and was 7.62. The remaining two mixtures produced a digestate with a slightly acidic pH value of 6.64 and 6.33, respectively, which means that it will not have a major impact on soil acidity if the digestates are used in agriculture.

If we take into account the fact that agricultural soils with low pH value prevail in our area, the properties of the soil in terms of acidity can be improved by applying digestate.

The result of the research, which is of particular importance, is the possibility of producing energy (biogas) and fertilizer (digestate) from livestock waste streams, because it is generally known that agriculture is a significant consumer of energy.

In this way, the production of energy and useful products from waste streams and their use at the point of origin of waste realizes one of the basic principles of a circular economy, but also of sustainable agricultural production.

CONCLUSIONS

The development and implementation of a system of renewable energy sources such as biogas from anaerobic digestion, based on national resources, will increase the stability of the national energy supply and reduce dependence on energy imports.

The production and use of biogas from anaerobic digestion has a positive effect on the environment and socio-economic benefits for society as a whole, but also for the involved farmers as end users

It is generally known that livestock waste has suitable characteristics for anaerobic processing, so the results of the analysis showed that the substrates used in this research represent potential raw materials for biogas production due to the favorable content of VS and COD, which represent the amount of organic matter from which it is obtained methane.

Due to the relatively high content of dry matter in all three types of manure that represented the basic substrates, waste sludge from the wastewater treatment plant was added in order to optimize the TS to optimal values for the wet digestion process. In addition, waste sludge also plays the role of inoculum because it contains a large number of anaerobic microorganisms.

In mixture 1, the process of anaerobic decomposition lasted twenty-six days, and in the remaining two mixtures, the process lasted ten days longer.

Cumulative production of biogas in mixture 2 (3869.98 ml) is significantly higher compared to the other two mixtures and especially compared to mixture 1 (1623 ml), which is the result of the duration of the anaerobic decomposition process.

Mixture 2 (sheep manure with sludge) produced the highest amount of biogas and methane on a daily basis, and the maximum production was recorded on the twelfth day of the experiment.

The mixture of chicken excrement and sludge has the highest biogas potential because in the shortest time it had the highest specific yield of methane (71.5 $mlCH_4/gVSi$) compared to the other tested samples (68.65 and 48.68 $mlCH_4/gVSi$).

The reduction of dry and organic matter is directly proportional to the specific production of methane and had the highest value in mixture 1, where the highest specific production of methane was recorded.

The production of energy (biogas) and fertilizer (digestate) from animal husbandry waste streams through anaerobic digestion, and their use at the point of origin of waste, is one of the basic principles of circular economy and sustainable agricultural production.

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