THERMAL PRETREATMENT OF CATTLE MANURE FOR ENHANCING BIOGAS PRODUCTION

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: The low degradability of waste materials containing lignocellulosic material is one of the factors that hinder the production of biogas. The increased need for advanced techniques in the anaerobic digestion process has led to the use of different pretreatment raw materials prior to the anaerobic digestion process in order to increase the yield of biogas. In order to maximize the yield of biogas from cattle manure in a mixture with waste sludge, the anaerobic digestion process was performed at mesophilic conditions for 54 days. As pretreatment, the thermal treatment of cattle manure at temperatures of 55 and 70 °C was applied. The highest biogas production was obtained in the sample of cattle manure, previously treated at 70 °C (M70), while the lowest was recorded in the control sample M. The specific biogas production in relation to the input quantity of volatile organic matter had the highest value in sample M70 and the lowest in the control sample. Overall results have shown that the thermal treatment of cattle manure before the anaerobic digestion process can increase both yield and biogas quality.

KEYWORDS: Anaerobic digestion, biogas, thermal pretreatment, cattle manure, waste sludge.

INTRODUCTION

One of the oldest and best researched processes by which the energy can be obtained from biomass is anaerobic digestion. Anaerobic digestion is a biological process of converting complex substrates of biogas and digestate by the action of various types of microorganisms without the presence of oxygen through four major steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis [1].

Today, biogas is commonly produced from raw materials that are easily degradable. Although there is a great potential for biogas production in organic raw materials, especially waste from agriculture, crop residues, animal waste, communal waste, food remains, these raw materials are characterized by a low degree of degradation and as such require longer retention time in the anaerobic digester [2].

Recently, the amount of manure produced on cattle farms has increased, most of which has been disposed in landfills or on agricultural land as a fertilizer without previous treatment. On the other hand, with application of the Nitrates Directive (91/676/EEC), the application of cattle manure for fertilization of agricultural land is limited[3]. In fact, anaerobic digestion provides an alternative solution for treatment, as well as for the recovery of energy from this type of waste [4].

In order to overcome the problem of slow degradation to ensure a shorter time of retention, with increased production of biogas and reduction of waste material that is being disposed, it is advisable to use certain methods for pretreatment of input raw material [5].

The optimal pretreatment method for use in the process of decomposing these raw materials should be economical, should increase the availability of raw materials to microorganisms, should not use or produce substances that inhibit biogas production, should not require high energy consumption and no environmentally harmful byproducts should be created.

MATERIAL AND METHODS

Fresh samples of cattle manure from the dairy farm "Spreča", which were thermally treated at temperatures of 55°C and 70°C and waste sludge from the municipal waste water treatment plant in Živinice, were used as substrates.

A laboratory reactor system for anaerobic digestion, consisting of six glass bottles of 500 ml volume, combined with eudiometric tubes which help to read the biogas production volume, was used for experimental studies. The constant temperature of 35°C was obtained by heating the water in the water bath (Figure 1). The pressure and the temperature of the ambient air were measured with the barothermo-hygrometer and the readings were used to convert the volume of obtained biogas into normal conditions.

Mixing of the substrate was performed mechanically using a magnetic stirrer.

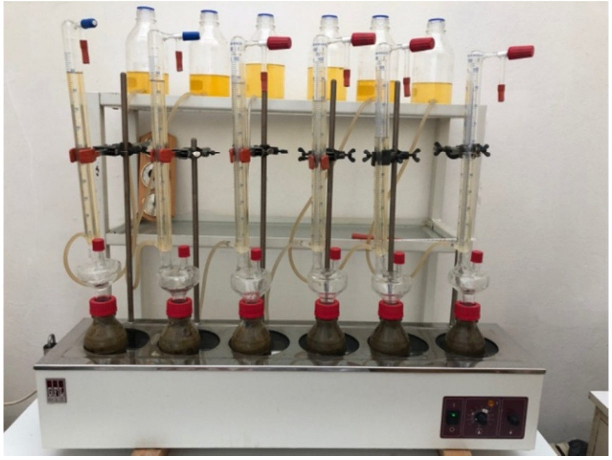

Figure 1. Laboratory reactor system for anaerobic digestion

An incubator with a thermo regulator for thermal pretreatment of cattle manurewas used (Figure 2). The samples were tempered for two hours in the incubator, with certain amounts of manure being subjected to temperatures of 55°C and 70°C.

Figure 2. Incubator with thermo regulator

The characterization of both raw materials, cattle manure and waste sludge, especially in the mixture, was performed before and after the anaerobic digestion by measuring the pH value and determining total dry matter (TS), volatile organic matter (VS), total Kjeldahl nitrogen (TKN) and chemical oxygen demand (COD). The methods used in the analysis of physico-chemical characteristics are standard methods and modified standard methods for wastewater testing (ISO and Standard Methods for Examination of Water and Wastewater (APHA)).

The pH value was measured by a digital measuring device with direct immersion of the electrodes in samples, using pH meter Mettler Toledo FE20/EL20. Prior to each measurement, the control of the measuring device was performed using standard buffer pH 4.01, 7.01, 10.01.

Determination of dry and volatile organic matter was carried out according to the standard Method *Method 2540-Solid B i 2540-Solid E. Standard Methods for the Examination of Water and Wastewater 21st edition* APHA, Washington, DC (2005) [6].

For the determination of the content of total Kjeldahl nitrogen, *Method 4500-*N_{org} *B. Standard Methods for the Examination of Water and Wastewater 20nd edition* APHA, Washington was used. The method consists of three parts: digestion at a temperature of 340 °C in the presence of concentrated sulfuric acid and Kjeldahl catalyst, distillation in the presence of NaOH where the distillate is absorbed into a 2% boric acid solution and titration with 0.1 M HCl in the presence of indicator bromocresol green [7].

Chemical oxygen demand was determined according to the modified standard method BAS ISO 6060:2000 [8].

The duration of the experiment was 54 days. The amount of biogas produced was read on a daily basis and the gas composition was determined on the gas chromatograph "PERKIN ELMER", equipped with the software package "Arnel".

RESULTS AND DISCUSSION

The experiment of anaerobic digestion of cattle manure and waste sludge mixtures was conducted at mesophilic conditions (35 ± 2 °C). Prior to the experiment, physico-chemical analysis of substrate, cattle manure (CM) and waste sludge (WS) was performed and the formed mixture was used as control sample (M). After the thermal processing of cattle manure at temperatures of 55 °C and 70 °C, two more mixtures (M55 and M70) were formed, which were subjected to the process of anaerobic digestion together with the control mixture.

In order to ensure the optimal value of dry matter content (about 8% mass) for the anaerobic digestion process, with respect to the results of the physico-chemical analysis, mixtures with equal ratio (by mass) of untreated or treated cattle manure and waste sludge (1:1) were formed. The physico-chemical characteristics of cattle manure and sludge, and the mixture of untreated and thermally treated cattle manure and sludge are shown in Table 1.

Table 1. Physico-chemical characteristics of cattle manure, sludge and mixture of CM:WS

parameter	Unit	CM	WS	M	M55	M70
pH	-	7.7	6.87	6.61	6.97	6.87
TS	%	14.99	3.82	9.47	10.09	9.56
VS	%	13.50	2.31	7.93	8.52	7.92
VS/TS	-	0.9	0.6	0.83	0.84	0.82
TKN	g/kg	3.68	2.85	3.20	3.07	3.26
COD	g/kg	178.90	46.39	70.98	89.06	93.97

TS-total solids VS-volatile solids; TKN-total Kjeldahl nitrogen; COD- chemical oxygen demand

The pH value measured in all three formed mixtures ranged from 6.61 to 6.97, while according to literature, the optimum pH value for an undisturbed process of anaerobic digestion ranged from 6.5 to 7.6 [9]. The content of dry matter in the control sample was slightly higher than the recommended value. The VS/TS ratio was approximately 0.8 in all formed mixtures, so the requirement for a sufficient amount of organic matter in reactors was satisfied [10].

The ratio of available organic matter and nitrogen, expressed through COD:N, ranged from 22:1 in control sample, 29:1 in sample M55, and 29:1 in sample M70, while the optimal value of this ratio was 30:1.

The differences in regard of pH value, dry matter content, VS/TS and COD:N ratios between M, M55 and M70 samples are mainly caused by the thermal treatment of the part of the M55 and M70 samples, although the inability to fully homogenize such mixtures should be considered, because it certainly has an influence on the parameters of the samples, but significantly lower than the influence of thermal treatment has.

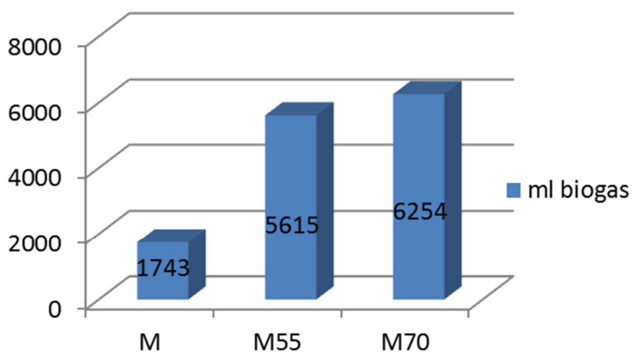

Diagram 1. Quantity of biogas obtained from untreated and thermally treated cattle manure and sludge in a period of 54 days

Diagram 1 shows the total amount of biogas produced during the time of substrate retention in reactors for 54 days. During the study, the amount of biogas produced in the reactor with a thermally treated cattle manure at 70°C (M70) was 6254 ml, a slightly smaller amount of biogas was recorded at 55°C (M55) (5615 ml), while the smallest biogas production in the amount of 1743 ml was recorded in the control sample (M). Also, the specific production of biogas based on the input VS expressed in [ml/g VSi] had the highest value for sample M70 (263.22), slightly smaller for sample M55 (219.68), while the lowest (73.27)for control sample (M) (Diagram 2).

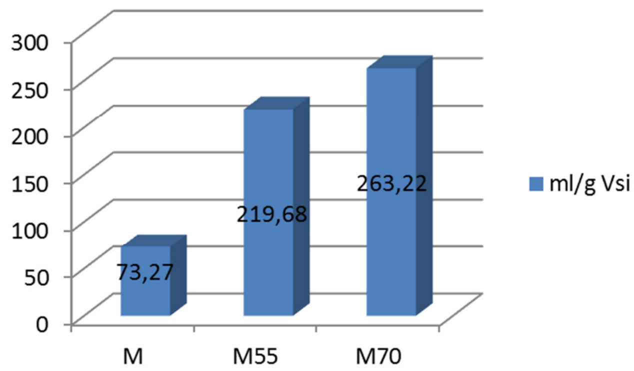

Diagram 2. Specific biogas production per g VSi

Table 2 shows the characteristics of the digestate remaining after the anaerobic degradation process, the amount of produced biogas, the specific biogas production in relation to the input volume of VSi, and the proportion of methane in the biogas. It is apparent that the values for certain parameters in the digestate were significantly lower than those prior to the digestion process, except for the pH value in samples M (7.03) and M70 (7.53), where the value was increased while slight reduction occurred in sample M55 (6.92), indicating that during the process there was no inhibition of the process with volatile fatty acids that represent an anaerobic degradation intermediate and the values remained within the range optimal for anaerobic digestion.

Reduction of dry and volatile organic matter suggests that part of organic matter was transformed into gas products. Also, significantly lower values of COD in the digestate (reduced by about 80%) were observed, in relation to the sample values prior to the start of the process. The TKN content in the samples prior to the start of the process was significantly higher than the TKN values in the digestate, due to the fact that nitrogen is a macronutrient necessary for anaerobic microorganisms for growth and development during degradation of organic matter.

The highest value for the proportion of methane in biogas was in sample M70 (49.44%), while the lowest was in control sample (M) in the amount of 45.14%, and in sample M55 was 45.16%.

Table 2. Physico-chemical characteristics of cattle manure/waste sludge mixture after the experiment

Parameter	unit	M	M55	M70
pH	-	7.03	6.92	7.53
TS	%	8.15	6.61	6.83
VS	%	5.50	4.95	4.81
TKN	g/kg	2.27	2.84	2.95
COD	g/kg	13.48	13.35	10.88
V biogas	ml	1743	5615	6254
W methane	%	45.14	45.16	49.44
V methane	ml	768.79	2535.73	3091.97
Specific production of biogas	ml/g Vsi	73.27	219.68	263.22

TS-total solids VS-volatile solids; TKN-total Kjeldahl nitrogen; COD- chemical oxygen demand;
V biogas – volume of biogas; W methane – share of methane in biogas; V methane – volume of methane;

CONCLUSION

Comparing the values obtained by physico-chemical analysis of the formed mixtures before and after the anaerobic digestion process, it could be concluded as follows:

- The pH value slightly increased in M and M70 samples.
- The reduction of volatile organic matter by 42% in sample M55 and 39.3% in M70 and about 30% for control sample (M), leads to the conclusion that a certain amount of organic matter was translated into gas products.
- The largest biogas production was recorded in sample M70 (6254 ml), while the smallest was obtained in the control sample M (1743 ml); in the M55 sample, 5615 ml of biogas was produced.
- The largest proportion of methane in biogas was in M70 (49.44%), while the values of this parameter for M and M55 samples were close to 45%.
- The specific production of biogas in relation to the input volume of volatile organic matter had the highest value for sample M70 (263.22 ml/g VSi), while for control sample (M) was the lowest and was 73.27 ml/g VSi.

This experiment has shown that the thermal treatment of cattle manure at temperatures of 55°C and 70°C in a mixture with waste sludge, increases biogas production by 3.22 and 3.59 times (respectively) compared to the control sample with untreated cattle manure. The increase in methane share in produced biogas of almost 9% compared to samples M and M55 was obtained in sample M70.

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