CHEMICAL PRETREATMENT OF CATTLE MANURE TO IMPROVE BIOGAS PRODUCTION

ORIGINAL SCIENTIFIC ARTICLE

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ABSTRACT:

Great potential in gas production is found in raw materials of organic origin, such as manure, waste sludge, food residues and the like. In order to speed up the process of biogas production, that is, the first stage of hydrolysis, it is necessary to pre-process the substrate. In order to obtain the maximum amount of biogas, the anaerobic digestion process was carried out in mesophilic conditions for 37 days. For the purpose of examining the effects of pretreatment, the substrate was chemically treated with the addition of dehydrated CaO in quantities of 0.75% and 1.5% in relation to the mass of the substrate. The results showed that by treating cattle manure with the addition of 0.75% CaO, higher daily production of biogas with a higher methane content is achieved. The total amount of biogas obtained with the addition of 0.75% CaO was 5247.21 ml, while the highest methane content was 61.24%.

KEYWORDS: anaerobic digestion; biogas; chemical pretreatment; cattle manure; biogas production; methane content.

INTRODUCTION

The process by which energy from biomass can be obtained is anaerobic digestion. In addition to the economic benefits it generates, this process of organic waste treatment is extremely current because it directly affects the reduction of greenhouse gas emissions, which ultimately does not lead to negative impacts on the environment. Anaerobic digestion is a biological process of decomposing organic matter without the presence of oxygen, a process that is part of the natural cycles of matter and energy [1].

For the production of biogas, raw materials of organic origin, such as municipal waste, food residues, agricultural waste, are huge potential, but given that most of these raw materials are difficult to decompose, which limits the production of biogas, today biogas is mostly produced from raw materials that can be easily decomposed and largely used [2]. The application of cattle manure for fertilization of agricultural land is limited with application of the Nitrates Directive (91/676/EEC) [3].

Although these raw materials are of enormous importance for gas production, due to their complex physico-chemical structure, they are more difficult to decompose, and ultimately result in less biogas production. In the process of anaerobic digestion by the action of different types of microorganisms, two main products are formed: biogas and digestate [4]. A possible solution for obtaining higher biogas production is the process of pretreatment of incoming raw materials, and their main task is to facilitate the anaerobic digestion process itself [5], [6].

The choice of pretreatment, in addition to being economical, should meet several important conditions to ensure its effectiveness and sustainability. Firstly, it should not require excessive energy consumption, as this would offset the potential benefits of biogas production and lead to an inefficient process. The energy demands of the pretreatment method should be optimized to ensure that the overall process remains cost-effective and energy-efficient. Furthermore, the pretreatment should not have a negative impact on the environment through the generation of harmful by-products or pollutants. Any waste products produced during the pretreatment should be manageable and ideally reusable, minimizing the ecological footprint of the process.

Another crucial aspect is that the pretreatment method should not involve or produce substances that could inhibit the subsequent stages of biogas production. Some chemicals or compounds might interfere with the anaerobic digestion process or hinder the microbial activity necessary for efficient biogas generation. Therefore, careful selection of chemicals and treatment conditions is necessary to ensure that no adverse effects on biogas production are introduced.

Chemical pretreatment typically involves processes that utilize chemical reactions to alter the structure of biomass, breaking down complex compounds and making the organic material more accessible for microbial degradation during anaerobic digestion. These chemical treatments may involve the use of acids, alkalis, or oxidizing agents, all of which can disrupt the lignocellulosic structure of the biomass, enhancing the release of fermentable sugars and other nutrients that are critical for the biogas production process. The ultimate goal of chemical pretreatment is to enhance the efficiency and yield of biogas production, while also ensuring that the process remains sustainable and environmentally friendly.

MATRERIALS AND METHODS

For the purpose of the research, samples from the dairy cow farm "Spreča" were used, which were chemically treated with the addition of CaO in quantities of 0.75% and 1.5% and waste sludge from the wastewater treatment plant Živinice.

To conduct this experimental research, a laboratory reactor system for anaerobic batch-type digestion was used, consisting of six glass eudiometric tubes that are connected to glass bottles with a volume of 500 ml (Figure 1). Eudiometric tubes are used to equalize the level and accept excess liquid, and thus they are used to read the production of biogas. By heating the water, a constant temperature of 35 °C is enabled.

In order to obtain a certain recalculated value of the volume of biogas, a baro-thermohygrometer for measuring pressure and a thermometer for temperature measurement were used, and the mixing of the substrate was carried out using a magnetic mixer.

Figure 1. Laboratory reactor system for anaerobic digestion

In the chemical pretreatment of cattle manure, dehydrated CaO was added in quantities of 0.75 and 1.5% to the total mass of the sample, and then after added CaO, mixing of the substrate was performed to homogenize the sample and added CaO. The samples were left at room temperature for three hours for CaO to act on the substrate.

An analysis of substrate (cattle manure and waste sludge, as well as a mixture of cattle manure and waste sludge) was performed before and after the anaerobic digestion process, which included the measurement of pH value and electroconductivity, determination of dry matter content (TS) and volatile organic matter (VS), content of total Kjeldahl nitrogen (TKN) and chemical oxygen demand (COD).

The methods used in the analysis of physicochemical characteristics are standard methods and modified standard methods for the 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.

Chemical oxygen demand was determined according to the modified standard method BAS ISO 6060:2000 [7].

Determination of the total content of dry matter and the total content of volatile organic matter of all samples was carried out according to *Metod 2540-Solid B.Standard Methods for the Examination of Water and Wastewater 21st edition*. APHA, Washington, DC (2005) [8]. The method used to determine the content of total Kjeldahl nitrogen is *Metod 4500-Norg B. Standard Methods for the Examination of Water and Wastewater 20nd edition*. APHA, Washington, DC (1998) [9].

The experimental part of this study lasted 37 days. The composition of the obtained biogas was analyzed daily on the clarus 500 gas chromatograph (PERKIN ELMER, India) equipped with thermal conductivity detector (TCD-R) and gas analyzer "Arnel".

RESULTS AND DISCUSSION

Before the experimental part, a physical-chemical analysis of cattle manure substrate (CM) and waste sludge (WS) was performed, and their mixture was used as a control sample (M). The experiment was conducted under mesophilic conditions at a constant temperature of 35 ± 1°C for 37 days. After the chemical treatment process, two mixtures M0.75 and M1.5 were formed, and in order to achieve a significant value of dry matter content (about 8%) a mixture of waste sludge and cattle manure was formed in a ratio of 1:1.

In chemical pretreatment of cattle manure, dehydrated CaO was added in quantities of 0.75 and 1.5% to the total mass of the sample. After the addition, mixing of the substrate was carried out to homogenize the sample and added CaO. Samples left at room temperature for three hours for CaO to act on the substrate. After the chemical pretreatment, physico-chemical characterization of pretreated samples was performed.

Table 1 shows the parameters of the physico-chemical characteristics of cattle manure and waste sludge, as well as mixtures of waste sludge with untreated and chemically treated bovine manure.

Table 1. Results of physicochemical characteristics of cattle manure mixture, waste sludge and CM:WS mixture

Parameter	Unit	CM	WS	M	M0.75	M1.5
pH	-	6.7	6.79	6.83	8.99	10.47
TS	%	15.35	4.13	9.77	10.97	10.60
VS	%	12.97	2.49	7.95	8.60	8.04
VS/TS	-	0.84	0.60	0.81	0.78	0.75
TKN	g/kg	3.69	1.87	2.27	3.9	3.03
COD	g/kg	118.15	52.92	68.90	102.67	89.89

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

In order to obtain a larger amount of biogas, it was observed that by adding a smaller amount of CaO (0.75%) with the previous pretreatment process, a higher production of biogas with a higher methane content compared to the control sample was obtained, as well as a sample in which cattle manure was treated with the addition of 1.5% CaO.

Certain changes in pH values, COD, the total amount of Kjeldahl nitrogen in the content of dry matter and volatile organic matter were also observed. The pH value for waste sludge was 6.79, the value of cattle manure was 6.7, and thus it was lower compared to the mixture of cattle manure and waste sludge that underwent the pretreatment process and which had a value of 7.03. According to literature, for an undisturbed process of anaerobic digestion the optimum pH value ranged from 6.5 to 7.6 [10]. 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 [11]. After chemical treatment, the value of this parameter increased to 8.99 with the addition of 0.75% CaO, and to 10.47 with the addition of 1.5% CaO, which could be expected, because the introduction of dehydrated CaO into the substrate with a high water content resulted in the formation of calcium hydroxide.

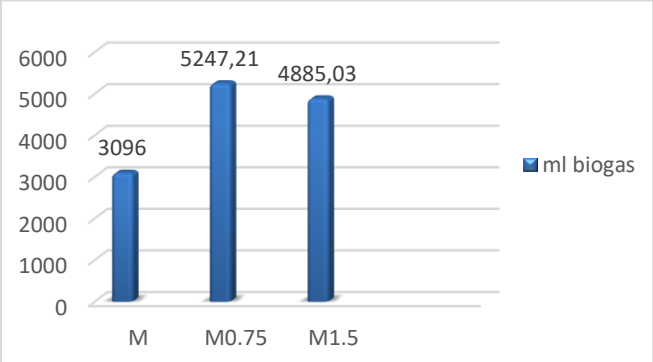

Diagram 1. Amount of biogas of untreated and chemically treated manure and waste sludge in a period of 37 days

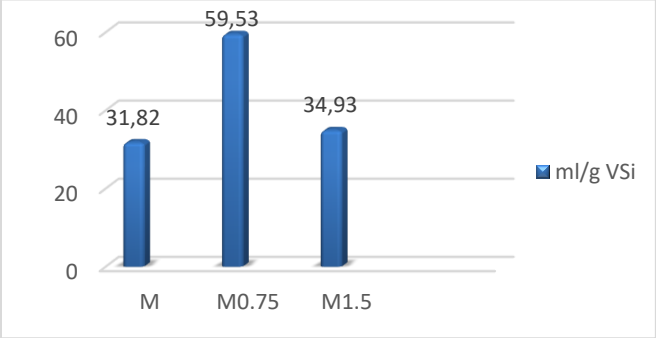

Diagram 2. Specific biogas production

Table 2 shows the characteristics of the remaining digestate after the process of anaerobic digestion, and the amount of biogas produced and specific production of biogas in relation to the parameter of volatile organic matter. From the table, it is noticeable that in the sample M1.5 pH value was significantly lower (7.17) compared to the pH values for samples M (7.3) and M0.75 (7.33).

Table 2. Physico-chemical characteristics of the mixture of cattle soil and waste sludge after conducting the experimental part

Parameter	Unit	M	M0.75	M1.5
pH	-	7,3	7,33	7,17
TS	%	7,44	7,32	6,53
VS	%	5,51	4,92	3,68
TKN	g/kg	2,59	2,74	2,09
COD	g/kg	64,40	74,76	58,11
V biogas	ml	3096	5247.21	4885.03
W methane	%	52.65	61.24	52.35
W CO_2	%	44.02	34.58	41.32
V methane	ml	758.83	1535.93	842.61
Specific production of methane	ml/g VSi	31.82	59.53	34.93

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; W CO_2 – share of CO_2 in biogas, V methane – volume of methane;

CONCLUSION

After conducting the entire experimental part, based on the physical-chemical characterization of waste sludge and cattle manure, the basic parameters of starting raw materials were obtained.

After the process by which the samples underwent pretreatment, in this case chemical pretreatment, and after the characterization of physico-chemical characteristics, results were obtained that determined a decrease in the dry matter content and an increase in the content of organic matter (due to the addition of CaO).

The pH value in both treated samples was significantly increased compared to the value of the untreated sample, which is an indicator of the consequence of $Ca(OH)_2$ due to the reaction of CaO and water present in the substrate.

The best results of daily production of biogas and methane, and specific biogas production were obtained using the addition of 0.75% CaO (5247.21 ml), with a methane content of 61.24% and a CO_2 content of 34.58%. The higher amount of CaO used for the research of 1.5% showed that it did not achieve significant yield and that it adversely affected the production and quality of the biogas obtained.

Mineral substances in the substrate for both treated samples resulted in an increase in the content of volatile organic matter with the addition of CaO, and as a result of the decrease in the proportion of dry matter, in both treated samples was the formation of CO_2.

Chemical pretreatment of cattle manure is a process by which improved biogas production is obtained, as well as the quality of which achieves a higher content of methane in biogas, compared to the same samples that have not been previously treated, and which were used in the process of anaerobic digestion.

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