Influence of novel $[Bi_6O_6(OH)_3](C_7H_7SO_3)_3$ complex on the biogas production

Anelia Tzanova
Department of Chemistry, Faculty of Electronic Engineering and Technologies
Technical University of Sofia
Sofia, Bulgaria
ntzanova@tu-sofia.bg

Alexander Zahariev
Department of Chemistry, Faculty of Electronic Engineering and Technologies
Technical University of Sofia
Sofia, Bulgaria
alexs_zahariev@tu-sofia.bg

Nikolay Kaloyanov
Department of Organic Chemistry, Faculty of Chemical Technologies
University of Chemical Technology and Metallurgy
Sofia, Bulgaria
nikolaykaloyanov@uctm.edu

Kamelia Ruskova
Department of Chemistry, Faculty of Electronic Engineering and Technologies
Technical University of Sofia
Sofia, Bulgaria
kruskova@tu-sofia.bg

***Abstract*—This article presents the results of the process of biomethanization and joint biodegradation of manure from cows (reference sample), a mixture of the same manure and household waste of fruit-vegetable origin (peelings), as well as a mixture of the manure and bismuth complex of p-toluenesulfonic acid. The samples are incubated at 34.5 degrees Celsius, under nitrogen atmosphere, during 30 days, periodically measuring the volume of biogas and the percentage of methane.**

From the results obtained, one can see that during entire period of the experiment, the mixture containing cow manure and household waste of fruit-vegetable origin produce the largest amount of biogas, compared to the other two samples. However, regarding the methane content in all samples, its amount in this mixture is the least.

During the measurement period, mixture containing the complex $[Bi_6O_6(OH)_3](C_7H_7SO_3)_3$ always show a larger amount of biogas produced, compared to the reference sample. It is noteworthy that the biogas produced by this sample always depicts the highest percentage of methane, compared to other two samples.

Keywords*— *anaerobic fermentation, biogas, biomass, Bi(III) complex, methane production.

I. INTRODUCTION

Biogas belongs to the renewable energy raw materials, being a source of methane, which is used as an alternative to gasoline and diesel fuel, for the production of electricity, as a high-calorie household fuel, etc. Another important advantage of methane is the fact that, unlike liquid and solid fuels, only carbon dioxide is emitted as a harmful emission upon its burning. The methane content in biogas is in the range of 50-65%, and besides methane, there are also carbon dioxide (25-45%), nitrogen ammonia, sulfur dioxide, hydrogen, hydrogen sulfide, etc. [1].

Recently, the production of biogas on biogas on the basis of various biological wastes, solid household waste, manure, organic waste, etc., has gained great importance and hence it is a subject of various studies. One of the most important factors in the process of anaerobic digestion is the acidity of the environment. According to [2], the maximum amount of biogas is obtained when pH is in the range of 6.8 to 7.2.

The formation of methane (methanogenesis) from various biological waste (biomass) is a process in which it is converted into methane under the action of methane-producing bacteria. This process is a fermentative decomposition of waste in an anaerobic atmosphere. This anaerobic degradation proceeds according to the following sequential steps: hydrolysis, fermentation (formation of acids) and methanogenesis. Methanogenic bacteria, e.g. green bacteria as *Azotobacter* sp., *Pseudomonas* sp., as well as other purple sulfur/non-sulfur bacteria which are present in cow manure and produce the maximum amount of methane [3], are developed in about 15 days, at optimal values of pH 6.6 - 8.0. Their growth and vital activity depend strongly on pH of the environment, as at the beginning of fermentation pH lies within the alkaline range. When passing from the second to the third stage, resulting acids are converted into methane, whereby pH of the medium slowly increases through neutral to slightly alkaline values.

In addition to the use only of cow dung for the production of biogas, its mixtures with fruit and vegetable waste, organic household waste, industrial organic waste, etc., are very often subjected to anaerobic fermentation. On one hand, this is done to improve the methane production [4], and on the other – to assist the biodegradation of hay contained in cow manure.

There are data in the literature that some biologically active substances, e.g. antibiotics (penicillin, tetracycline, tylosin, lincomycin, sulfamethazine and carbadox) have an effect on the production of biogas, and in particular methane, during anaerobic fermentation of cow manure [5]. In this regard, the aim of the present work is to study the influence of both the complex $[Bi_6O_6(OH)_3](C_7H_7SO_3)_3$, previously synthesized by the team [6] and showing good antibacterial properties [7], and the combination of cow manure and household waste of fruit-vegetable origin (peelings), on the production of biogas and methane in particular.

II. MATERIALS AND METHODS

A. Laboratory installation

The experiments were carried out using a laboratory installation (Fig. 1), consisting of a water bath equipped with a thermostat and a magnetic stirrer, three anaerobic bioreactors and the corresponding number of gas collectors. Each of the collectors was connected to a gas analyser in order

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to determine the percentage of methane. The bioreactors are chemically inert, hermetically sealed plastic containers with a working volume of 400 cm^3, equipped with silicone hoses and one-way gas valves leading to the biogas-collector system, with a volume of 2000 cm^3 (Fig. 1).

Bio-fermentation was carried out in the described bioreactors, for a period of 30 days, under a nitrogen atmosphere and in the absence of light. The temperature maintained during the experiment was 34.5 ± 1 °C.

Before and after the digestion process, the acidity of the medium (pH) of the studied mixtures was also determined.

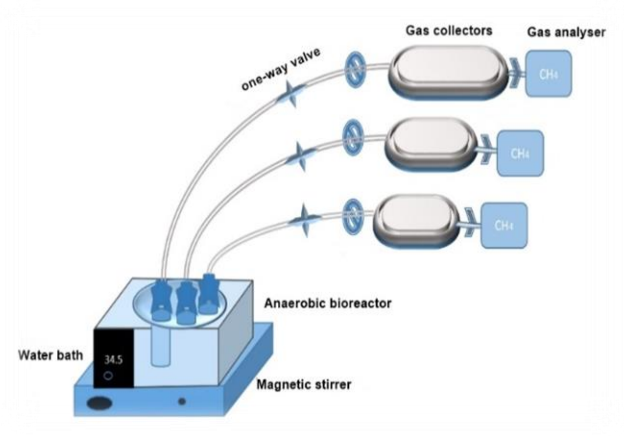

Fig. 1. Scheme of laboratory installation

The volumes of biogas accumulated in the gas collectors were measured periodically every 48 or 72 hours, and the samples were taken using a gas-sampling syringe.

The methane content (% vol.) in biogas was measured using Gas analyser MS104K Diffusion Type, equipped with IR sensor, working within temperature range -40 ÷ +70 °C.

pH of the mixtures was measured using Hanna instrument pH 211, pH measuring range 0 ÷ 14, with accuracy 0.01 pH and temperature range 0 ÷ 100 °C.

B. Mixtures preparation

Three types of mixtures were prepared, based on fresh biomass from cow manure (Vrana cow farm, Sofia, Bulgaria). The first mixture (CM1) is a pure manure diluted with distilled water in a ratio of 1:1 (control sample). The second mixture (CM2) contains 55% pure manure diluted with distilled water in a ratio of 1:1 and 45% household waste of fruit-vegetable origin. The third sample (CM3) is a mixture of pure manure diluted with distilled water in a ratio of 1:1 and 10 mg of bismuth complex of p-toluenesulfonic acid with a composition $[Bi_6O_6(OH)_3](C_7H_7SO_3)_3$.

In order to increase the biogas content, the initial substrate was separated to a particle size of 0.5 mm, distilled water was added in a ratio of 1:1 and stirred until a homogeneous suspension is formed [2]. In mixture CM2, the peels of fruits and vegetables were ground and mixed with cow manure diluted with distilled water in a ratio of 1:1. The diluted manure was mixed with the peels in a ratio of 55:45, respectively.

The so prepared mixtures (CM1, CM2, CM3) were sampled in order to determine total solid, volatile solid, moisture content and pH. These parameters were measured both before and after the fermentation process. After the analyses performed, the mixtures (CM1, CM2, CM3) were tempered in a water bath to 34.5 ± 1 °C and left under inert nitrogen atmosphere for anaerobic fermentation for 30 days.

C. Analysis of the mixtures before and after fermentation

Total solid (TS), volatile solid (VS), as well as moisture content of three mixtures, were determined using methods according to BDS EN25934, EN15935 and BDS EN ISO 18134-1, respectively.

III. RESULTS AND DISCUSSION

It can be seen from Table I, that initial TS value of the control sample (CM1) is 6.59% and that of the mixture (CM2) containing peelings is 8.82%, which means that both samples contain TS < 10%. According to [2], these values determine the belonging of all three mixtures to the main class of anaerobic decomposition technologies, known as "conventional wet". According to the literature data, it is known that when the moisture content is between 60 and 80%, then methane production is maximal [2]. In the case of anaerobic fermentation, a tendency to decrease VS content and increase moisture content is observed compared to the mixtures before fermentation [2] which correlates well with the data presented in Table I and Table II.

TABLE I. OPERATING PARAMETERS OF THREE MIXTURES BEFORE ANAEROBIC FERMENTATION

Mixture	Mixture assignment	Total solid (TS), %	Moisture content, %	Volatile solid (VS), %	pH
CM1	Control sample	6.59	93.41	82.64	7.23
CM2	Cow manure + household waste	8.82	91.18	85.23	6.82
CM3	Cow manure + bismuth complex	6.59	93.41	82.64	7.23

TABLE II. OPERATING PARAMETERS OF THREE MIXTURES AFTER ANAEROBIC FERMENTATION

Mixture	Mixture assignment	Total solid (TS), %	Moisture content, %	Volatile solid (VS), %	pH
CM1	Control sample	1.26	98.70	61.38	7.80
CM2	Cow manure + household waste	5.47	94.50	84.77	4.79
CM3	Cow manure + bismuth complex	3.92	96.08	76.48	7.03

The highest TS content is observed for CM2, both at the beginning and at the end of the measurement, which according to [2] is associated with increased biogas production and a tendency to decrease methane production. This is explained by accumulation of volatile fatty acids, which leads to a decrease in pH in the reactor from 6.82 at the beginning to 4.79 at the end of fermentation process (Tables I, II).

For mixture CM3, the highest relative amount of the methane produced is observed, which is explained by a small amount of TS throughout the entire period of measurements - from 6.59% to 3.92% at the end of the process (Tables I, II). This is also confirmed by pH values, which vary in the slightly alkaline region (from 7.23 to 7.03), which favours the development of methanogenic bacteria [3].

It is known from the literature that the greater the amount of VS, the greater the amount of biogas produced [2]. From Tables I and Tables II, it can be seen that in mixture CM2, the VS content throughout the measurement period is the highest compared to the other two mixtures, which correlates with the highest biogas content. In the case of control sample (CM1), a similar dependence is observed: the production of biogas is the lowest, because during the measurement period, VS has the smallest relative value (from 82.64 % to 61.38 %).

A. Production of biogas and methane from three investigated mixtures

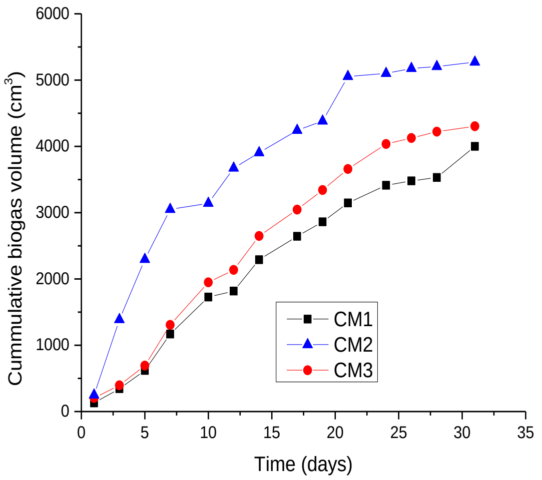

Fig. 2. Cumulative biogas volume (cm^3) of three mixtures investigated, measured over 30 days.

Fig. 2 represents data concerning cumulative biogas volumes (cm^3) of the three investigated mixtures, measured during 30 days of the experiment. From this figure it is clearly seen that during the experiment the mixture containing manure and fruit-vegetable peelings (CM2) produces the largest amount of biogas, compared to the other two mixtures. It is noteworthy, that the percentage of methane in this mixture is the least, and this trend appears after the fourth day of measurement (Fig. 3). These results could be explained by the fact that the added peels of fruits and vegetables ensure an acidic environment during the fermentation process, which is visible by the pH values at the beginning and end of the experiment - 6.82 and 4.79, respectively.

The mixture containing $[Bi_6O_6(OH)_3](C_7H_7SO_3)_3$ demonstrates throughout the measurement period a larger volume of biogas produced, compared to the control sample (Fig. 2). However, it is noteworthy that to the third day of the experiment, the percentage of methane in the biogas produced by this mixture (CM3) is similar to that of control sample (CM1). Then, a tendency to increase the methane content of CM3 compared to sample CM1 is outlined, and both samples show a significant increase in this content compared to CM2 until the end of experiment (Fig. 3).

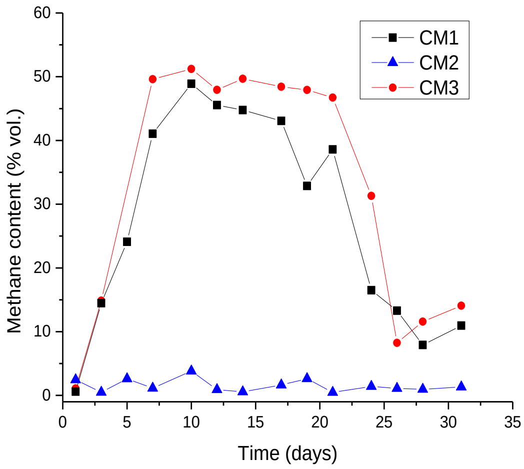

Fig. 3. Methane content in biogas (% vol.) of three mixtures studied, measured over 30 days.

The fact that CM3 produces the highest relative amount of methane could be explained by good antibacterial activity of the p-toluenesulfonic acid bismuth complex added to this mixture. It is known from the literature [7] that this complex shows an inhibitory effect against *Staphylococcus aureus* - ATCC 29213 and *Escherichia coli* - ATCC 47093 and ATCC 25922. This could mean that the substance attacks these gram-positive and gram-negative bacteria, presenting into the diluted cow manure, thereby it facilitates development of methane-producing bacteria. It is worth noting that in the period between the 7th and 22nd day, a plateau is established, corresponding to maximum methane content in CM1 and CM3 (45-50%). After the 22nd day, the relative amount of methane from mixture containing the bismuth complex and from the control sample begins to decrease sharply, indicating that fermentation process enters its final phase.

IV. Conclusion

The following conclusions can be drawn from the obtained results: maximum amounts of biogas are gained from mixture CM2, containing diluted cow manure and fruit-vegetable peelings. However, when compared to the other two mixtures investigated, the percentage of methane from CM2 is the lowest. During the measurement period, mixture containing the complex $[Bi_6O_6(OH)_3](C_7H_7SO_3)_3$ shows a higher amount of biogas than the control sample. It is worth noting, that the percentage of methane obtained from CM3 is always the highest, compared to the other two mixtures.

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