ANIMAL MANURE AS SUBSTRATE FOR BIOGAS PRODUCTION

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Abstract. Lately, anaerobic fermentation of animal manure is considered a promising way for biogas production through the anaerobic digestion process. Anaerobic digestion technology is viewed as a method not only for solving environmental problems, but also for contributing to energy production and resolving economic and social issues. This paper investigated the potential of cow and pig manure for biogas production obtained through the anaerobic digestion process. The retention time in the digester was 20 days and the operating temperature was kept in mesophilic domain of 35 ± 1.5 ºC. The most important factors influencing the gas composition are the characteristics of the substrate. The samples of the tested substrates were collected and analysed for pH, total soluble solids (TSS), ash, the content of soluble proteins and sugar content. The results showed that the total biogas production derived from pig manure was higher (about 2.5 $m^3 \cdot batch^{-1}$) compared to that derived from cow manure (about 2 $m^3 \cdot batch^{-1}$). During the anaerobic digestion, it was observed that the values of TSS and pH were slightly decreasing due to the growth and multiplication of bacterial cells, the consumption of substrate and the accumulation of metabolites. Reducing sugars and soluble proteins were found in a relatively stable range, between 0.4 and 0.9 $mg \cdot ml^{-1}$ for proteins and the concentration of sugars was maintained between 2.8 and 4.6 $mg \cdot ml^{-1}$.

Keywords: biogas, cow and pig manure, soluble protein, sugar content, anaerobic digestion.

Introduction

In recent years, animal farms produce a large quantity of manure that posed serious pressure on environment. Therefore, it is very important to find effective methods for animal manure treatment [1]. At present, anaerobic digestion as proven to be an optimum process for the treatment of waste from agriculture and animal husbandry, is offering multiple advantages, such as reduced pollution and emissions of greenhouse gases [2; 3].

Animal manure can be a beneficial resource for the renewable energy production and a source of nutrient-rich agricultural fertilizers [4]. Moreover, from a socio-economic point of view, biogas not only provides environmental benefits, but also has a low feedstock cost [5].

In the absence of air, biogas is produced through the anaerobic digestion process by several species of microorganisms, in four main stages, namely: hydrolysis, acidogenesis, acetogenesis and methanogenesis [6; 7]. The anaerobic digestion of bio-solids involves biological conversion of soluble, dissolved organic matter into biogas, alcohols, volatile fatty acids and nitrogen-rich organic residues [4].

The stability of the anaerobic digestion process is highly influenced by the composition of the used feedstock in the bioreactor. Many different types of substrates can be used as feedstock in the anaerobic digester for biogas production including animal manure (36 %), agro-industrial wastes (30 %) and municipal solid wastes (34 %) [8].

Animal manure is rich in a wide variety of nutrients necessary for bacterial growth. It has been recognized that using animal manure alone may not represent the most efficient way to produce biogas due to its low carbon/nitrogen ratio.

Livestock manure contains high nitrogen content, such as: fresh goat manure (1.01 %), chicken manure (1.03 %), dairy manure (0.35 %) and swine manure (0.24 %) [9].

According to the Mid-West Plan Service Publication [10], the carbon/nitrogen (C/N) ratio for swine manure is around 6 to 8, which is too low for an anaerobic digester. In this case, it is recommended to use for biogas production animal manure in co-digestion with crop residues in order to maintain a balanced C/N ratio, to enhance bacterial growth and decrease the risk of ammonia inhibition and acidification [11; 12].

The most important problem of biodegradable wastes is that these are rich in lipids, cellulose and proteins. Many research papers have demonstrated that combining different organic wastes for the anaerobic co-digestion process results in a substrate better balanced that leads to a significant increase in biogas production. Wu et al. [13] reported significant biogas production increases in the co-digestion process by combining carbon rich agricultural residues with swine manure.

The organic mixture, which provides the substrate for the anaerobic digestion process can comprise a wide variety of organic carbon sources, ranging from raw sewage sludge to municipal wastes, or biomass material such as plants and crop wastes [14].

Biogas production from the anaerobic digestion process offers multiple benefits such as alternative fuel, high-quality fertilizer, electricity, heat, waste recycling, greenhouse gas reduction and environmental protection [15].

Not all types of feedstocks are suitable for biogas production and in some cases biogas production might not be profitable. In order to assess the suitability and profitability of biogas feedstocks, a reliable way of characterising and analysing feedstocks is necessary [16].

The biogas composition depends on the chemical composition of substrates, the technology used and the operational parameters. The anaerobic digestion process is very sensitive to changes in ambient conditions due to the groups of microorganisms involved [17].

The aim of the present study was to determine the starting point of biogas production and the maximum level reached by biogas production. More specifically, the feedstock characterization was investigated by determining the total soluble solids (TSS), content of soluble proteins, reducing sugar, ash and pH value.

Materials and methods

The cow and pig manure used in this study were collected from the farm located in the Teleorman County, in June 2015.

Anaerobic fermentation was performed in a batch anaerobic digester with 60 litres total capacity during a 20 days period for each type of substrate. The anaerobic digester is insulated on the outside with mineral wool and the content is heated by an electric boiler powered by photovoltaic panels. Water was used as heating fluid and was heated up to 70^{o}C in the 200 litres electric boiler. The substrate is mixed using a paddle stirrer driven by an electric motor, the stirrer being set to start automatically at an interval of 30 minutes, with a time of mixing of 3 minutes.

For each batch 45 kg of substrate (effective quantity) were used composed of 10 litres of added water and 35 kg of manure (cow or pig). The water was added because only the solid part of the animal dejection was used for the experiments and also to improve the digestion process.

The temperature and pH are automatically monitored by means of a temperature and pH sensor placed along the reactor and connected to the biogas plant. The inoculum was not used in the anaerobic digestion process.

Analytical methods

The biogas volume was measured using a Sacofgas Milano gas meter. The methane content was analysed using a portable Mentor/COMB/IR Series gas analyser, equipped with a sensor for methane. The ash quantity was determined by sample calcination in an oven at 600 ºC for one hour.

The temperature and pH were automatically monitored by means of a temperature and pH sensor placed along the reactor and connected to the data acquisition system. The experiment was carried out in the mesophilic range, and the temperature was gradually raised (in approximately 4 hours) from 23.5 ºC to 35 ± 1.5 ºC, this value being kept constant throughout the experiment. Mesophilic temperatures are well documented to display good operating performance [18].

The content of total soluble solids (TSS) was determined with a thermo-balance, after the centrifugation of the initial samples at 5000 rpm followed by filtering through a membrane with pores of 0.45 μm. The TSS was used as an indicator of the quantity of the dissolved nutrients that can be absorbed by microorganisms inside the fermenter. It represents the soluble fraction of dry organic matter composed of both organic and inorganic substances.

The content of soluble proteins was determined according to the Lowry method [19] and the concentration of sugars was achieved by the method in which 3.5-dinitrosalicylic acid (DNS) is used [20]. In both cases, the absorbance is measured using a T92+ UV VIS spectrophotometer, PG Instruments.

Results and discussion

In order to assess the suitability and profitability of animal manure feedstock for biogas production, the following parameters were monitored: pH, TSS, soluble proteins, reducing sugars, moisture and ash.

The moisture of pig manure was 84.46 % and for cow manure it was 77.76 %, while the determined ash was of 0.1634 g for pig manure substrate and 0.11304 g for cow manure substrate.

Tables 1 and 2 show the characterization of the tested substrates at different intervals of the anaerobic digestion process.

The optimal pH for methanogenesis is around 7.0, while it is between 5.5 and 6.5 for hydrolysis and acidogenesis, as reported in numerous studies [21; 22]. The pH value is the pivotal factor influencing the methane production efficiency and it has been proved that the optimal range of pH to obtain maximal biogas yield in anaerobic digestion is 6.5-7.5 [23].

The initial pH values for the tested substrates were above 6.0 in both cases. After 5 days, the pH values increased slightly and then stabilized and reached values above 7.0 for both tested substrates.

During the anaerobic digestion process, a slight decrease of TSS content was observed for pig manure from 1.26 % to 0.71 % and for cow manure from 1.17 % to 0.23 %, the fact that can be attributed to the presence of easily degradable compounds within the soluble fraction.

Table 1

Cow manure characteristics during the anaerobic digestion process

Cow manure	Day 1	Day 5	Day 10	Day 15	Day 20
pH	6.2	6.5	7.03	7.25	7.27
TSS, %	1.17	1.07	0.74	0.51	0.23
Soluble proteins, $mg \cdot ml^{-1}$	0.70	0.64	0.6	0.52	0.47
Reducing sugars, $mg \cdot ml^{-1}$	4.2	3.9	3.5	3.1	2.8

Table 2

Pig manure characteristics during the anaerobic digestion process

Pig manure	Day 1	Day 5	Day 10	Day 15	Day 20
pH	6.5	6.8	7.2	7.34	7.39
TSS, %	1.26	1.22	1.14	0.97	0.71
Soluble proteins, $mg \cdot ml^{-1}$	0.9	0.85	0.7	0.63	0.5
Reducing sugars, $mg \cdot ml^{-1}$	4.6	4.4	4.0	3.2	3.0

The amount of methane and biogas production from cow and pig manure showed the expected differences, as it can be seen in Figures 1 and 2. These differences can be attributed to the different ingredients of the tested substrates.

Regarding biogas production, we observed a delayed start in both cases, this phenomenon being due to the absence of inoculum in digester. The lower level of biogas produced by cow manure is also due to the lower values of reducing sugars and soluble proteins compared to those derived from the pig manure substrate.

For pig manure feedstock, after day 2, the biogas production increased until day 14 from 0.015 m^3 to 0.180 m^3, with some fluctuations, and thereafter, the gas production almost stopped after day 20.

The maximum value of total biogas production during the 20 days of anaerobic digestion of animal manure was about 2.5 $m^3 \cdot batch^{-1}$ for the pig manure substrate compared to that derived from the cow manure substrate, which was about 2 $m^3 \cdot batch^{-1}$.

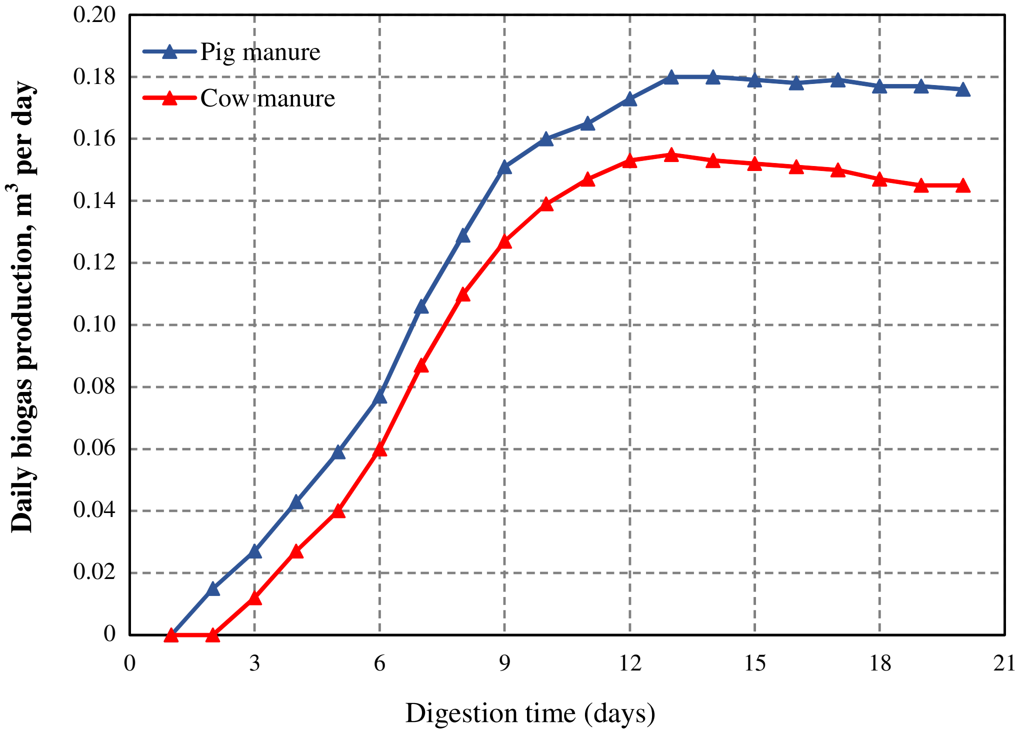

Fig. 1. **Daily biogas production from pig and cow manure**

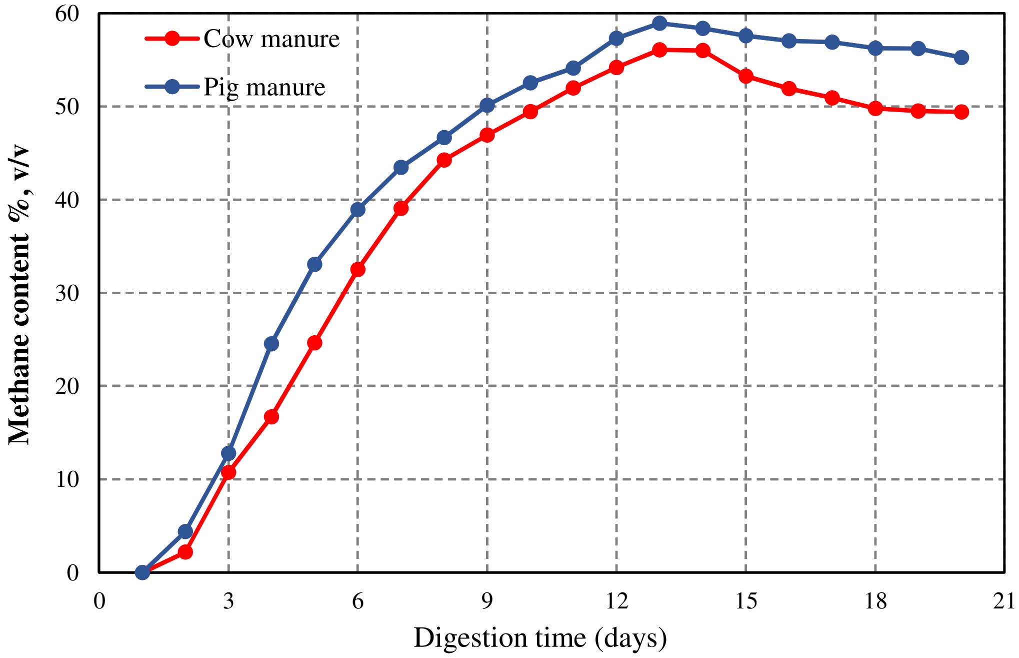

Fig. 2. **Daily CH_4 content (% v/v) of the produced biogas**

Conclusions

1. In this paper were evaluated the biogas production, methane yield and the time variation of the substrate characteristics consisting of pig and cow manure. The experiments were conducted by using a small capacity biogas plant at a temperature of 35 (±1.5) ºC, neutral pH and intermittent mixing process. The plant was operated for 20 days as we were interested to find when the biogas production begins and what the maximum biogas level was. The maximum biogas level, respectively methane, was reached after 13 days of digestion and maintained relatively constant

(with a slight decrease) until the 20th day, when we decided to stop the process (the anaerobic digestion could have been continued).
2. The maximum level of biogas obtained after 20 days of anaerobic digestion of pig manure was about 2.5 $m^3 \cdot batch^{-1}$ compared to that derived from the cow manure substrate that was about 2 $m^3 \cdot batch^{-1}$. In addition, there were some differences in the methane levels between pig and cow manure. The used substrate was not totally consumed and the total biogas production is unowned, because this was not the aim of this study.
3. The concentration of soluble protein was in a relatively stable range, between 0.47 and 0.7 $mg \cdot ml^{-1}$ for cow manure substrate, and between 0.5 and 0.9 $mg \cdot ml^{-1}$ for pig manure substrate, the phenomenon is explained by the relatively low consumption and by the formation of protein specific to bacterial cells.
4. The concentration of sugars was maintained between 2.8 and 4.2 $mg \cdot ml^{-1}$ for cow manure substrate, and between 3 and 4.6 $mg \cdot ml^{-1}$ for pig manure substrate. These values demonstrate that the phenomenon of growth, cell multiplication and biogas generation is a complex one.
5. Animal manure is rich in a wide range variety of nutrients necessary for bacterial growth. However, it is recommended to use animal manure in co-digestion with crop residues in order to maintain a balanced C/N ratio, to enhance bacterial growth and decrease the risk of ammonia inhibition.

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