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ZOOTECHNICAL WASTE AS RAW MATERIAL FOR BIOGAS PRODUCTION AND AS FERTILIZER FOR AGRICULTURE

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Abstract

In recent times, the anaerobic fermentation process of animal waste has become a promising solution for biogas production through anaerobic digestion. Anaerobic digestion technology is considered not only an environmental solution but also a potential source of energy, contributing to solving economic and social issues. This research has explored the potential of using poultry, cow and pig manure, to produce biogas through the anaerobic digestion process. Animal farming produce significant quantities of waste and thus exert a negative action on the environment. The animal waste resulting from zootechnical activities can represent an important resource to produce renewable. Furthermore, by using animal waste and plant residues as organic materials to produce biogas, we are not only reducing the quantities of waste illegally dumped along riverbanks or in landfills. In this research paper, the objective was to develop an optimal mixture of animal waste and agro-food byproducts to produce biogas.

Key words*: anaerobic digestion, biogas, cow manure, pig manure, poultry manure.*

INTRODUCTION

Animal farming takes place both in individual households and large specialized farms. A significant aspect of this activity involves the accumulation of substantial quantities of residual organic materials, which can be solid, liquid, or semi-liquid (Artun & Saltuk, 2019). Typically, these residues, which contain significant amounts of organic fertilizers, are used for the fertilization of nearby agricultural lands.

The manure generated from zootechnical activities contains significant levels of nitrogen, such as: fresh poultry manure (1.03%), fresh cow manure (0.35%), and fresh pig manure (0.24%) (Zhang et al., 2013). The nitrogen in this fertilizer is typically in the form of ammonium, which contains enzymes with fast-acting properties. Thus, the use of poultry manure as a fertilizer is easy and doesn't require much care. However, it is important to consider the significant loss of nitrogen in the form of ammonia. Due to this nitrogen loss, it is not recommended to mix poultry manure with alkaline materials such as wood, ash, or regular lime (Annex 9. Code of Good Agricultural Practice, 2018).

These alkaline materials can easily release ammonia when they meet poultry manure, which can lead to nitrogen loss. Poultry manure can become an excellent fertilizer when mixed with another compost. This can help balance the nutrients and improve the quality of the fertilizer (Annex 9. Code of Good Agricultural Practice, 2018).

The waste generated by the agro-industrial sector could represent a real source of income if it is properly managed. The production of biogas is the most efficient way to utilize this waste (Hălmaciu et al., 2021). Currently, the anaerobic digestion process has become highly sought after in the management of agricultural and animal farming waste, but it also offers numerous advantages, such as reducing pollution and greenhouse gas emissions (Chae et al., 2008; Khalid et al., 2011).

Biogas is an alternative to livestock waste management. However, it leaves a sludge which is contains organic composition that can be used as a solid organic fertilizer (Kurnani et al., 2018). Biogas is produced in the absence of

oxygen through the process of anaerobic digestion, which involves various species of microorganisms (Bardeanu et al., 2021; Yaylaci, & Erdal, 2021). This process consists of four phases: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Khalid et al., 2011; Markowski et al., 2014). Biogas production was influenced by various factors, such as pH, temperature, dry matter content, oxygen, C/N ratio, agitation, time, and activity of microorganisms in a digester (Deublein & Steinhauser, 2008).
The anaerobic digestion process involves the biological transformation of soluble organic matter into biogas, alcohols, volatile fatty acids, and nitrogen-rich organic residues (Anitha et al., 2015).

MATERIALS AND METHODS

Since there are no research studies that use animal waste from different animals in the same biodigester, an experiment with various mixtures containing poultry, cow and pig manure was chosen. In this research paper, the primary objective was to develop an optimal mixture of animal waste and agro-food byproducts to produce biogas.

Equipment description

Using an automatic gas flow measurement system (Gas Endeavour), BPC Instruments AB, Sweden, experiments were carried out on the anaerobic co-digestion process (Figure 1).
Unit A is equipped with the following components: 15 glass bottles, 500 mL as reactors, 15 plastic caps with agitators, 15 plastic screw caps with hole, 15 helical couplings, 14 short motor cables, 1 long motor cable (from Motor Controller to first motor unit), 1 signal cable (from the Gas Volume Measuring Device to Motor Controller), 15 plastic stoppers with 2 tubing ports and rotating shaft for mixing, 1 thermostatic water bath (18 L), 1 plastic glass lid for the water bath, with 15 circular opening, 15 evaporation minimizing rings for the lid and reactors, 15 plastic tubing clamps.
Unit B contains: 1 bottle holder for 15 glass bottles, 15 glass bottles, 100 mL, 15 plastic screw caps with hole, 15 plastic stoppers with 2 tubing ports.
Unit C contains: 1 gas volume measuring device (including 15 flow cell chambers, 15 injection mold flow cells containing magnetic metal pieces, frame, and plastic covering), 30 check valves, 1 plastic syringe, 1 power adapter.
Other components: 1 shielded Ethernet cord, 1 Motor Controller, 1 power adapter, boxes of 15 m flexible Tygon tubing, 1 number markers kit for tubes, 15 plastic lids.

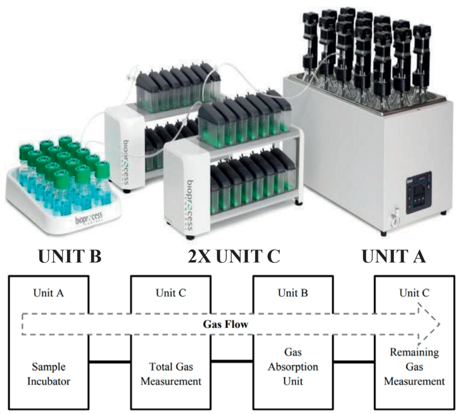

Figure 1. Biogas Production Plant - Gas Endeavour. Continuous profile of total gas and CH_4 production
Source: BPC Instruments AB, 2002

The installation is also equipped with optional equipment: 15 glass bottles, 1 L (bottles with one port designed for continuous pH monitoring during the batch fermentation) and 15 stirrers adjusted for 1 L bottles, 6 glass bottles, 2 L (bottles with one port designed for continuous pH monitoring during the batch fermentation) and 6 stirrers adjusted for 2 L bottles, 1 plastic glass lid for the water bath, with six circular openings for reactors, gas sampling units (BPC Instruments AB, 2002).
With Gas Endeavour, the data analysis and recording are completely automated (Figure 2).
The testing vessels (500 mL) from Unit A, containing small quantities of a microbial inoculum sample, are incubated at a temperature of 37°C in the incubation unit, within a thermostatic water bath.
The samples in each vessel are mixed using a slow-rotation agitator, while gas is continuously produced from the material. In the gas absorption unit (Unit B), the gas produced in each flask passes through an individual flask

containing a solution capable of absorbing specific gas fractions. If we use an alkaline solution such as NaOH, acidic fractions like CO_2 and H_2S are retained, and only CH_4 and H_2 will pass to the gas monitoring unit. To monitor the acid-binding capacity of the solution, we can add a pH indicator to each flask.

In Unit C, the volume of gas released from either the incubation unit or the gas absorption unit is measured using a wet gas flow measurement device with 15 multiplexed cells. This measurement device operates on the principles of liquid displacement and buoyancy and can monitor ultra-low gas flow rates. When a defined volume of gas flows through the device, it generates a digital pulse, and the data are recorded and displayed, with the apparatus analyzing the results.

The system can measure both the total gas and a specific fraction remaining after absorption, such as CH_4, for seven parallel vessels. This can be achieved by directing the gas produced from a test vessel into a flow cell chamber in Unit C, measuring the total gas, and then connecting the outlet of this chamber to a flask containing an absorption solution, such as NaOH, to remove CO_2 and H_2S. Afterward, the outlet of this flask is connected to a second flow cell (BPC Instruments AB, 2002).

Figure 2. Optimal mixtures of animal waste and agro-food byproducts for biogas production using Gas Endeavour

Operating mode

The animal waste used in this study was collected in August and September 2023 from farms located in Teleorman County. Three different samples of animal waste were characterized to study the anaerobic co-digestion process. The physico-chemical properties were assessed through laboratory analyses. The equipment used for the determinations to calculate total nitrogen was the Dionex Aquion Ion Chromatograph and the CARY60 UV-VIS Spectrophotometer, while for calculating phosphorus and potassium, the equipment used was the PerkinElmer 8300 ICP-OES and the Milestone Ethos Easy System.

Tables 1, 3 and 5 show the calculation of total nitrogen from different samples of animal waste (from poultry, cows and pigs) and Tables 2, 4 and 6 show the calculation of phosphorus and potassium. Animal waste samples were stored at -4ºC during the preparation of the mixtures. The inoculum was obtained from a wastewater treatment plant in Teleorman County.

The substrate was a mixture of organic materials with a concentration of 10% solids (animal waste, plant residues, food waste) and the remaining portion is water.

Table 1. Analyses of nitrates, nitrites, nitrogen and total nitrogen (calculated) for poultry waste

Determinations	U/M	Poultry Waste
Nitrites	mg/kg	< 2.5
Nitrates	mg/kg	< 50
Nitrogen Kjeldahl	g/kg	19.1
Total nitrogen (calculated)	mg/kg	19100

Table 2. Analyses of poultry waste

Determinations	U/M	Poultry Waste
Phosphorus	mg/kg	11300
Potassium	mg/kg	27600

Table 3. Analyses of nitrates, nitrites, nitrogen and total nitrogen (calculated) for cow waste

Determinations	U/M	Cow Waste
Nitrites	mg/kg	< 2.5
Nitrates	mg/kg	< 50
Nitrogen Kjeldahl	g/kg	15.6
Total nitrogen (calculated)	mg/kg	15600

Table 4. Analyses of cow waste

Determinations	U/M	Cow Waste
Phosphorus	mg/kg	4760
Potassium	mg/kg	7970

Table 5. Analyses of nitrates, nitrites, nitrogen and total nitrogen (calculated) for pig waste

Determinations	U/M	Pig Waste
Nitrites	mg/kg	< 2.5
Nitrates	mg/kg	< 51.7
Nitrogen Kjeldahl	g/kg	25.0
Total nitrogen (calculated)	mg/kg	25000

Table 6. Analyses of pig waste

Determinations	U/M	Pig Waste
Phosphorus	mg/kg	7760
Potassium	mg/kg	15500

To achieve a uniform distribution of anaerobic bacteria throughout the substrate for the anaerobic co-digestion process, we combined multiple substrates with a 10% solids concentration with 40 g of inoculum (which is a previously prepared culture of anaerobic bacteria) and then introduced them into fermentation reactors with a usable volume of 400 g (Tabel 7). It is advisable for raw material mix recipes to adhere to a C/N ratio ranging from 15 to 25 and to have a moisture content of at least 90%. The reactors provide the conducive environment in which the anaerobic co-digestion process will take place. The experiments considered are presented in Tables 8, 9, 10 and 11.

Experiment number 5 - Blank test - it involved the use of 40 g of cellulose and 360 g of inoculum (Table 12).

Table 7. The quantities of materials required for the anaerobic co-digestion process

Total volume	500	g
Usable volume	400	g
Substrate	320.0	g
10% solids	40.0	g
Inoculum	40.0	g

Table 8. Experiment number 1 using green organic waste (tomato leaves)

Raw material	C/N	Exp. 1	Solid necessity	Solid requirement	TO BE FED		
					Fresh plant material	Water	Inoculum
		%	g	%	G	g	g
Green leaves (tomatoes)	20.4	20	8.00	20.00	40.000	172.29	40.00
Pig		40	16.00	22.73	70.392		
Cow		10	4.00	17.00	23.529		
Poultry		30	12.00	22.31	53.786		
TOTAL		100	**40.00**		**187.710**	**172.29**	**40.00**

Table 9. Experiment number 2 using green organic waste (tomato leaves) and wheat straw

Raw material	C/N	Exp. 2	Solid necessity	Solid requirement	TO BE FED		
					Fresh plant material	Water	Inoculum
		%	g	%	g	g	g
Green leaves (tomatoes)	25	10	4.00	20.00	20.00	172.29	40.00
Wheat straw		10	4.00	10.00	40.39		
Pig		40	16.00	22.73	70.39		
Cow		10	4.00	17.00	23.53		
Poultry		30	12.00	22.31	53.79		
TOTAL		**100**	**40.00**		**207.71**	**172.29**	**40.00**

Table 10. Experiment number 3 using grass as green organic waste

Raw material	C/N	Exp. 3	Solid necessity	Solid requirement	TO BE FED		
					Fresh plant material	Water	Inoculum
		%	g	%	g	g	g
Grass	17.2	20	8.00	20.00	40.000	172.29	40.00
Pig		40	16.00	22.73	70.392		
Cow		10	4.00	17.00	23.529		
Poultry		30	12.00	22.31	53.786		
TOTAL		**100**	**40.00**		**187.710**	**172.29**	**40.00**

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Table 11. Experiment number 4 using potato as green organic waste

Raw material	**C/N**	**Exp. 4**	**Solid necessity**	**Solid requirement**	**TO BE FED**		
					Fresh plant material	Water	Inoculum
		%	g	%	g	g	g
Potato	15.8	20	8.00	20.00	40.000	172.29	40.00
Pig		40	16.00	22.73	70.392		
Cow		10	4.00	17.00	23.529		
Poultry		30	12.00	22.31	53.786		
TOTAL		100	**40.00**		**187.710**	**172.29**	**40.00**

Table 12. Experiment number 5 using Blank test

Raw material	cellulose	inoculum
	g	g
	360	40.00
TOTAL	360	40.00

RESULTS AND DISCUSSIONS

Organic fertilizers with a low C/N ratio, such as straw less manure, tend to decompose rapidly. For instance, in the case of pig manure nitrification, this process can occur within a relatively short timeframe, typically ranging from three to five weeks.

On the other hand, fertilizers with a high C/N ratio, such as straw-bedded manure, undergo slower decomposition. This is due, in part, to the type of hydrocarbon substances present in the organic material, which can be degradable. Additionally, the specific nature of the waste (e.g. the chemical composition of animal droppings) can influence the rate of mineralization.

In general, fertilizers with a low C/N ratio tend to release nitrogen more rapidly, while those with a high C/N ratio can release nitrogen more slowly, which can be beneficial for a gradual and longer-lasting nutrient release. However, proper management of organic fertilizers with different C/N ratios is essential to maximize agricultural benefits and to avoid potential issues related to soil or water pollution.

Experiments were carefully monitored to maintain the best conditions for the development of anaerobic bacteria in the fermentation reactor: optimal temperature, pH level, and continuous substrate feeding. Mixing the substrate with the inoculum accelerated the anaerobic fermentation process.

The maximum biogas level was obtained after 5 days of anaerobic digestion of the animal manure and green grass substrate, reaching approximately 300 m³/day, compared to that derived from the animal manure with green leaves and straw substrate, which was approximately 200 m³/day (Figure 3). The highest recorded flow was 165 m³/day for the green grass and vegetable (potato) substrate (Figure 4).

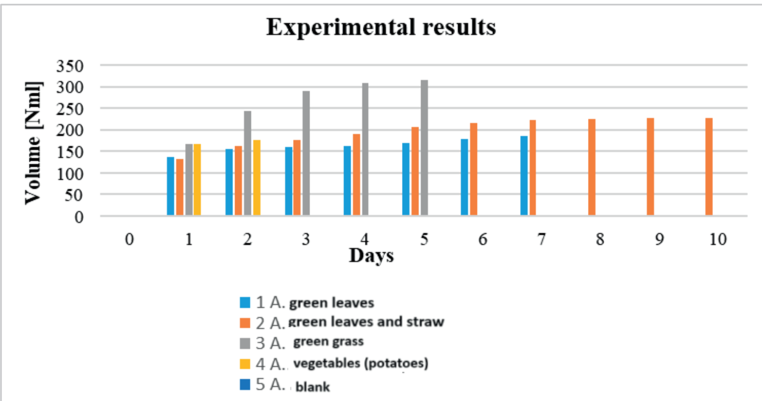

Figure 3. Experiments results - Volume [Nml]

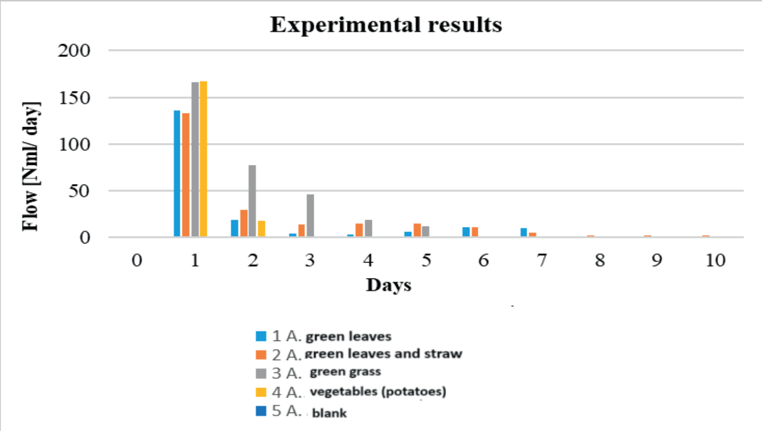

Figure 4. Experiments results - Flow [Nml/day]

CONCLUSIONS

Mixing animal waste with the inoculum is a crucial initial step in biogas production and ensures the efficiency of the anaerobic digestion process.

In this study, we conducted an evaluation of biogas production using poultry waste, cow waste, and pig waste as substrates.

The experiments were conducted using the Gas Endeavour biogas production facility, which is of small capacity, at a temperature of 37°C.

Our goal was to determine when biogas production begins and when the maximum level of production is reached.

In the first days, the installation recorded efficient biogas production, with the optimal mixtures being the mixture with green grass, the mixture with green leaves and straw, and the mixture with vegetables (potatoes).

After ten days of carrying out the experiments, the apparatus no longer recorded any signals, and the experiments were ended. This could indicate the depletion of organic matter resources in the anaerobic digestion process.

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