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VALUATION OF THE ENERGY POTENTIAL OF AGROZOOTEHNIC WASTE

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ABSTRACT. The anaerobic digestion of animal manure is a promising treatment solution allowing its partial conversion to energy, in the form of biogas. Anaerobic digestion technology is thus considered not only as a way to solve environmental problems, but also as a potential source of energy, while also contributing to solving economic and social problems.

This research investigates the potential of poultry, cattle and pig wastes for biogas production through the anaerobic digestion process. A number of 15 recipes had been prepared and studied, each consisting of a mixture of organic materials with a concentration of 10% total solids (animal waste, vegetable waste, food waste), in different proportions. The raw material mixtures (representing the substrates) respected a C/N ratio between 15 and 25. The substrate composition influence on the production of biogas was investigated. Different types of animal manure have been found to produce varying rates of biogas, with certain types yielding higher or more stable levels. In this installation, efficient biogas production was observed after seven days of anaerobic digestion, with the most effective mixtures being those with a higher proportion of grass.

Keywords: *animal waste, organic waste, anaerobic digestion, biogas, agro-food byproducts.*

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INTRODUCTION

Biogas can be generated in many ways, using different materials as substrates: plants, trees, grass, seeds, fruit and vegetable solid wastes, animal farm manure, algae, sludge, sewage, agri-food wastes and even urban solid organic materials (household wastes) [1, 2]. Table 1 presents typical examples of raw materials used in anaerobic digestion (AD) processes.

Table 1. Raw materials used in the anaerobic digestion process [3]

Waste	Types of waste
Agricultural waste and crop residues	Straws, green grass, potatoes, etc
Animal manure	Cattle, pig, and poultry manure

The AD process (anaerobic fermentation) is one of the most suitable for organic materials (wastes) valorization. It consist in a sequence of biological processes, in which the biodegradable part of the substrate is broken down into simple products, in the presence of bacteria. Overall, the process follows four slightly distinct steps of fermentation: hydrolysis, acidogenesis, acetogenesis and methanogenesis, occurring simultaneously in an oxygen free medium (Figure 1A). Each stage is well defined by specific chemical reactions (Figure 1B).

The final product is biogas (a mixture of gases, mainly methane and carbon dioxide) and digestate as byproduct (or sludge, as can be seen in Figure 1A). The amount of biogas that can be theoretically obtained from different substrates can be estimated using Buswell approximate equation taking elementary composition into account [4]:

$$C_cH_hO_oN_nS_s + y\,H_2O \rightarrow x\,CH_4 + (c-x)CO_2 + n\,NH_3 + s\,H_2S,$$

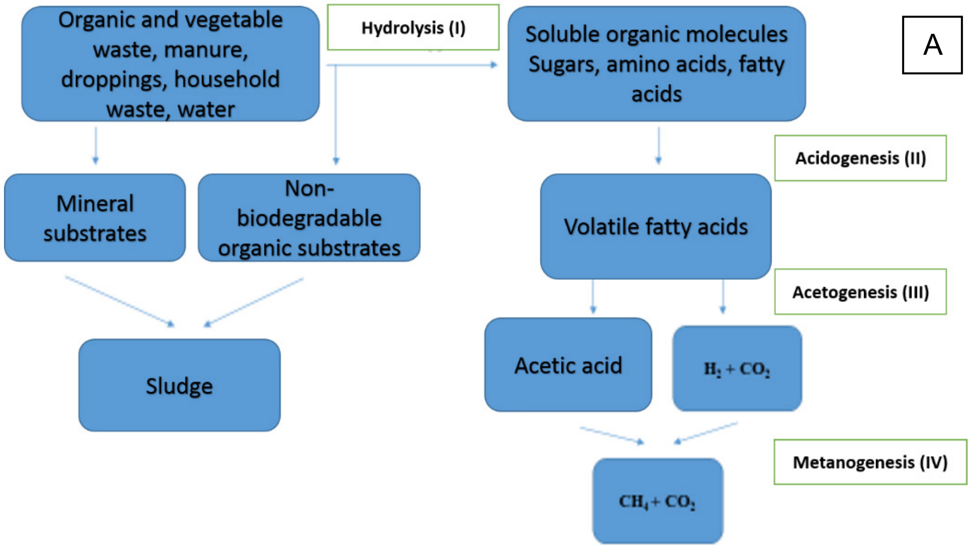
where

$$x = 0.125\,(4c + h - 2o - 3n + 2s)$$
$$y = 0.250\,(4c - h - 2o + 3n + 2s)$$

or, simplified

$$C_cH_hO_o \rightarrow (c/2 + h/8 - o/4)CH_4$$

For instance, carbohydrate is represented by $C_6H_{12}O_6$, fat by $C_{16}H_{32}O_2$, and protein by $C_6H_{10}O_2$ characterizing formulas.



B

AD Phase	Associated Chemical Reactions
Hydrolysis	$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2$
Acidogenesis	$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2$
	$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O$
	$C_6H_{12}O_6 \rightarrow 3CH_3COOH$ $C_3H_7O_2N + 2H_2O \rightarrow C_2H_4O_2 + NH_3 + CO_2 + 2H_2 + ATP$ $C_4H_9O_3N + H_2O \rightarrow C_3H_6O_2 + NH_3 + CO_2 + H_2 + ATP$ $4CH_3COCOO^- + 4H_2O \rightarrow 5CH_3COO^- + 2HCO_3^- + 3H^+$
Acetogenesis	$CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^- + HCO_3^- + 3H_2$
	$C_6H_{12}O_6 + 2H_2O \leftrightarrow 2CH_3COOH + 2CO_2 + 4H_2$
	$CH_3CH_2OH + 2H_2O \leftrightarrow CH_3COO^- + 2H_2 + H^-$
Methanogenesis	$CH_3COOH \rightarrow CH_4 + CO_2$
	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
	$2CH_3CH_2OH + CO_2 \rightarrow CH_4 + 2CH_3COOH$

Figure 1. A) Pathways for biomass conversion into biogas; **B)** Chemical reactions in anaerobic digestion (AD) phases [5]

Organic wastes are rich in carbohydrates, proteins and fats, which are important energy sources and generate considerable amounts of methane in biogas [6], as can be seen in Figure 1A.

Animal manure, in particular, is suitable for anaerobic digestion for several reasons: it has a high-water content, which facilitates the dilution of concentrated by-products and simplifies the pumping process; it has a high buffering capacity, essential to prevent sudden fluctuations in the pH value; and contain a wide range of nutrients necessary for the development of microorganisms [7]. Poultry manure however, has a low availability of nutrients, which makes regular supplementation with carbon sources necessary to ensure a stable and efficient anaerobic digestion process and therefore the exclusive use of poultry manure is not recommended, because the anaerobic fermentation process will be slow and will not produce a high yield of biogas [8]. However, this disadvantage can be compensated by co-digestion with other raw materials.

In this work was chosen to explore complex substrate compositions, including poultry, cattle, and pig waste, given the limited number of studies addressing the use of various animal wastes in a single digester. Thus, the main objective of the research is the development of an optimal mixture of animal manure and agro-food by-products to obtain high yield biogas conversions. Higher biogas production minimizes methane emissions into the atmosphere and contributes to a net reduction in greenhouse gas emissions [1,9].

The process of obtaining biogas through anaerobic digestion is a focus of research and is considered the best solution for managing animal waste, transforming organic waste into green energy and organic fertilizer for agriculture.

Since the topic of obtaining biogas is very current, I noticed that in the specialized literature only mixtures of organic matter with animal wastes that come from a single category of animals are presented, which is why I chose to study some waste mixtures that to lead to higher biogas yields than in the specialized literature, using both poultry manure, cattle manure, and pig manure in the same digester.

RESULTS AND DISCUSSION

As shown before, the complex process of AD is typically described as comprising four main stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Initially, lipids, carbohydrates, and proteins are broken down by fermentative bacteria into smaller components and soluble organic substrates, such as fatty acids, glucose, and amino acids. This step is often the rate-limiting factor in the AD of solid organic wastes, and various pre-treatment methods, including mechanical grinding, ultrasound, microwave, thermal, chemical, and biological treatments, have been proposed to enhance hydrolysis. In the second stage, the intermediate compounds are converted into volatile fatty acids (VFAs) like acetate, propionate, and butyrate, along with by-products such as NH_3, CO_2, and H_2S. In the next stages, VFAs are further digested into acetate, H_2, and CO_2, which serve as precursors for the production of CH_4 and CO_2 by methanogens [10].

The 15 experiments that were conducted had as a substrates complex mixture of organic materials with a concentration of 10% solids (animal waste, vegetable waste, food waste) based on the same materials, but in different proportions to see how the composition influences the production of biogas.

In order for the distribution of anaerobic bacteria to be uniform throughout the substrate, and to achieve the anaerobic co-digestion process, we combined several substrates with 40 g of the inoculum and then we introduced them into the fermentation reactors, having a useful volume of 400 g, as can be seen in Table 2.

The raw material mixtures respected a C/N ratio between 15 and 25.

The reactor uses the technique of continuous stirring in the fermentation process in order to maintain a constant and uniform movement of the mixture of substances. Thus, the uniform distribution of nutrients, or other essential elements in the fermentation solution is ensured.

In the sample incubation unit, up to 15 test vessels containing small amounts of a sample with appropriate microbial inoculum were incubated at the desired temperature in a thermostatic water bath.

In the gas absorption unit, the gas produced in each flask passes through an individual vessel containing a solution that can absorb certain fractions of the gas, undesired in biogas. In this case the produced gas was directed through an alkaline solution. Several gas fractions were retained through chemical interaction with the solution: when the alkaline solution like NaOH here is used, acidic fractions like CO_2 and H_2S are retained. Only CH_4 (and remaining traces such as H_2) will then proceed to the gas monitoring unit. A pH indicator was added to each vessel to monitor the acid-binding capacity of the solution.

In the gas volume measurement device, the volume of gas released from the incubation unit or from the gas absorption unit was measured using a wet gas flow meter with a multi-cell arrangement (15 cells). This measurement device operates on the principle of liquid displacement and buoyancy, and it can monitor ultra-low gas flow rates. A digital pulse is generated when a defined volume of gas flows through the device (2 ml or 9 ml, depending on the chosen resolution). An integrated data acquisition system is used to record, display, and analyze the results [11].

Table 2. Experiment Composting with Green Grass, Potatoes, and Wheat Straw

Exp.	Raw material (g)							
	Grass	Potatoes	Straw	Pig	Cattle	Poultry	Inoculum	Total
EXP 1	20.00	20.00	0.00	70.39	23.53	53.79	212.29	400.00
EXP 2	40.00	10.00	0.00	70.39	23.53	53.79	202.29	400.00
EXP 3	50.00	20.00	0.00	70.39	23.53	53.79	182.29	400.00
EXP 4	60.00	10.00	0.00	16.00	17.14	12.63	284.23	400.00
EXP 5	70.00	10.00	0.00	12.00	17.14	12.63	278.23	400.00
EXP 6	60.00	20.00	0.00	12.00	17.14	12.63	278.23	400.00
EXP 7	50.00	30.00	0.00	12.00	17.14	12.63	278.23	400.00
EXP 8	40.00	40.00	0.00	12.00	17.14	12.63	278.23	400.00
EXP 9	45.00	35.00	0.00	12.00	17.14	12.63	278.23	400.00
EXP 10	45.00	25.00	10.00	12.00	17.14	12.63	278.23	400.00
EXP 11	20.00	10.00	10.00	70.39	23.53	53.79	212.29	400.00
EXP 12	50.00	10.00	10.00	16.00	17.14	12.63	284.23	400.00
EXP 13	60.00	10.00	10.00	12.00	17.14	12.63	278.23	400.00
EXP 14	30.00	30.00	20.00	12.00	17.14	12.63	278.23	400.00
EXP 15	50.00	0.00	20.00	12.00	17.14	12.63	288.23	400.00

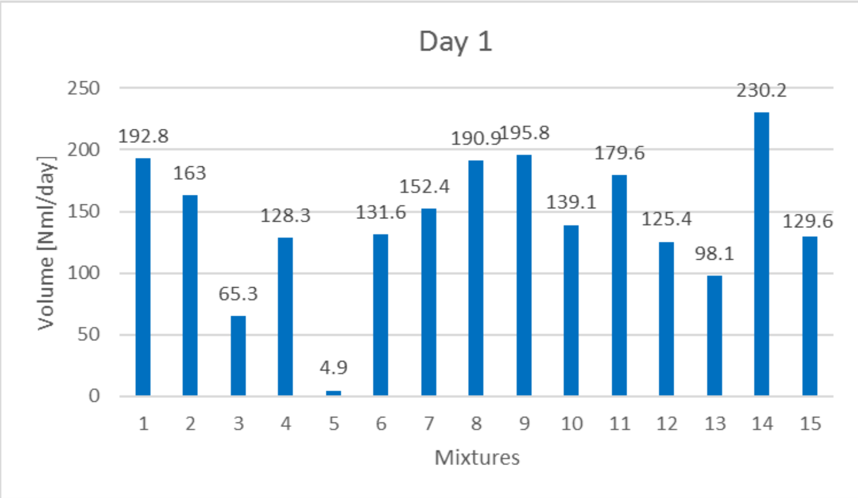


Figure 2. Results of biogas experiments generated using a mixture of pig manure, poultry manure, cattle manure, green grass, potatoes and straw, Volume [Nml] – Day 1

On the first day of anaerobic digestion, experiment no. 14 generated the largest volume of biogas, which had as raw material: green grass 30 g, potatoes 30 g, straw 20 g, pig manure 12 g, cattle manure 17.14 g and poultry manure 12.63 g.

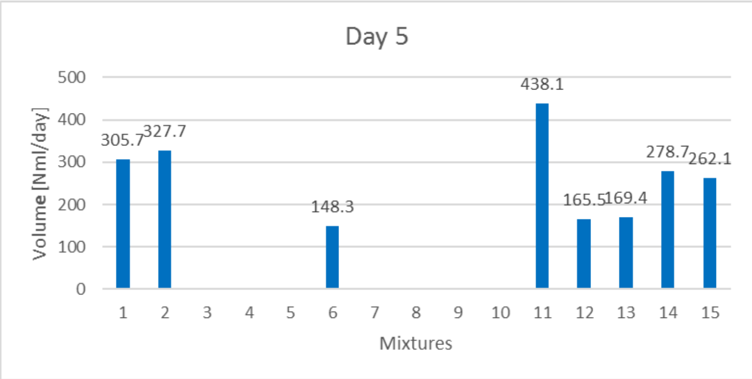


Figure 3. Results of biogas experiments generated using a mixture of pig manure, poultry manure, cattle manure, green grass, potatoes and straw, Volume [NmL] – Day 5

A low rate of biogas production was observed after the fifth day of anaerobic digestion, indicating that the anaerobic digestion was largely complete after this period. The maximum level of biogas was obtained after 5 days of anaerobic digestion.

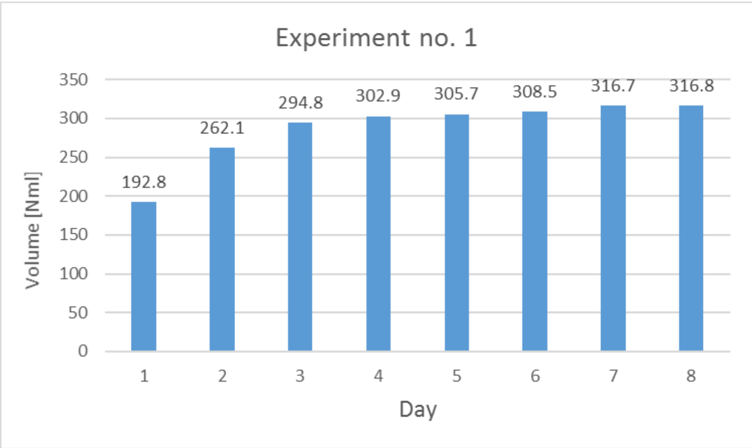


Figure 4. Results of experiment no. 1 biogas generated, using a mixture of pig manure 70.39 g, poultry manure 53.79 g, cattle manure 23.53 g, green grass 20 g, potatoes 20 g, Volume [Nml]

Starting with the sixth day of biogas production, the laboratory experiment recorded a decrease in the volume of biogas generated.

The highest volume of biogas generated was recorded in experiment no. 1 which consisted of a mixture of green grass 20 g, potatoes 20 g, pig manure 70.39 g, cattle manure 23.53 g, poultry manure 53.79 g, inoculum 212.29 g, followed by experiment no. 2 which it consisted of a mixture of green grass 40 g, potatoes 10 g, pig manure 70.39 g, cattle manure 23.53 g, poultry manure 53.79 g and inoculum 202.29 g.

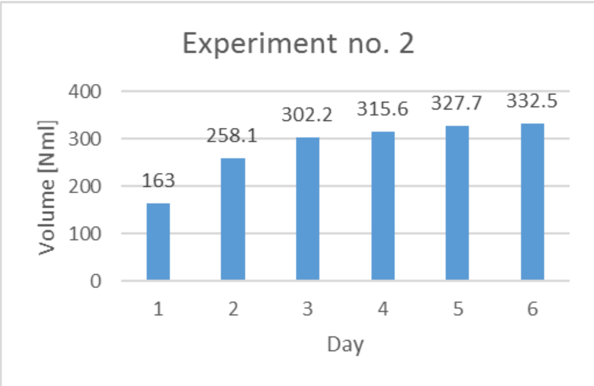


Figure 5. Results of experiment no. 2 biogas generated, using a mixture of pig manure 70.39 g, poultry manure 53.79 g, cattle manure 23.53 g, green grass 40 g, potatoes 10 g, Volume [Nml]

The level of biogas generated recorded the highest flow on the first day of anaerobic digestion, then started to decrease in the following days.

The highest flow of biogas generated by experiment no. 1 consisted of a mixture of green grass 20 g, potatoes 20 g, pig manure 70.39 g, cattle manure 23.53 g, poultry manure 53.79 g, inoculum 212.29 g was recorded on the first day, having the value of 192.75 m^3/day for the substrate with green grass and potatoes.

The observation that mixtures containing green grass generated a higher volume of biogas than those also containing wheat straw may be the result of differences in the chemical composition and degradation characteristics of these materials. Green grass may have a higher content of fermentable substances, such as carbohydrates and other water-soluble components, which are more easily accessible to the microorganisms involved in the anaerobic digestion process. This can lead to more efficient decomposition and higher biogas production. In contrast, wheat straw contains higher amounts of components that are more resistant to degradation. These components, such as lignin [12], may require more extensive degradation conditions or more intense microbial activity to be fully broken down, which could explain the lower volume of biogas generated in mixtures containing wheat straw. Wheat straw is a suitable substrate for biogas production, although its lignin content slows down the degradation process. Song and Zhang [13], in a study in 2015, investigated the monodigestion and codigestion of wheat straw, which they pretreated with four concentrations of H_2O_2 (1%, 2%, 3%, and 4%) before digesting it with cattle manure. They recorded a higher methane yield when the wheat straw was treated with H_2O_2 and codigested with cattle manure, while the codigestion of untreated wheat straw resulted in a lower yield.

The low biogas production may be due to a lack of water. Sadaka and Engler [14] reported that the solid and water content are key parameters in biogas production, directly influencing anaerobic digestion. Water facilitates bacterial movement and growth, aids in nutrient transport, and reduces mass transfer limitations.

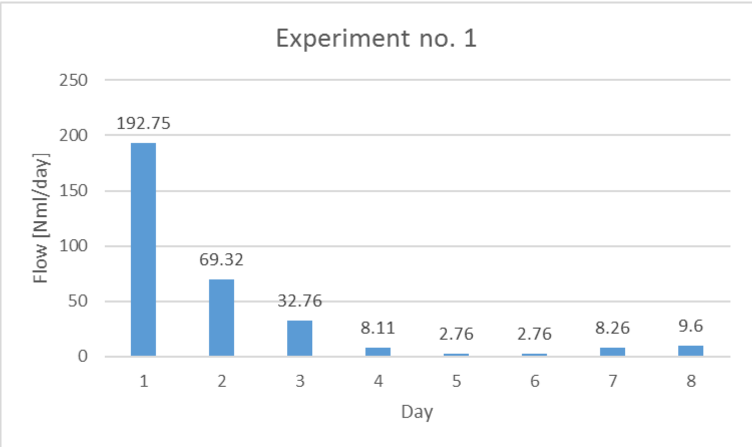


Figure 6. Biogas flow rate generated by experiment no. 1, using a mixture of pig manure 70.39 g, poultry manure 53.79 g, cattle manure 23.53 g, green grass 20 g, potatoes 20 g, Flow [Nml/day]

Figure 7 includes a centralized presentation of the experiments:

- Experiment no. 3 which consisted of a mixture of green grass 50 g, potatoes 20 g, pig manure 70.39 g, cattle manure 23.53 g, poultry manure 53.79 g, inoculum 182.29 g recorded the highest flow of biogas generated with the value of 392.21 m^3/day.

- The mixture that generated biogas for 6 days is mixture no. 3 which it consisted of a mixture of green grass 50 g, potatoes 20 g, pig manure 70.39 g, cattle manure 23.53 g, poultry manure 53.79 g and inoculum 182.29 g.
- The best yields were given by the experiments that had in their composition both green grass and animal droppings.

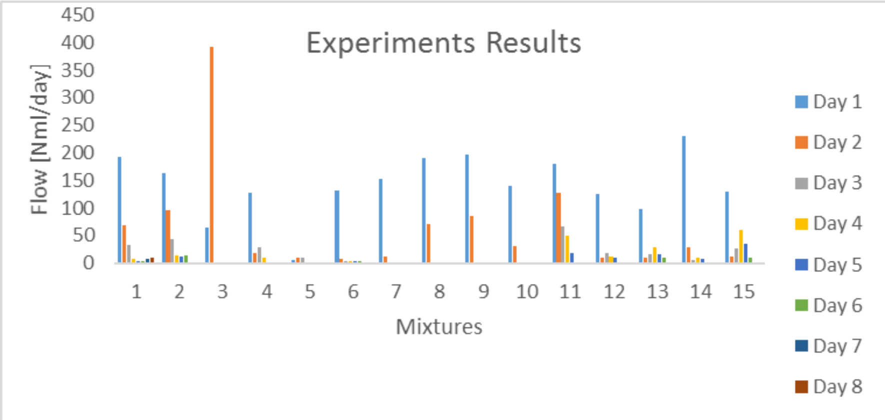


Figure 7. Experimental results using a mixture of pig manure, poultry manure, cattle manure, green grass, potatoes and straw, Flow [Nml/day]

CONCLUSIONS

The aim of the research was to develop an optimal mixture of animal manure and agro-food by-products in order to obtain high yields of biogas.

The experimental research consisted in the preparation and testing of 15 mixture recipes in which we used droppings from poultry, pig and cattle farms located in Teleorman county. We kept the animal manure samples at a temperature of (– 4) °C, in a closed container, protected from light. To speed up the anaerobic digestion process, we used wastewater as inoculum, collected from a sewage treatment plant located in Teleorman county.

The experiments were carried out using the Gas Endeavor biogas plant with a small capacity (15 glass reactors of 500 ml) and a constant temperature of 37°C.

Each set of experiments was carried out in four phases that included the collection and preparation of samples, the calculation of recipes, the preparation and commissioning of the installation and the collection and analysis of experimental data.

The installation has registered an efficient production of biogas since the first days, while the maximum level being recorded after 5 days of anaerobic digestion, the optimal mixtures being those that have a greater amount of green grass in their composition.

These differences between mixtures containing green grass and those containing wheat straw highlight the importance of biomass composition and characteristics in the biogas production process. The detailed analysis and understanding of these differences can provide valuable information for optimizing the composition of the mixtures used in biogas production and for increasing the efficiency of the process.

EXPERIMENTAL SECTION

The experiments were carried out using the Gas Endeavor biogas plant with a small capacity (15 reactors of 500 ml) and a constant temperature of 37°C.

The experiments were carried out in four phases:

Sample preparation phase: it consisted in the collection of samples from the site and the characterization of the organic substance by determining the content of dry substance and volatile substance. The samples were collected in the morning, to keep the biological characteristics intact and not to contaminate the samples.

The recipe calculation method was made taking into account that the C/N ratio should be between 15 and 25 and that the mixture should have solids content of 10%.

Preparation and commissioning of the installation Gas Endeavour consisted in the preparation and loading of the 15 glass reactors with substrate, according to the previously calculated mixture recipes.

After completing these phases, the installation is ready to be put into operation, and the reactors will be connected to the biogas treatment module, where the CO_2 retention takes place. The monitoring and control of the installation was done with the help of a laptop, which recorded and processed the data.

Recording of experimental data was carried out over a period of 8 days, during which the installation worked continuously. The installation calculated the value of the biogas production potential for each experiment.

The experiments were carefully monitored to maintain the best conditions for the development of anaerobic bacteria in the fermentation reactor: an optimal temperature, pH, continuous supply of substrate.

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