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Study of Technological Process of Fermentation of Molasses Vinasse in Biogas Plants

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Abstract: The volume of ethanol production waste—molasses waste in Ukraine—reaches up to 4 million m^3 per year. It is not easy to dispose of and is polluting the environment. Currently, the development of an effective technology for using molasses in biogas plants to obtain energy gas—biogas—is an urgent problem. The purpose of our work is to determine the rational volume of loading molasses bard into the methane tank in a quasi-continuous mode to obtain the maximum volume of biogas. To achieve this goal, the following experimental studies were carried out: mono-fermentation of molasses and combined fermentation of cattle manure and molasses on a laboratory biogas plant in a periodic mode; on the basis of the obtained laboratory studies, a special simulation model of biogas output during the quasi-continuous fermentation of substrates was established and the amount of molasses added to obtain the maximum biogas output was determined. The maximum output of biogas under the periodic system of loading the methane tank when adding 10.5% molasses to cattle manure is 1.462 l/(h kg DOM); when adding 26.1% molasses to cattle manure, it is 3.594 l/(h kg DOM). In order to increase the yield of biogas, it is advisable to add molasses in the amount of 30% of the volume of the substrate to the substrate based on cattle manure, which allows the discounted payback period of the biogas plant to be reduced to 1.2 years.

Keywords: biogas; vinasse; cattle manure; methane fermentation; biogas plant; methane tank; fermentation

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1. Introduction

As a renewable energy source, the production and utilization of biogas are of great benefit to mitigate greenhouse gas emissions, reduce the dependency on fossil fuels, and promote the utilization of livestock manure and crop straw. However, the operation of household biogas reactors in China does not always live up to expectations. In work [1], it was established that the lack of technical training and subsidies for the operation of household biogas reactors were key obstacles for households to continue using them. Conversely, a warmer local climate and larger domestic biogas reactors have had a positive effect on households choosing to continue to use them. As noted in works [2,3], in the general rating of the criteria for the use of industrial biogas plants, the involvement of interested parties is most important, followed by more significant subsidies for small and medium-sized plants and the principle of self-sufficiency, which is applied at the interregional level.

Nowadays, the actual problem comes from using large sizes of furniture in biogas plants. At the same time, there is a certainty that comes from using only such a load volume that is used in biogas plants and it helps to achieve maximum biogas output. In order to increase the yield of biogas from cattle manure, it is advisable to use the waste from agricultural and processing production as co-substrates, which also eliminates the need to dispose of them. Such co-substrates include sediments of vegetable oils [4,5], soapstock [6,7], substandard flour [8,9], extruded straw [10,11], and extruded straw along with bird droppings [12,13]. One of such co-substrates is crude glycerine [14,15], which is formed as a by-product of biodiesel production [16–20]. One method to resolve this problem is by carrying out an experimental project of methane fermentation of cattle manure with molasses vinasse in laboratory biogas plants for the periodic mode of loading of methane tank and determining the dependence of increasing output biogas on loading volumes of methane tank with molasses vinasse. However, modern biogas plants typically operate in a quasi-continuous substrate loading mode, meaning that there needs to be a loading volume of molasses vinasse in the methane tank in a quasi-continuous mode for maximum biogas production.

Post-alcohol vinasse is a waste of ethanol production. Molasses vinasse is obtained from the production of ethanol from molasses, and grain vinasse from grain. Around 4 million m^3 of molasses and 3.6–3.8 million m^3 of grain vinasse [21] are produced in Ukraine every year. Fifty per cent of dry matter (DM) molasses ferments during the process of alcohol fermentation, and the rest become vinasse [22]. In fact, it is very acidic (pH = 4.0–4.3) with a high biological and chemical oxygen demand (BOS = 52–58 kg/m^3, ChOC = 92–100 kg/m^3) and a large amount of suspended solids (2.0–2.5 kg/m^3) [23]. It is unsuitable for use as animal feed because it has a large amount of minerals [24]. High concentrations of sulphites in molasses vinasse [25] limit its use as a fertiliser because of the possibility of soil certification [26]. Molasses vinasse can be processed into biogas from anaerobic digestion, which decreases acidity. As a result, molasses vinasse can be used as an organic fertiliser.

In [27,28], it is noted that the transition vinasses in biogas plants are reduced by environmental loading, and in [29–32], there is also an opportunity to gain extra energy. In [33], it is recommended to treat the vinasse with ozone before methane digestion, which will decrease the vinasses' ChOC by 30%. However, as indicated in [34], the inhibition of methanogens by sulphates is already being observed at a ratio of SO_4^{-2} anions to ChOC equal to 0.1, and at SO_4^{-2}/ChOC = 0.2, methane fermentation stopped, and it was impossible to restore it. In [23,35], it is noted that the molasses vinasse must be diluted in a large amount of water before methane fermentation. In [36], it is recommended to add the vinasse to the substrate in a small amount, or to neutralise it to reduce the effect of strong acidity. A single addition of a saturated solution of Na_2CO_3 to the vinasse increases its pH from 4.6 to 5.7, and twice increases it to 6.4, as stated in [37]. It is noted that the vinasse has a low ratio of carbon to nitrogen, so it is necessary to add additional substances (animal manure, organic industrial waste, and lime products) to improve the use of biogas, as [38] recommends.

Biogas output was 0.536 l/g volatile solids (VS) when removing methane and 0.305 l/g VS when vinasse was added to cattle manure, as reported in [39]. These indicators of biogas output are higher than the mono-fermentation of cattle manure (0.456 l/g VS, 0.245 l CH_4/g VS) and the fermentation of cattle manure with the addition of a leather production waste (0.505 l/g VS, 0.288 l CH_4/g VS). In [40], the biogas output at vinasse fermentation was 5.37 m^3/day.

The vinasse can be disposed of by using it as a co-substrate for biogas production, as we can see from previous research [41]. It is recommended to add a small amount of molasses to the substrate because it can cause methanogen inhibition [42]. However, the literature does not indicate the amount of vinasse that must be added to the substrate in order to avoid the inhibition of methane-forming bacteria.

The purpose of this work is to determine the rational volumes of loading the molasses vinasse into the methane tank in a quasi-continuous mode in order to obtain maximum volumes of biogas.

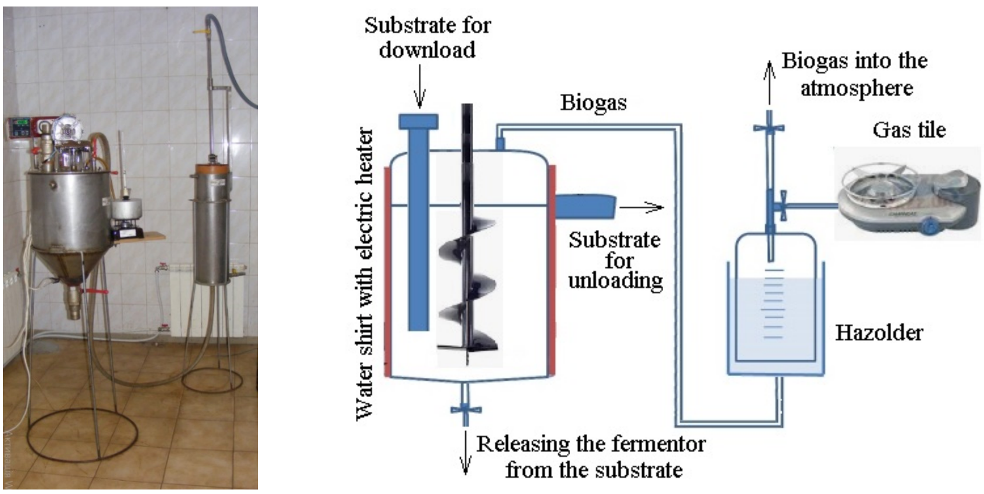
2. Materials and Methods

The following experimental research was performed to achieve this goal: the mono-fermentation of molasses vinasse and the co-fermentation of cattle manure and molasses vinasse in a laboratory biogas plant in a periodic mode; a special simulation model of biogas production was quenched for the quasi-continuous fermentation toes and rational volumes of molasses vinasse were added for maximum biogas output, based on the obtained laboratory studies.

The Gnidavsky Sugar Mill was used for research. It was tested at the Ukrainian Laboratory for Quality of AIC Products. According to the protocol of research, results of the molasses bard sample after bioethanol production No 0406H dated 2 April 2018 contains 14.1% of dry matter, including 3.72% crude protein, 0.4% raw fat, and 0.93% soluble carbohydrates. The mass fraction of potassium in molasses vinasse is 12.33 g/l, or 1.23%, the mass fraction of potassium in terms of K_2O—14.79 g/l, or 1.48%, the mass fraction of sodium—2.51 g/l, or 0.25%, the mass fraction of magnesium—38.99 mg/l, or 0.0039%, the mass fraction of magnesium in terms of MgO—38.99 mg/l, or 0.0039% and the mass fraction of iron—13.22 mg/l, or 0.0013%.

The dry organic matter (DOM) is made up of proteins, fats, and carbohydrates, so the DOM content of the Gnidavsk Sugar Mill is: 3.72 + 0.4 + 0.93 = 5.5%. The pH of the molasses vinasse was 4.7, measured on a pH-009 pH meter.

Experimental studies of methane fermentation of molasses vinasse were carried out on a laboratory biogas plant consisting of a methane tank with a working volume of 30 l and a "wet" type gas holder (Figure 1a,b).



(**a**) (**b**)

Figure 1. Laboratory biogas plant: (**a**)—appearance; (**b**)—plant a layout.

Biogas release was determined with the help of a wet gasholder. In doing so, the heating of the digester is provided by a water jacket with an electric heater placed between the outer and the inner hull. The substrate is pumped into the active zone of the inner shell through a pipe that almost reaches the bottom.

At the same time, the processed digestate is fed through a pipe located at the level of the substrate and biogas boundary. The digester is refuelled to ensure not less than 1/3 of the processed digestate has uterine bacteria culture in it. The release of biogas is recorded on a scale graduated in centimetres on the raised cylinder gauge of the wet gasholder. The calorific value of the biogas is determined by burning it on a gas stove while heating the water in the calorific value measurer.

The substrate is prepared by mixing cow manure with water and adding flour to it. The methane tank is 3/4 filled with the substrate in a periodic loading mode.

Research at the temperature regime of the methane tank at 40 °C was conducted in several stages. At the initial stage, the fermentation of molasses vinasse was explored without adding cattle manure. Finally, fermentation research into the substrate consisting of a mixture of cattle manure, water, and molasses was carried out.

Experimental research was carried out into the mono-fermentation of molasses vinasse. In the first phase of research, 30 l of biosolids were added to the laboratory meth tank—10 l of biosolid and 20 l of molasses. The substrate pH was 4.7.

The DOM mass of the molasses vinasse loaded into the methane tank was determined by the formula:

$$M_{DOMc} = \frac{M_{MV} \cdot DOM_{MV}}{100\%} \quad (1)$$

where:

M_{DOMC}—mass of dry organic matter of the molasses vinasse loaded into the methane tank, in kg;

M_{MV}—mass of molasses loaded into the methane tank, in kg;

DOM_{MV}—content of dry organic matter in molasses, as a %.

The DOM mass of the molasses vinasse loaded into the methane tank by formula (1) was:

$$M_{DOMc} = \frac{20 \cdot 5.05}{100} = 1.01 \text{ kg, or } \frac{1.01 \cdot 100}{20} = 5.05\%.$$

The second stage of research was on the mono-fermentation of molasses bard. 17.5 l of biosludge and 8.5 l of molasses were loaded into the laboratory meth tank. The substrate acidity was reduced by the addition of baking soda—104 g of baking soda was added to 26 l of substrate and biosludge, which was dissolved in them by stirring. The pH of the substrate was raised to 6.7. The DOM mass of the molasses vinasse loaded into the methane tank was calculated by formula (1):

$$M_{DOMc} = \frac{8.5 \cdot 5.05}{100} = 0.4293 \text{ kg, or } \frac{0.4293 \cdot 100}{8.5} = 5.05\%.$$

$$\frac{0.4293 \cdot 100}{8.5} = 5.05\%.$$

At the third stage of the research into the mono-fermentation of molasses vinasses, it was suggested that biogas does not contain methane due to the high content of DOM vinasses. At this stage, 10 l of biosludge and 20 l of substrate consisting of the 3 l of vinasse and 17 l of water were loaded into the laboratory meth tank. Soda was not added to the substrate to reduce the acidity. The pH of the substrate was 6.3 due to the neutral reaction of water. The DOM mass of the molasses vinasse loaded into the methane tank was calculated by formula (1):

$$M_{DOMc} = \frac{3.0 \cdot 5.05}{100} = 0.1515 \text{ kg, or } \frac{0.1515 \cdot 100}{20} = 0.76\%.$$

Experimental studies of the combined fermentation of cattle manure and molasses. A substrate consisting of 3.5 kg of cattle manure, 5 l of water and molasses was added to a laboratory methane tank with a useful volume of 30 l, in which 18.5-20.5 l of biosludge remained. It was planned that the weight of the added molasses bard would be 1 kg, then 3 kg, and would increase by 2 kg each time until the biogas combustion was stopped.

However, after adding 3 kg of bard to the substrate, the obtained biogas burned; the customer was satisfied with the results, since according to the project, the content of bard in the substrate of the designed biogas plant should not exceed 30%. Therefore, further experiments were stopped.

The weight of the COP substrate based on cattle manure with the addition of molasses is:

- 0.5125 kg at a bard weight of 1 kg, or 5.39% of the mass of the substrate;
- 0.6135 kg when the bard weighs 3 kg, or 5.33% of the mass of the substrate.
- At the same time, the content of bard in the substrate is:
- 10.5% when the bard weighs 1 kg;
- 26.1% when the bard weight is 3 kg.

3. Results and Discussion

Experimental studies of mono-fermentation of molasses bard. The first stage. For three to four days, a lag phase was observed during which methane-forming bacteria became accustomed to the unusual conditions: high acidity, the absence of a traditional substrate—cattle manure, and the presence of a new substrate—molasses vinasse. After adapting to the new conditions, the bacteria began intensive activity and active reproduction, which was accompanied by a significant release of biogas. Biogas was released far more than the digestion of any substrate we studied. The only downside was that the resulting biogas did not burn. Hydrogen sulphide was not observed, so it can be predicted that the basis of the biogas was carbon dioxide. Since there was no biogas combustion, on the sixth day at the stage of the stationary phase, the fermentation was stopped by completely unloading the substrate from the methane tank.

The second stage of research on mono-fermentation of molasses bard. It was assumed that biogas does not contain methane due to high acidity. The acidity of the substrate was reduced by adding baking soda. Since the mother culture of bacteria was already accustomed to molasses during the previous experiment, no lag phase was observed. For two days, the fermentation underwent a logarithmic phase, a very short stationary phase and a dying phase. Starting from the third day of fermentation until the end of the experiment on the sixth day, the yield of biogas did not change. The total level of biogas, as can be seen from the graph of the accumulated biogas output, was slightly lower than in the previous experiment, but still much higher than the biogas output during the fermentation of all the substrates we studied. However, the obtained biogas still did not burn; there was a faint smell of hydrogen sulphide. Therefore, the assumption about inhibition of methane formation due to high acidity was confirmed.

The third stage of mono-fermentation of molasses bard research. The dynamics of fermentation were similar to the previous experiment, though the biogas output decreased by about a quarter. The biogas still did not burn, though this time there was a very strong smell of hydrogen sulphide. The results of the mono-fermentation study of molasses vinasse are presented in Figure 2 (biogas output in time) and Figure 3 (cumulative biogas output).

Experimental research continued into the joint digestion of cattle manure and molasses. Since the mono-fermentation of molasses vinasse did not give results on the energy saturation of the obtained biogas, it was decided to study the joint fermentation of molasses vinasse and cattle manure.

A 30-L volume comprising 18.5–20.5 l of biosludge with a substrate consisting of 3.5 kg of cattle manure, 5 l of water, and molasses was added to the laboratory methane tank. It was planned that the weight of the added molasses vinasse will be 1 kg, then 3 kg, and would increase by 2 kg each time until the biogas stops burning.

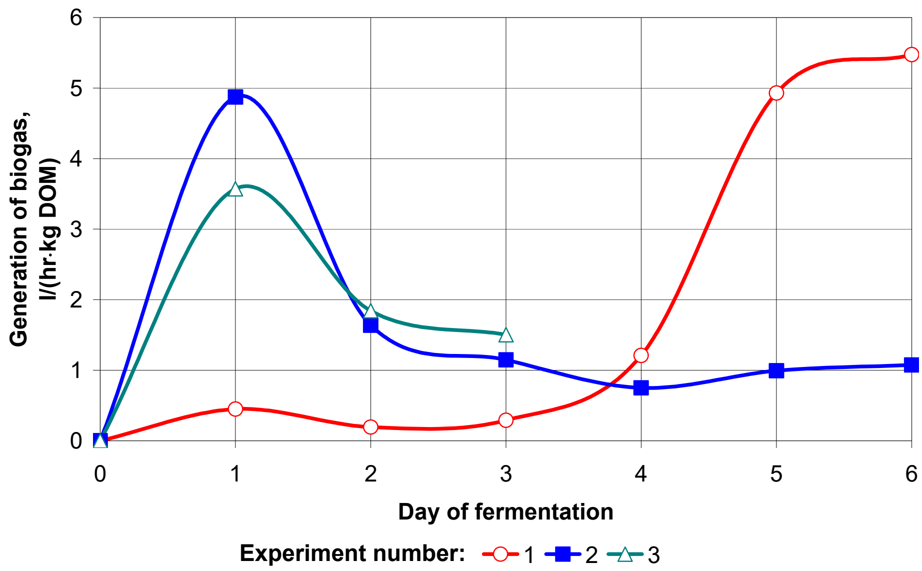


Figure 2. The output of biogas in the mono-fermentation of molasses vinasses at a fermentation temperature of 40 °C: 1—20 l of vinasse, pH = 4.7 was added to 10 l of biosludge; 2—8.5 l of vinasse, pH = 6.7 was added to 17.5 l of biosludge; 3—20 l of substrate, consisting of 3 l of vinasse and 17 l of water, pH = 6.3, was added to 10 l of biosludge.

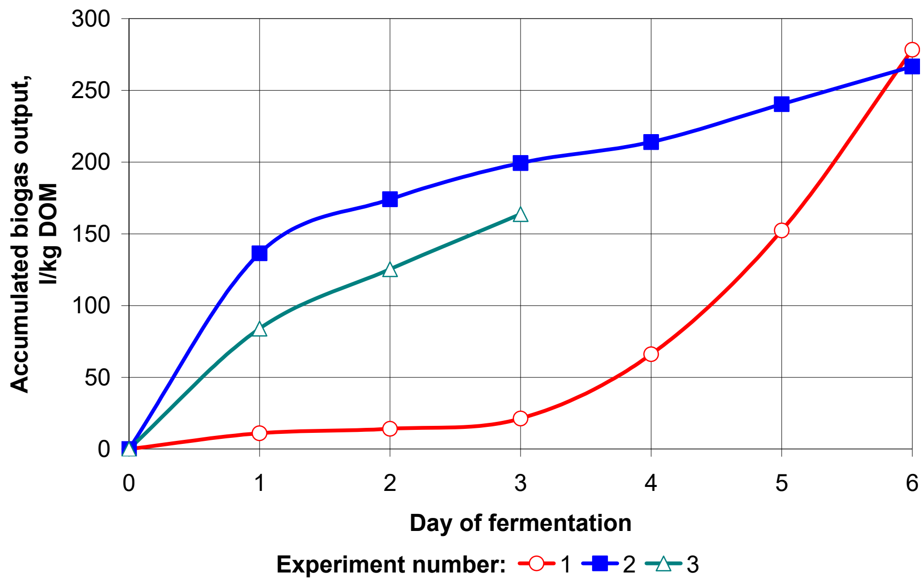


Figure 3. Accumulated biogas output in the mono-fermentation of the molasses broth at a fermentation temperature of 40 °C: 1—20 l of broth was added to 10 l of biosludge, pH = 4.7; 2—8.5 l of vinasse, pH = 6.7 was added to 17.5 L of biosludge; 3—20 l of substrate, contains of 3 l of vinasse and 17 l of water, pH = 6.3, was added to 10 l of biosludge.

However, since biogas was able to burn when 3 kg of vinasse was added to the substrate, the client was satisfied with the results, since the vinasse content in the substrate of the projected biogas plant should not exceed 30%. Therefore, further experiments were discontinued. The weight of the DOM substrate based on cattle manure with the addition of molasses vinasse was:

– 0.5125 kg at a vinasse weight of 1 kg, or 5.39% by weight of the substrate;
– 0.6135 kg with a vinasse weight of 3 kg, or 5.33% by weight of the substrate.
– The content of the vinasses in the substrate was:
– 10.5% at a vinasse weight of 1 kg;

– 26.1% when weighing 3 kg of vinasses.

The results of the study on joint digestion of cattle manure and molasses are presented in Figure 4 (dynamics of biogas output in time) and Figure 5 (cumulative biogas output).

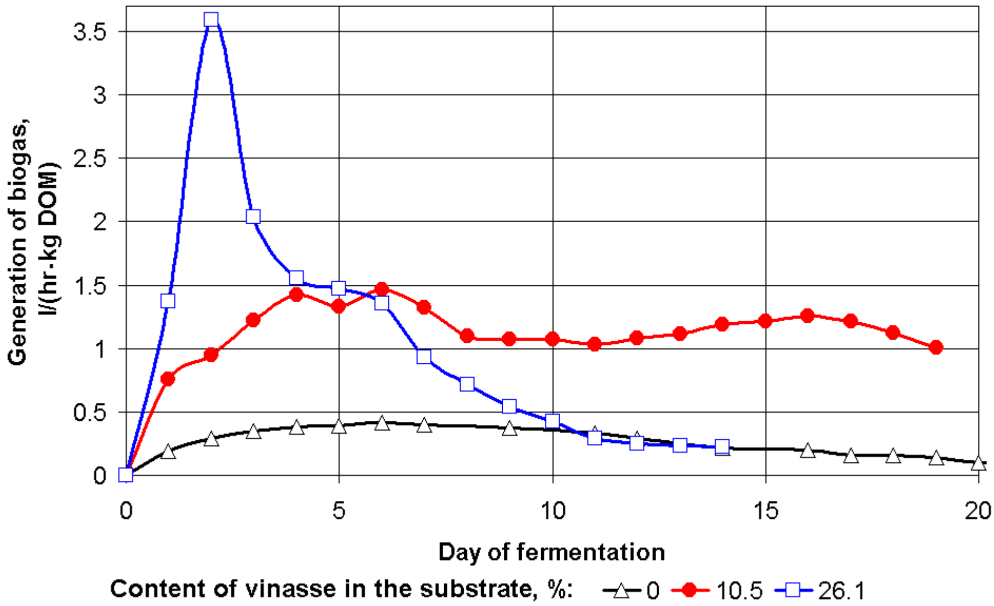


Figure 4. The output of biogas at the combined fermentation of cattle manure and molasses at a fermentation temperature of 40 °C.

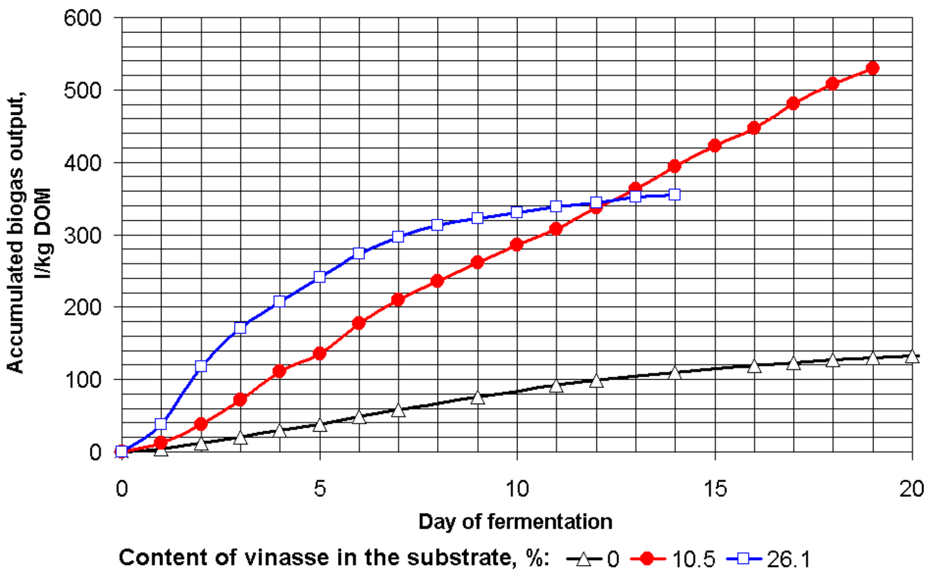


Figure 5. Accumulated biogas output from the joint digestion of cattle manure and molasses at a fermentation temperature of 40 °C.

As can be seen from Figure 4, there is diauxic growth with the joint digestion of cattle manure and molasses vinasse. Biogas output is large enough and its level does not decrease for quite a long time; as a result of this, the accumulated biogas output constantly increases (Figure 4), exceeding the level of biogas output during the digestion of other studied substrates. By increasing the vinasse content of the substrate from 10.5% to 26.1%, the biogas output increases.

The maximum biogas output in the periodic methane tank loading system with the addition of 10.5% molassic vinasse to the cattle manure is 1.462 l/(h·kg DOM), and with the addition of 26.1% molassic vinasse to the cattle manure, it is 3.594 l/(h·kg DOM). The conversion factor of biogas output from the dimension l/(h·kg DOM) to the dimension l/(h·kg) with the addition of 10.5% molasses vinasse to the cattle manure is 18.573 kg/kg DOM; with the addition of 26.1% molasses vinasse to the cattle manure, it is 18.745 kg/kg DOM.

The accumulated biogas output from cattle manure digestion with the addition of molasses vinasse at a fermentation temperature of 40 °C is approximated by the Newton polynomial:

$$V_b = b_n \cdot t^n + b_{n-1} \cdot t^{n-1} + b_1 \cdot t + b_0, \quad (2)$$

where:

V_b—the accumulated biogas output, l/kg DOM;
t—fermentation time in days;
n—the degree of the polynomial.

The coefficients of the polynomial (2) are given in Table 1.

Table 1. Polynomial coefficients describe the average accumulated biogas output from the digestion of cattle manure with the addition of molasses vinasse at a fermentation temperature of 40 °C.

The Content of Molasses Vinasses in the Substrate,%	Polynomial Coefficients				R^2
	b_3	b_2	b_1	b_0	
0	−0.0258	0.3325	14.27	−7.7	0.9998
10.5	-	−0.14	31.1	−12.0	0.9986
26.1	0.129	−5.2	73.7	−11.5	0.9964

The coefficients of determination of the approximated curves (2), with the polynomial coefficients given in Table 1, approaching one, indicating that the obtained regression equations accurately reflect the experimental data. The Fisher test verifies the significance of the determination coefficients. The Student's criterion showed that all the coefficients of polynomials (2) in Table 1, in addition to the coefficient b_3 for the expression describing the accumulated biogas output when the molasses vinasse content in the substrate is 26.1%, are significant. The coefficient b_3 is unreliable, but when it is extracted, the coefficient of determination significantly deteriorates.

On the first day of fermentation, the biogas did not burn, after which the biogas combustion stabilised with a lower combustion heat of 16.5–20.5 MJ/m^3 (Figure 6).

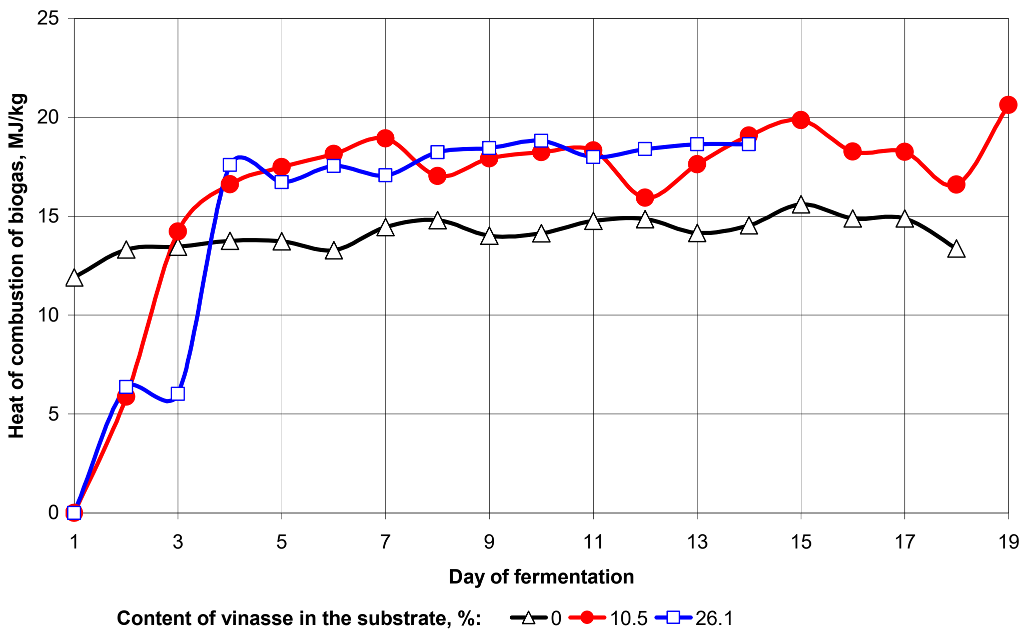


Figure 6. Dynamics of changes in heat of combustion of biogas over time.

A model of biogas output given quasi-continuous loading for cattle manure digestion with the addition of molasses vinasse was worked out, using the methane tank of the biogas plant to conduct experimental research into the fermentation of substrates on the basis of cattle manure with the addition of co-substrates were carried out, suitable for the periodic loading of the substrate. The gradual loading of the substrate is quite difficult. At the same time, the periodic mode of methane tank loading is rarely used in practice in current biogas plants, with quasi-continuous loading used more often, where the substrate is loaded with small portions into the methane tank after a certain period of time (usually about an hour). In this case, the biogas output reaches the maximum that can be achieved with the periodic system of loading and value, and is maintained at the same level throughout the life of the biogas plant. Therefore, based on the experiments with the periodic methane tank loading system, it is possible to simulate the biogas output at a quasi-continuous loading system. Based on the data presented in [15] and our own studies, it can be argued that the biogas output of a quasi-continuous loading system will be close to the maximum biogas output of a periodic loading system.

The maximum biogas output for the periodic system of methane tank loading with the addition of 10.5% molasses vinasse to the cattle manure is 1.462 l/(h·kg DOM); with the addition of 26.1% molasses vinasse to the cattle manure, it is 3.594 l/(h·kg DOM). The simulated biogas output at cattle manure digestion with the addition of molasses vinasse for quasi-continuous loading of methane tank at a fermentation temperature of 40 °C is shown in Figure 7.

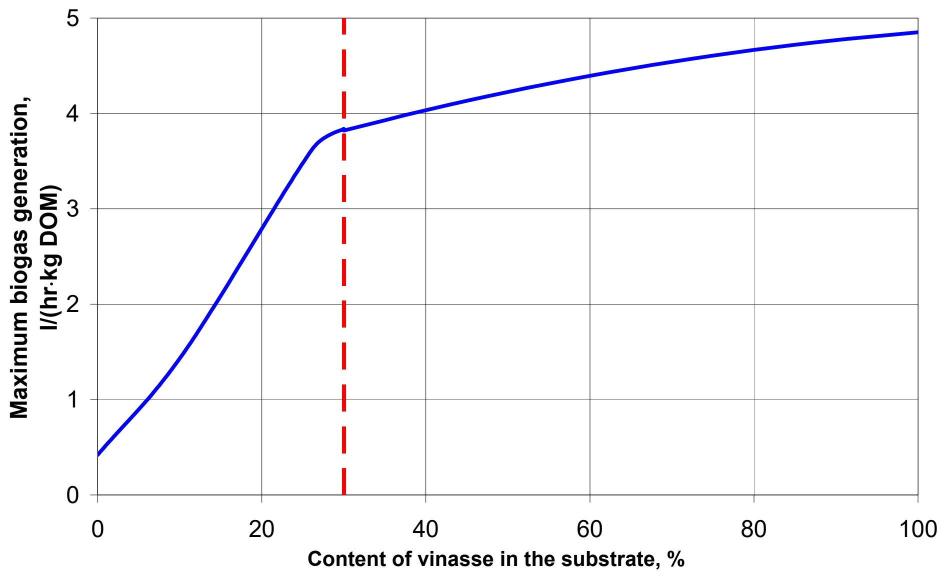


Figure 7. Modelled biogas output from cattle manure digestion from molasses vinasse for the quasi-continuous loading of a methane tank.

The simulated biogas output from cattle manure digestion with the addition of molasses vinasse for quasi-continuous loading of methane at a fermentation temperature of 40 °C is approximated by a third-order Newton polynomial that outputs reliable results only at the points obtained in the experiment. At other points, when predicted, the values obtained from one Newton polynomial do not correspond to the accepted trend. Therefore, it was decided to approximate the simulated biogas output using two Newton polynomials:

$$\begin{gathered} V_{b\,\text{mode}} = -0.00018 \cdot MW^3 + 0.0079 \cdot MW^2 + 0.039 \cdot MW + 0.42 \\ \text{for } MW \leq 30 \text{ with } R^2 = 0.9999, \\ V_{b\,\text{mode}} = -0.00011 \cdot MW^2 + 0.029 \cdot MW + 3.05 \text{ for } MW \geq 30 \\ \text{with } R^2 = 0.9995, \end{gathered} \quad (3)$$

where:

$V_{b\ \mathrm{mode}}$—the modelled output of biogas for the quasi-continuous loading of methane, l/kg DOM;

MW—the content of molasses vinasse substrate, %.

Since the experimental data for their approximation and correct determination of the coefficient of determination were not enough, the existing experimental data were used to construct graphical dependencies (see Figure 6), at which additional points were established by interpolation and extrapolation at regular intervals to determine their regression equations and determination coefficients.

The coefficient of determination of the approximated function (3), which describes the simulated biogas output when cattle manure is digested with the addition of molasses vinasse for the quasi-continuous loading of the methane tank at a fermentation temperature of 40 °C, is close to one, indicating that the obtained regression equation displays the received data. The Fisher test verifies the significance of the determination coefficient for α = 5%. The Student's test showed that all Newton's polynomial coefficients (3) are significant.

Simulation modelling of the dynamics of biogas output during substrate digestion based on cattle manure with the addition of molasses vinasse was carried out by solving the Simulink differential equation system package:

$$\begin{cases} \frac{dC}{dt} = \left(\frac{\mu_m \cdot S}{k_a + S} - \frac{\mu_d \cdot k_b}{k_b + S} - p\right) \cdot C \\ \frac{dS}{dt} = p \cdot (S_0 - S) - \left(k_\alpha \cdot \mu_m \cdot C + \frac{k_\beta \cdot S \cdot \mu_m}{k_a + S} \cdot C + k \cdot \rho_\mathrm{b} \cdot \rho_c \cdot \frac{dV_b}{dt}\right), \\ \frac{dV_b}{dt} = \frac{K_\gamma \cdot S}{\rho_c} \end{cases} \quad (4)$$

where: *C*—the biomass concentration of methane-forming bacteria, kg/m^3; *S*—the concentration of nutrients of the substrate absorbed by bacteria, kg/m^3; S_0—the initial nutrient concentration of the substrate, kg/m^3; dV/dt—dynamics of biogas output, m^3/(kg·day); *p*—the dilution factor of the culture by the molasses vinasse of fresh substrate, day^{-1}; *k*—the nutrient conversion factor of the substrate into biogas, kg/kg; ρ_b, ρ_c—the density of biogas and substrate, kg/m^3; k_α, k_β—dimensionless substrate absorption coefficients; k_α—a constant equal to the nutrient concentration of the substrate at which the growth rate reaches half the limit, kg/m^3; k_β—the empirical coefficient, kg/m^3; μ_d —the maximum specific rate of death of methane-forming bacteria, day^{-1}; μ_m—the maximum specific growth rate of methane-forming bacteria, day^{-1}; K_γ—the rate of conversion of substrate nutrients into biogas, m^3/(kg·days); *t*—time in days.

The known parameters of system (4) are as follows: k = 0.27 kg/kg [16], ρ_c = 1050 kg/m^3, and ρ_b = 1.212 kg/m^3 (according to their own research results); for the periodic loading of the methane tank, p = 0 days^{-1} [17], and for the quasi-continuous, p = 0.05 days^{-1}. The initial conditions for the solution of system (4) are: C_0 = 1 kg/m^3, S_0 = 115 kg/m^3 (was determined from the results of experimental studies: 8.5 kg of substrate was loaded into methane tanks with a working volume of 30 l, including 3.5 kg of cattle manure and 5 kg of water; therefore, S_0 = 3.5/(30 1000) = 115 kg/m^3), and V_0 = 0 m^3/kg. The parameters μ_m, μ_d, k_α, k_β, k_a, k_b, K_γ are unknown and depend on the temperature of the methane tank and the type of co-substrate. As a result, the dynamics of biogas output during periodic (Figure 8a) and quasi-continuous loading (Figure 8b) of the substrate were obtained.

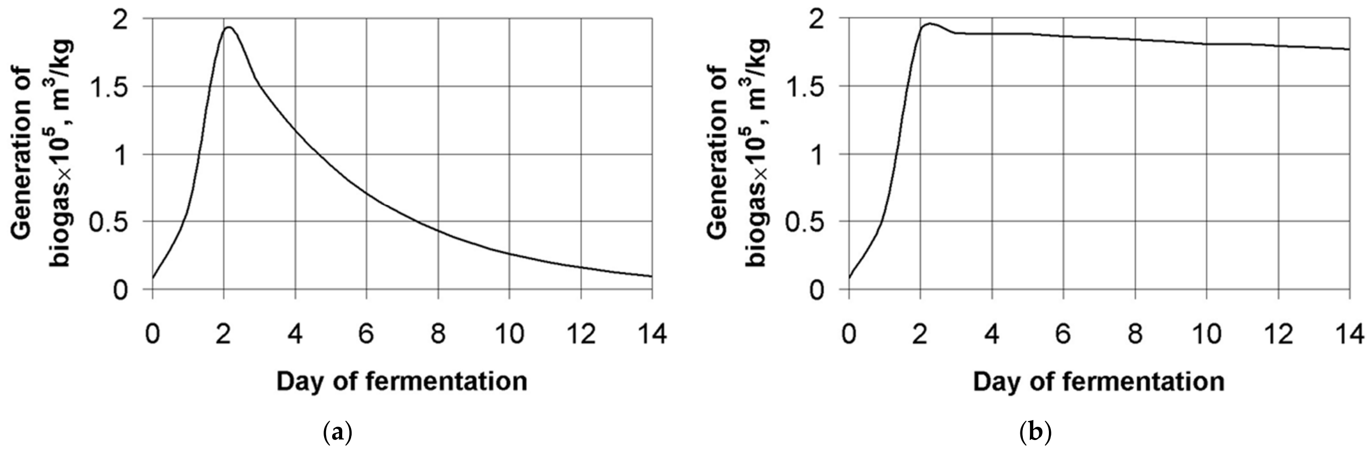


Figure 8. Dynamics of biogas output, obtained as a result of modelling the functioning of the methane tank of the biogas plant during the digestion of cattle manure with the addition of molasses: (**a**)—for the periodic mode of loading of the methane tank; (**b**)—for the quasi-continuous loading of methane tank.

By selecting the parameters μ_m, μ_d, k_a, k_b, k_α, k_β, and K_γ of the simulation model (3) and comparing the results of simulation modelling of the dynamics of biogas output during the periodic loading of the methane tank with the results of experimental research, we achieved (Figure 9) a simulated model closest to the dynamics of biogas output over time, which was obtained experimentally. The similarity criterion was the approximation of the determination coefficient R^2 to one. In the simulation modelling of all the substrates, it was assumed that $k_\alpha = 10^{-9}$, $k_\beta = 5$, $k_a = 14$ kg/m^3, and $k_b = 0.01$ kg/m^3.

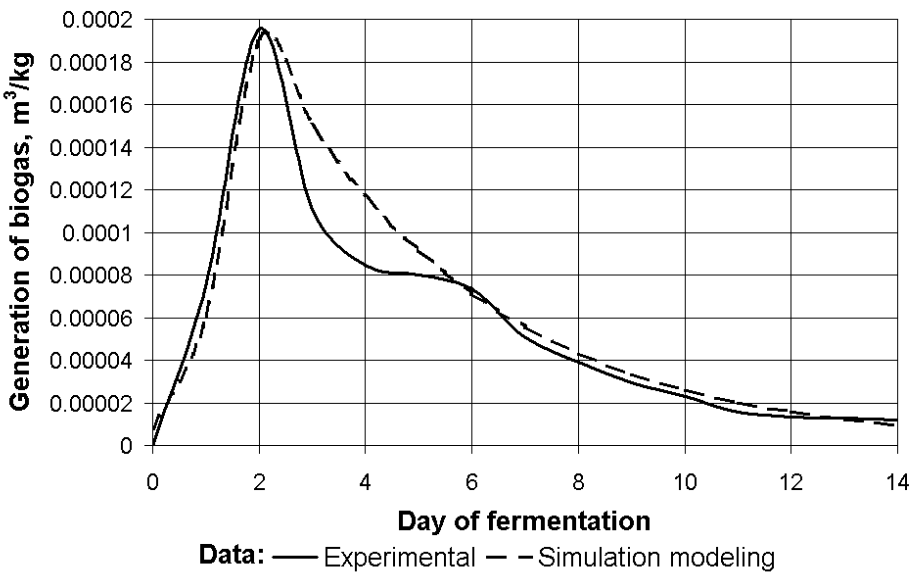


Figure 9. Results of comparison of simulation data with experimental data for cattle manure fermentation with the addition of 26.1% molasses vinasse at a fermentation temperature of 40 °C.

The coefficients of simulation models of biogas output during cattle manure digestion with the addition of molasses vinasse at a fermentation temperature of 40 °C are shown in Table 2.

Table 2. The coefficients of the simulation model of biogas output during cattle manure digestion with the addition of a molasses broth at a fermentation temperature of 40 °C.

Contents, %	μ_m, day^{-1}	μ_d, day^{-1}	K_γ, m^3/(kg·day)	R^2
10.5	0.725	0.03	0.0000033	0.8974
26.1	2.3	0.25	0.000008	0.9677

The mathematical model of the functioning of the biogas plant with determined coefficients allows the main product of the technological process to be predicted: the magnitude of the biogas output in the case of loading through the system of feeding and dosage of the substrate in a quasi-continuous mode based on cattle manure with the rational part of the molasses.

It is also important to look at the ecological efficiency of using molasses vinasse for methane digestion in a biogas plant. The methane fermentation of molasses vinasse allows it to be processed into a quality organic fertiliser, increasing the pH of the generated substrate. The filtrate can be used to fertilize crops, while the digestate helps to restore soil fertility [32]. It does not smell unpleasant, like a molasses vinasse, when it merges into the filtration fields.

Is the co-digestion of a molasses broth with cattle manure a cost-effective solution? When fermenting cattle manure from 1000 cows with the addition of 30% molasses vinasse, the estimated discounted payback period of the biogas plant (with a useful volume of 1800 m^3 worth 5.8 million euros with a cogeneration plant worth 4.8 million euros) at the "green" tariff (12.38 €ct/kWh) will be low for biogas plants and will be just 1.2 years at a discount rate of 10% (without the "green" tariff, it would reach up to 2.6 years), compared with 10.5 years for the mono-fermentation of cattle manure with the condition of sale of electricity produced from burning biogas at a "green" tariff.

So, in the process of our research, we established that a large output of biogas is observed during the mono-fermentation of molasses. However, the obtained biogas does not burn, since it contains only carbon dioxide and almost no methane, which is consistent with the studies of Barrera et al. [34], who claim that the methanogens are inhibited by sulphites that enter the molasses bard during the production of ethanol from molasses. Diluting the molasses bard with a large amount of water, as recommended by Arimi et al. [35], and neutralising the molasses with baking soda, as recommended by Miroshnichenko et al. [36], Rabii et al. [37], helps reduce its acidity to a pH of 6.7, but this does not affect the increase in methane content in the obtained biogas. Only the compatible methane fermentation of molasses with cattle manure, as recommended by Parsaee et al. [38] to increase the ratio of carbon to nitrogen, made it possible to achieve the presence of methane in biogas on the second day of methane fermentation. Therefore, molasses can be recycled by using it as a co-substrate for biogas production, as reported in the study by Kiani et al. [41]. At the same time [42], the yield of biogas will be higher compared with the yield of biogas during the mono-fermentation of cattle manure, which is consistent with the results of research by Singh et al. [39] and Siqueira et al. [40].

4. Conclusions

In the case of the combined methane fermentation of cattle manure with molasses through the periodic loading of the methane tank system, there is a more than a five-fold increase in biogas output compared with the mono-fermentation of cattle manure.

The maximum yield of biogas under the periodic system of loading the methane tank when adding 10.5% molasses to cattle manure is 1.462 l/(h kg DOM); when adding 26.1% molasses to cattle manure, it is 3.594 l/(h kg DOM).

To increase the yield of biogas, it is advisable to add molasses in the amount of 30% of the volume of the substrate to the substrate based on cattle manure.

In addition to environmental protection, the compatible fermentation of cattle manure with molasses vinasse helps reduce the discounted payback period of the biogas plant to 1.2 years at a discount rate of 10%.

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