Визначено, що найбільший вихід біогазу характерний для відходів необроблених шкір свиней. Раціональний вміст субстрату при 20 добовому зброджуванні – 7,5 %. При скороченні часу зброджування до 12 діб раціональною концентрацією субстрату є 2,5 %. Концентрація метану в біогазі складає 65–70±3,2 %, в залежності від концентрації субстрату та складу відходів виробництва

Ключові слова: переробка жировмісних відходів, біогаз, анаеробне зброджування, переробка відходів виробництва шкіри

Определено, что наибольший выход биогаза характерен для отходов необработанных шкур свиней. Рациональное содержание субстрата при 20 дневном сбраживании – 7,5 %. При сокращении времени сбраживания до 12 суток рациональная концентрация субстрата составляет 2,5 %. Концентрация метана в биогазе составляет 65–70±3,2 %, в зависимости от концентрации субстрата и состава отходов производства

Ключевые слова: переработка жиросодержащих отходов, биогаз, анаэробное сбраживание, переработка отходов производства кожи

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OBTAINING BIOGAS DURING FERMENTATION OF FAT-CONTAINING WASTES OF LEATHER PRODUCTION

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1. Introduction

The production of leather has been increasing over recent years in Ukraine and throughout the world. Production output in Ukraine currently reaches 4,000 m^2/year, and global production reaches 0.6 million m^2/year [1, 2]. Starting from 2015, an increase in the export of products of leather manufacturing has been observed [3].

A rise in the rate of production leads to the increased formation of amount of organic wastes (fats, scrapings, wool, and blood). This has negative environmental consequences, because there are no technologies for proper handling of such wastes in Ukraine. In addition, the generated organic wastes contain a large amount of inorganic salts and surface-active substances (SAS), which also complicates recycling technology.

The main waste of this industry is the fat-containing raw material that includes chemical impurities, which are added in the process of manufacturing of the product (sodium chloride, calcium hydroxide, sodium sulfide, sodium carbonate, etc.). This limits the possibilities of using these wastes for the production of soap, detergents and materials for leather greasing [4].

At the same time, fat-containing raw materials can serve as a source of feed of microorganisms and be renewable raw material for obtaining biogas. That is why the study of the possibility of formation of biogas from wastes of leather industry is relevant.

2. Literature review and problem statement

World leather industry annually manufactures about 3–3.5 million tons of solid wastes [5] that require proper handling in accordance with the standards of environmental protection [6].

The main organic waste is fat, which contains inorganic substances, SAS and other components, which are used at different stages of leather treatment. One of the main methods of recycling of fat-containing wastes of leather industry and their analogues is direct combustion or gasification with production of liquid fuel [7]. These technologies lead to pollution of the environment with greenhouse gases and the loss of the organic component, which can be used as a fertilizer.

The most effective method of recycling of fat-containing raw material is anaerobic fermentation with obtaining of biogas [7, 8]. As a rule, when using fatty waste, co-fermentation with the cellulose-containing raw material is applied to stabilize pH value.

Addition of organic fraction of solid domestic wastes as a co-substrate to fatty wastes from the slaughter house decreases the yield of methane. Biogas, obtained at co-fermentation, contained 61.9±1.4 % of methane, and without adding of substrate it contained 65.6±0.3 %. In this case, fat removal was 83 % (duration of hydraulic keeping in the laboratory setup was 50 days) [8].

A decrease in the content of methane in biogas at co-fermentation with solid domestic wastes at the ratio of 1:5 was observed when using pre-treated waste from the slaughter house (20 min at 133 °C, at a pressure higher than 3 bars). Methane content in biogas without adding co-substrate was 59.8±0.4 %, with co-substrate it was 53.5±1.0 % [9].

The method of obtaining biogas from liquid wastes of production of wet blue leather of cattle is considered in literature [10]. Recycling includes fermentation of chrome leather wastes in the form of shavings and gelatin that were thermally pre-treated, the latter is separated from chromium hydroxide in the process of initial treatment. Daily yield of biogas was 165 m^3 at loading of modified UASB reactor of 2 t, the content of methane in biogas was 51 %.

At co-fermentation of fat-containing wastes of leather manufacture (scrapings) with silt of treatment plants at the ratio of 3:2, the yield of biogas is 62.4 m^3 from a ton of raw material per day with methane content of 73 %. In this case, the 60 % degree of recycling of fatty wastes is achieved [11].

With the help of accelerated fermentation, fertilizers are obtained from wastes of leather production, for which scrapings are used simultaneously with deposits of wastewaters from an enterprise, which contain Cr^{3+} [12]. Existence of chromium makes the use of this fertilizer problematic.

In paper [13], wastes of leather industry, obtained at the stage of fleshing, are used. The wastes are characterized by alkaline pH value of 11.4, minimal ratio of C:N for the fermentation process and high content of ammonium ions. For optimization of parameters of the process, organic domestic wastes were used as co-substrate. Co-fermentation of wastes of different origin increases the yield of biogas by 16.5 % in relation to the use of pure scrapings.

There is information on studies [13] into fermentation of wastes of leather industry, obtained at the stage of fleshing, which have minimum for fermentation ratio of C:N and alkaline pH of 11.4, with organic household wastes. Addition of co-substrate in the form of organic domestic wastes optimizes a range of C:N and pH to minimize the effect of NH_4^+ ions and increases the yield of biogas by 16.5 % (from 5,600 cm^3, using only the faction of scrapings, to 6,518 cm^3 with the optimal ratio at adding organic wastes from 1 dm^3 of useful capacity of the reactor).

The industry uses the biotechnology of recycling leather treatment wastes with addition of wastewater [14]. With the help of the similar technology, the system of wastewater treatment and organic waste recycling with obtaining of biogas was created at the ECCO plant in the Netherlands in 2012. This technology allows the company ECCO Tannery to decrease the amount of wastes and replace natural gas consumption with biogas.

In the paper [15], anaerobic recycling of wastes of the leather industry with addition of rice waste as co-substrate is used. Fermentation was carried out at temperature of 35 °C with addition of a specially selected inoculate. Addition of rice waste changes the ratio of C: N, which leads to twice increased yield of biogas (from 23 to 47 dm^3 from 1 kg of raw material).

Thus, production of biogas from wastes of fat-containing raw material of leather industry is most appropriate because the use of such waste recycling technology makes it possible to solve the problems of environmental protection and obtaining power carrier and fertilizers [16, 17].

Currently existing research and technological solutions use co-fermentation with wastes from other industries to produce biogas and, basically, scrapings as water-containing raw material. At the same time, different methods of leather production are used, which gives grounds for development of the technology of obtaining biogas from wastes of leather industry, acquired at different stages. Today, there is no technological solutions regarding the use of fat wastes, which have a high concentration of mineral salts and antiseptics that are used at different stages of production. That is why it is necessary to develop technological solutions for carrying out the fermentation process for obtaining biogas from all fat-containing wastes of leather production without adding co-substrates.

3. The aim and objectives of the study

The aim of present research is to establish conditions for the fermentation of fat-containing wastes of leather manufacture to obtain a stable biogas yield.

To accomplish the set goal, the following tasks had to be solved:

– to explore the influence of the composition of the fat-containing substrate, formed at different stages of leather production, on the yield of biogas;

– to determine the rational concentration of fat-containing wastes for obtaining the maximum yield of biogas;

– to develop the technological schematic of recycling of fat-containing wastes of leather industry, which have a high content of mineral salts.

4. Materials and methods for research into fermentation process of leather production wastes and obtaining of biogas

4. 1. The examined materials and equipment, used in the experiment

The study was conducted using the wastes of various production stages of tannery “Chinbar” (Kyiv, Ukraine). Depending on technological conditions of the leather production process, fat-containing wastes differ in content of salts, superficially active substances (SAS) and other components that influence technological parameters of fermentation. The content of salts in the composition of wastes is shown in Table 1.

Table 1

Content of components in the composition of fat wastes of leather production

Entry order	Sample	Content of components
1	Product of treated skins of pigs	Na_2CO_3, $Ca(OH)_2$, Na_2S, SAS, wool, antiseptics
2	Pure swine fat	NaCl
3	Product of treated skins of cattle	$Ca(OH)_2$, Na_2CO_3, Na_2S, SAS, kaolin, wool, antiseptics
4	Product of untreated skins of pigs	Na_2CO_3, SAS

The pH of the medium was determined using the ionometer MI-150 (made by "Measurement equipment", Russia).

The mass of raw materials was determined using the analytical scale Scout PRO of model SPE-123 with an error not exceeding 0.01 g.

The moisture content of raw material was determined by drying it in the drying chamber 2B-151 (Ohaus, USA) at a temperature of 110±5 °C. Percentage of mass fraction of dry residue (X) was calculated from the formula:

$$X = \frac{m_1 - m_2}{m} \cdot 100, \ \%, \quad (1)$$

where m_1 is the mass of dry residue with the weighing bottle, g; m_2 is the mass of the weighing bottle, g; m is the mass of the batch, g.

Ash content of substrates was determined after combustion in the muffle furnace VEBKEWH (VEBKEWH, Germany) at temperature of 800 °C. Percentage of mass fraction of ash (Z) was calculated from formula (1), where m_1 is the mass of the crucible with the batch after ashing, g; m_2 is the mass of the crucible, g; m is the mass of the batch, g.

The content of ash-free dry organic substance (DOS) for loading of laboratory methane tanks was calculated from formula:

$$COP = \frac{w_{dry} \cdot (100 - w_{ash})}{100}, \ \%, \quad (2)$$

where w_{dry} is the mass fraction of dry substance, w_{ash} is the mass fraction of ash.

Moisture, ash content and content of the dry organic substance were determined three times according to standard procedures [18].

Qualitative and quantitative composition of components of biogas were determined using the gas chromatograph LCM-8-D (Moscow Experimental Plant "Chromatograph", USSR) according to the standard procedure [19].

4. 2. Procedure for conducting fermentation of fat-containing wastes to determine parameters of biogas obtaining process

To determine the yield of biogas depending on the composition of the substrate, fermentation was carried out in anaerobic reactors of volume of 0.5 dm^3 with coefficient of filling of 0.8. Temperature of fermentation was 38±2 °C (mesophyll mode) without stirring. The content of dry organic substance in the methane tank is 5 %. Fermented residue of the laboratory methane tanks of the Department of Ecobiotechnology and Bioenergetics at the National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute (Ukraine)". The amount of inoculate was 8 g.

To achieve the uniformed distribution of fatty wastes in the middle of the methane tank and to prevent phases' distribution, the substrate was applied to the surface of a fibrous inert carrier.

To determine the influence of concentration of the substrate on biogas yield and methane content in it, the authors studied concentration of fat-containing raw material in the methane tank from 2.5 to 10 % at intervals of 2.5 %. In this case, wastes of leather production were used as a substrate, which was characterized by stable yield of biogas and high content of methane in it.

5. Results of research into obtaining biogas from fat-containing wastes of leather industry

Depending on the stage of leather production, fatty wastes contain different content of organic and inorganic substances, which affects the process of obtaining biogas from the substrate. Table 2 gives composition of wastes of leather production.

Table 2

Content of dry substance and ash content of organic wastes of leather production

Sample	Moisture, %	Ash content, %	DOS, %
Product of treated skins of pigs	62,4±3,12	20,6±1,03	17±0,85
Pure swine fat	1,9±0,095	0,13±0,007	97,97±4,90
Product of treated skins of cattle	64,95±3,25	24,49±1,22	10,56±0,53
Product of untreated skins of pigs	56,88±2,84	8,13±0,41	34,99±1,75

As Table 2 shows, the highest content of inorganic salts is characteristic for the wastes, obtained after treatment of skins of cattle and pigs. The lowest content of salt is found in swine fat. The highest content of DOS is characteristic for pure swine fat, and the lowest – for wastes from cattle.

Fig. 1 shows daily yield of biogas during 12 days of fermentation for wastes from various stages of the process. As it can be seen from Fig. 1, biogas is not formed when wastes of cattle are used as a substrate. Depending on the type of wastes, the lag phase is 2–3 days. In the first six days of fermentation, the yield of biogas is higher for the substrate from treated skins of pigs, than the yield from untreated skins. For pure swine fat, the yield of biogas is lower than the one from the treated skins. In this case, at the beginning of biogas formation, methane content is 5–10 % and subsequently it increases. Starting from day 5, the concentration of methane in biogas is 50 % and reaches its maximum of 70 % on day 12 (Fig. 2). For other types of wastes, there is a similar dependence, but the maximum methane content does not exceed 68 %.

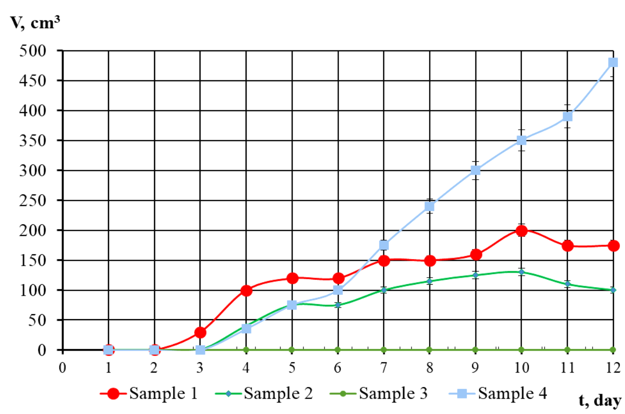

Fig. 1. Dependence of biogas yield (V) in the process of fermentation (t) on raw material of various stages of leather production: 1 — product of treated skins of pigs, 2 — swine fat, 3 — product of treated skins of cattle, 4 — product of untreated skins of pigs

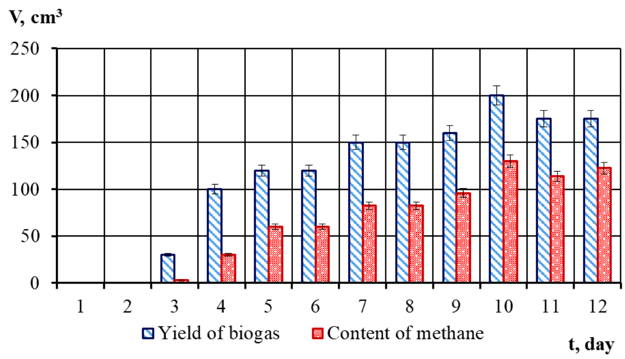

Fig. 2. Yield of methane (CH_4) and biogas (V) in the process of fermentation (t) of treated skins of pigs

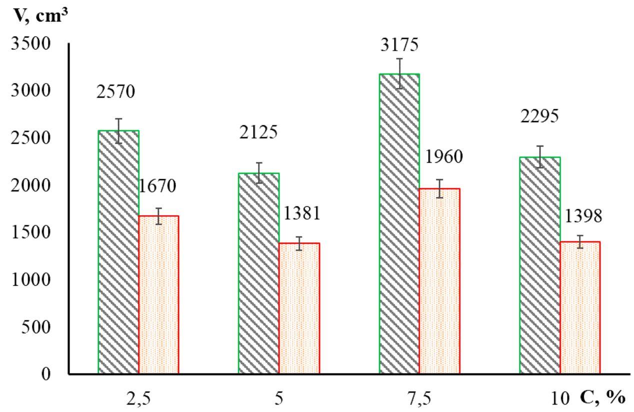

Fig. 4. Total yield of biogas and methane (V) depending on the concentration of wastes (C) in bioreactor in the process of fermentation within 28 days

Taking into account the amount of wastes, formed in the leather production process, the product of treated skins of pigs was selected as substrate when determining the optimum concentration of the substrate for obtaining maximum yield of biogas and methane content in it. Results of the research into the yield of biogas depending on concentration of fat-containing wastes in the process of fermentation are shown in Fig. 3. Fig. 4 shows the total yield of biogas and averaged content of methane for 28 days of carrying out the process. It should be noted that in this case, association of microorganisms from the previous stages of fermentation of fat-containing wastes was taken as inoculate.

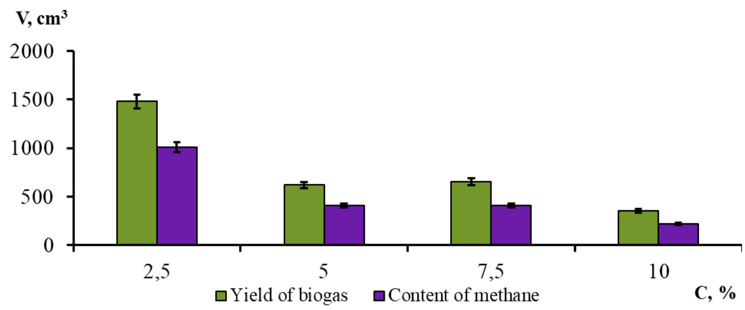

Fig. 5. Yield of biogas and methane (V) per 1 g of DOS depending on concentration of raw material (C) in fermenter

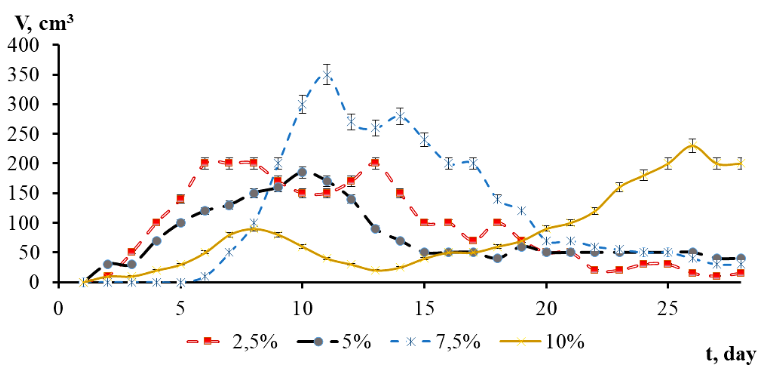

Fig. 3. Yield of biogas (V) in the process of fermentation (t) for different concentrations of fat-containing raw material: 2.5; 5; 7.5; 10 %

As Fig. 3 shows, at an increase in the concentration of substrate larger than 5 %, the duration of lag phase increases. In this case, at concentration of the substrate of up to 5 %, after day 12, the yield of biogas decreases. For concentrations of 7.5 and 10 %, the period of maximum yield of biogas is within 8–18 and 20–28 days, respectively.

As Fig. 3, 4 show, rational concentration of fat wastes for maximum yield of biogas and methane content in it is 7.5 % if the fermentation process lasts 20 days or longer. At a decrease in the duration of fermentation to 12 days, the rational concentration is 2.5 %. The concentration of 10 % is not rational for the fermentation process, since the rate of biogas yield increases only after 20 days of fermentation. This is due to the rapid formation of volatile organic acids and a decrease in pH of the medium. In this case, the content of methane in biogas at the beginning of fermentation does not exceed 20 %.

As Fig. 5 shows, the yield of biogas and methane per 1 g of DOS for fatty wastes is the highest for waste content in the medium of 2.5 %, the yield is twice as low at a concentration of 5 % and 7.5 %. That is, by increasing the concentration of substrate by 3 times, the yield of biogas increases only by 20 %, which leads to a decrease in the formation of biogas per unit of DOS.

6. Technological scheme for obtaining biogas when recycling fat-containing wastes of leather production

According to the results of research, the authors developed technological solutions of anaerobic recycling of fat-containing wastes with high concentration of mineral salts. Generalized schematic of recycling of fat-containing wastes with a high content of mineral salts with simultaneous obtaining of biogas is shown in Fig. 6.

Collection of wastes from various stages of leather production for averaging by concentration of mineral salts takes place in the tank T-1 at the auxiliary stage AS-1. Fat-containing organic wastes are sent to the stage of their crushing and homogenization to mechanical crusher Cr-2 (auxiliary stage AS-2). After crushing, the substrate by means of a screw conveyor C-3 comes for pre-treatment to the collector T-4 (stage AS-3), where there is the process of substrate moistening to the value, optimal for fermentation (90–98.5 %).

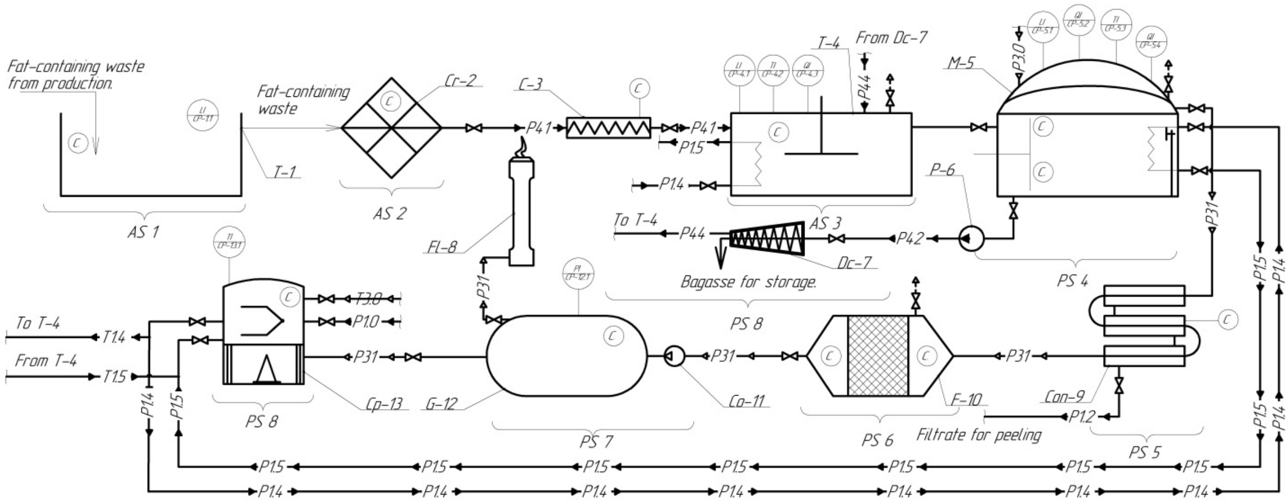

Fig. 6. Generalized schematic of recycling fat-containing wastes with high content of mineral salts and simultaneous obtaining of biogas: T-1 – waste collection tank, Cr-2 – screw crusher for crushing fat-containing wastes, C-3 – auger of feeding substrate, T-4 – tank for bringing substrate to optimal moisture, M-5 – methane tank, T-6 – pump for removal of fermented residue, Dc-6 – decanter centrifuge , Fl-8 – flame for emergency biogas combustion, Con-9 – system of moisture removal (drying) from biogas, F-10 – filter of system of purification from hydrogen sulfide, Co-11 – contactless compressor for creation of dilution and gasholder filling, G-12 – gasholder for biogas storage, Cp-13 – cogeneration plant

From the collector T-4, the substrate arrives at the production stage (PS-4) to the methane tank M-5, where the immediate fermentation process goes on for 20 days (technological parameters: T is 37±2 °C, pH is 6.8–7.2, Q_{day} is 5 % V_p).

Biogas, formed in the process of recycling of fat-containing wastes, gets into a temporary gas tank, which is located above the fermentation capacity and is a dual gas bag. From it, with the help of air injection into the intermembrane space, biogas comes to the stage of moisture removal Con-9 (PS-5) and the filter for purification from hydrogen sulfide F-10 (PS-6). Biogas, purified from moisture and noncombustible components, with the help of the contactless compressor Com-11 is blown to the gas tank G-12, from where the power carrier is used in the congregation plant Cp-13. Electric power and heat, formed in this process, may be used for own needs of an enterprise.

Fermented residue is removed from the capacity of the methane tank M-5 using the sewer pump P-6. Fermented residue enters the dehydration system, which is a decanter centrifuge Dc-7 (stage PS-8 repeat). Dehydrated bagasse, the volume of which is 15–20 times less than the amount of waste, generated after leather production, arrives to be stored on the territory of an enterprise or may be taken away to silt grounds of nearby sewage stations, the filtrate after cleaning may be re-used in the technological process.

To take all measures of safety and labor protection, the process implies the use of flame Fl-9 for emergency combustion of obtained biogas or its excess.

7. Discussion of results of biogas formation during fermentation of fat-containing wastes of leather production

The absence of fermentation process, which is typical for wastes from cattle skin (Fig. 1), can be explained by significant concentration of salts, as indicated by the value of ash content of the sample (Table 2) and composition (Table 1). Significant concentration of salts leads to inhibition of vital activity of microorganisms that participate both in the process of destruction of fat-containing substance, and in methanogenesis.

Increased content of salts (ash content of 20 %) and increased amount of SAS in wastes (Tables 1, 2) lead to a decrease in the yield of biogas in fermentation process (Fig. 1, 2). Existence of soda in wastes makes it possible to maintain pH values of the medium that are optimal for methanogenesis process. Because volatile fatty acids are formed in the course of fermentation of fat-containing wastes, it may lead to acidification of the medium and a decrease in the yield of biogas, as typical for pure fat (Fig. 1, sample 2).

In addition, due to release of CO_2, a hydrocarbon buffer is formed:

$$HCO_3^{+} + H^{+} \leftrightarrow H_2CO_3 \leftrightarrow H_2O + CO_2, \quad (3)$$

that is activated in acidic medium, but its capacity is insufficient to maintain pH value in the range of 6.5–7.5 in the case of using pure fat, as indicated by lower biogas yield and methane content (55 %) in it (Fig. 1). Pure fat also contains a small amount of mineral salts (Table 2), which also has a negative impact on development of microorganisms that need existence of microelements in habitat to provide for vital processes.

A decrease in the yield of biogas from treated skins of pigs in relation to untreated (Fig. 1) can also be explained by existence of antiseptics and organic additives in wastewater, which have a negative impact on development and vital activity of microorganisms. This leads to destruction and requires a long time for adaptation and formation of association of microorganisms, which is not only tolerant, but also able to utilize them.

Based on Fig. 3, it may be stated that the yield of biogas, depending on the concentration of the substrate, is determined by duration of fermentation. At an increase in concentration of up to 10 %, impurities, contained in waste water, have a significant impact, as their concentration increases. Accordingly, a longer term for adaptation of association of microorganisms is required, as indicated by an increase in the yield of biogas after day 20 of fermentation. An increased concentration also leads to fast acidification of the medium, since in the process of fermentation, larger amount of volatile fatty acids are formed and the yield of methane decreases (Fig. 4). Based on the obtained results, it may be stated that 10 % concentration of the substrate is not cost-effective for obtaining methane in the process of recycling fatty wastes.

Maximum yield of biogas for 28 days of fermentation was obtained by using 7.5 % of the substrate's content (Fig. 4). As Fig. 3 shows, after day 20, the yield of biogas decreases significantly and duration of the process for such fermentation should not exceed this term. A steady high rate of methane formation lasts for 10 days, and a long term of adaptation of association of microorganisms is characteristic for such concentration of the substrate as well as for the 10 % concentration. Content of methane in biogas is lower than while using 2.5 % concentration of fat-containing wastes (Fig. 4). This can be explained by the lower pH value of the process due to rapid formation of volatile fatty acids and CO_2 at degradation of raw materials.

At a concentration of the substrate of 2.5 %, a steady yield of biogas is observed, but it is lower than total yield from the unit of DOS by 23 % relative to the concentration of 7.5 %.

Lower rate of biogas formation at a lower concentration of raw material can be explained by insufficient arrival of nutrients to microorganisms and removal of metabolites from them because stirring was not applied in the fermenter.

Higher percentage of utilization of fat-containing raw material is characteristic for 2.5 % content of the substrate in the fermenter, which is proved by the value of yield of biogas and methane per 1 g of DOS (Fig. 5). A lower yield of biogas per 1 g of DOS for other concentrations can be explained by both larger amount of impurities, contained in the waste water, and greater number of acids, formed during fermentation.

Thus, to carry out the process of fermentation of fat-containing wastes from various stages of production for the purpose of obtaining biogas, the concentration of the substrate in the methane tank should not exceed 13 g/dm^3

The direction of this research makes it possible subsequently to develop the technology of recycling fat-containing wastes with a high content of inorganic salts with obtaining of power carriers in the form of biogas, which currently has no analogues. In subsequent research, it is planned to determine other technological parameters (concentration of volatile fatty acids, contents of C:N) of recycling fat-containing wastes at the pilot setup with the possibility of interpolation on industrial samples.

8. Conclusions

1. We obtained results that make it possible to state that the yield of biogas from fat-containing wastes, formed at various stages of leather production, depends on the content of impurities, which are used in the process (salts, SAS, antiseptics, etc.). The highest yield of biogas is characteristic for wastes of untreated skins of pigs that contain soda and insignificant amount of SAS. The yield of biogas by day 12 of fermentation was 480 cm^3, which is 50 % higher than that while using fat-containing wastes from other technological stages of leather production.

2. It was determined that rational concentration of fat-containing raw material for obtaining biogas should not exceed 7.5 % or 13 g (DOS)/dm^3. Under such conditions, the yield of biogas and methane for treated skins of pigs is 601 cm^3/g of DOS and 402 cm^3/g of DOS, respectively. At such content of fat-containing wastes from treated skins of pigs, effectiveness of biogas formation is 22.4 % higher than that at other ratios.

3. The proposed technology allows us to carry out the process of biogas fermentation at 10 % content of salts with the yield of biogas of 594 dm^3/g of DOS at hydraulic time of keeping in the reactor for 20 days.

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