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Prospects of Improving Biogas Technologies by Increasing Productivity of the Methane Generation Process due to Complex Processing of Organic Waste

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Abstract

This paper aimed at analysing the current state of methods of increasing methane generation during treatment of organic sewage sludge. The authors considered the theoretical principles of biogas production and the main directions of intensification of methane fermentation processes. A chemical study of sediments produced at sewage treatment plants in the city of Kharkiv, Ukraine, showed that the C/N ratio in the investigated excess activated sludge is 4-5, in the mixture of primary and secondary sediment - 5-6, in sediment from sludge sites - 6 -10, which is significantly less than the ratio of 20:1, which limits the negative impact of increased nitrogen content in organic substrate for methane fermentation. The directions for rising speed of the first phase of sediment fermentation and directions for increasing methane output during fermentation of a complex organic substrate have been determined. The promising technologies of adding organic substrates, richer in carbon compared to sewage sludge, have been noted. This solution will not only make it possible to improve productivity of fermenters, but at the same time resolve the issue of organic waste management.

Introduction

According to an approximate estimate, the total amount of sewage sludge produced at sewage treatment plants in Ukraine per year is more than 5 million tons of dry substance. The accumulation of these wastes leads to creation of dangerous ecological situations in territories adjacent to treatment plants due to the occurrence of fires, emissions of greenhouse gases and toxic substances, contamination of groundwater with environmentally hazardous compounds. At the same time, according to its chemical composition, this sediment can potentially be used as a fertilizer, and is also a highly promising substrate to produce gas fuel.

Among the positive results of realization of anaerobic fermentation of organic substrate, it is possible to note:

- Reduction of greenhouse gas emissions;
- Reduction of coal, oil, natural gas and wood use;
- Increase of safety of sewage water (anaerobic fermentation kills pathogenic microorganisms due to high temperatures and anaerobic regime);
- Increase soil fertility due to the use of non-conventional fertilizers based on digestate;
- Reducing discomfort from unpleasant smell and proliferation of insects [1-4].

Nowadays, technologies of anaerobic fermentation of sewage sludge are implemented in a very limited way at municipal treatment plants of Ukraine, for example, at Bortnytska aeration station in the city of Kyiv, at the wastewater treatment complex in the city of Lviv. Nevertheless, the issue of implementation and improvement of processes of sludge processing remains sharp and up-to-date.

During the construction of new sewage treatment plants and complexes for sludge processing, development of modernization and renovation projects of existing water drainage systems, the introduction of modern intensive technologies of anaerobic sludge processing should be provided. In addition, the issue of processing organic waste of treatment facilities should be approached in a comprehensive manner, taking into account the need to process municipal solid waste (MSW), solid and liquid organic industrial waste, animal and plant waste, waste of forest industry complex, etc.

The quality and volume of biogas (gas received from biomass) is an important aspect of this problem. Possible sources of biogas: waste of animal farms, sewage or organic substances on waste landfills. Biogas is a mixture of methane (60-70%), CO_2 and small amounts of other gases. Biogas can be used as an energy carrier for electricity generation and for heating or cooking needs. Now biogas is used mainly for combined electricity and heat generation in the block mini-thermal power plants [2].

Biomethane gas (almost 100% methane) formed either by enrichment of biogas or by gasification of solid biomass. Enriched biomethane is not different from natural gas, so it can be transported and used in the same way. Biomethane has the advantages of natural gas, while remaining carbon neutral [3].

Biogas is considered to be the most efficient sources of bioenergy, as it is a product of a rather cheap and environmentally safe way of utilization of organic waste. Designing of sludge processing plants should be directed not only and not so much at the own stabilization of organic substance, but also increase of quantitative and qualitative characteristics of biogas received.

According to the International Energy Agency IEA for the potential of biogas 570 million tons of oil equivalent (toe), its actual production in 2018 amounted to 35 million toe. The pace of development of biogas production in different countries varies depending on availability of raw materials and the level of technological processes. The largest producers of biogas in the European Union are Germany, Czech Republic, Great Britain, Italy and France. It was developed EU countries that first introduced alternative energy transition programs and systematically supported initiatives aimed at introducing new biogas technologies. According to the number of operating biogas complexes, the leaders are Germany and Italy, from the point of view of the scale of application of biogas - Denmark [1, 2]. In European practice 75% of biogas is produced from agricultural waste, 17% from organic waste of private households and enterprises, and 8% from municipal sewage and sewage effluent of separate production. In Asia, the largest number of domestic biogas stations exist in China, in Latin America - in Brazil. According to the American Biogas Association, in 2017 in the USA there were more than 2,100 biogas plants [3].

According to [4] the volume of energy produced in Ukraine from renewable sources in the final energy use in 2018 averaged 3,582 thousand toe to 7% of the total final energy consumption. Of these, the largest contribution is made by bioenergy - 77.3%. According to the energy balance of Ukraine for 2018, the total supply of primary energy from biofuels and waste amounted to 3,195 thousand toe, equivalent to the replacement of 4 billion m^3/year of natural gas. The share of biofuels in total primary energy supply is 3.4% (more than 70% of total renewable energy supply). The growth of the sector during 2010-2018 was 31% per year on average.

According to the Energy Strategy of Ukraine for the period up to 2035, the contribution of biomass, biofuels and waste to the total supply of primary energy in 2035 had to be 11 million toe, which is 50% of the contribution of all renewable sources [4]. The number of biogas producers in Ukraine was about 50 with a total installed capacity of about 100 MW. It is clear, that taking into account the large-scale military invasion of Ukraine, the existing infrastructure damage and the economic downturn, the planning of actions to achieve the development goals of the bioenergy sector will be revised.

Theoretical bases of the process of methane generation during fermentation of organic substrates

As is known, the processing of organic raw materials for methane takes place in four stages (fig. 1) in the process of metabolism and complex interactions in mixed populations of the bacterium consortium. During the process of disintegration of organic substance, products of metabolism of each group of bacteria act as a living substrate for bacteria of the next stage of decomposition. The last stage, namely the generation of methane is carried out by microorganisms (known under the general name of methanogens) belonging to the group of archea [5].

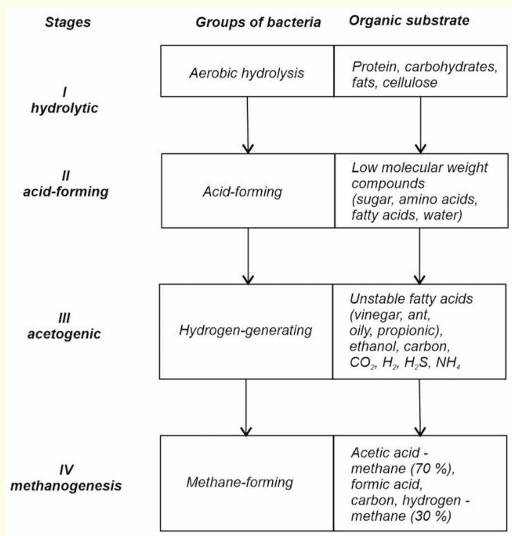

Figure 1: Stages of decomposition of organic substrate.

The disintegration of organic substances into components up to conversion into methane can only occur in water environment. Thus, for fermentation of solid substrates it is necessary to add water.

Modern biogas plants are divided into two types according to the technology of preparation and fermentation of raw materials: liquid-phase technology (humidity of fermentable organic mass more than 85%) and solid-phase (humidity of organic mass less than 85%). The solid-phase fermentation is a series of consecutive operations. Raw substance, for example, biological wastes, manure, sludge, fats or green masses, put in hermetically sealed fermenter and, as a rule, warm and stir. Thus, as a result of anaerobic processes, biogas is formed. Applying of liquid-phase technological processes is more common in practice of use of biogas plants. This process consists in continuous introduction of small portions of incoming raw material into the fermenter, which is a tank-mixer without access of air, where humidity and temperature are maintained [6].

Stage-by-stage decomposition of organic substance occurs unevenly because different groups of bacteria work at different speeds. Acid-forming bacteria work the fastest processing organic substrates for a period of time from several hours to two days. Ideally, between stages of decomposition is established a dynamic balance in the concentration of substances, namely between the supply of nutrients and their dissolution [5].

The main technological parameters determining efficiency of the process of anaerobic fermentation of sediments are their chemical composition, temperature and duration of fermentation, loading on organic substance, concentration of loading sludge, as well as mode of loading and mixing of contents of fermentation chamber.

The chemical composition of sewage sludge (absolute concentrations of biological elements - carbonic, nitrogen, phosphorus and their ratio, concentration of individual compounds - carbohydrates, proteins, lipids, etc.) influences on the composition of biogas produced, and kinetic indices of individual stages of fermentation. This influence is carried out both directly (as the sediment is the source substrate of fermentation) and indirectly, as the chemical composition of sludge is also a parameter that makes selection of the composition of microbiological consortium that carries out the process.

The main components of the ash-free part of sediment and activated sludge are protein, fat, carbon-containing substances, which in sum make up 80-85%. The other 15-20% comes from the part of lignin-humus complex compounds, which, as literature data [5] show, are practically not subject to destruction during anaerobic enzymatic metabolism and are an inert substrate for this process.

The most frequent mistake is overload of bacteria with substrate which is quickly fermented. It leads to accumulation of acids as a result of life activity of acid-forming bacteria. In this connection, a very sharp fall in pH level may occur, which other types of bacteria cannot withstand. In addition, excessive concentration of the produced substance leads to delay growth of a group of bacteria that produce it.

Dynamic balance is also determined by ease of the substrate decomposition. Sugar and starch, for example, because of its simple structure are decomposed very quickly and require only a short stay in the fermenter. The more complex structure of the substrate, the longer the decomposition will take. Cellulose and hemicellulose - high molecular polysaccharides - have wide-spread structure and are decomposed slowly [5]. Lignin is a lignified substance of plants, heterogeneous aromatic polymer, the amount of which increases with the age of the plant, is decomposed by bacteria very bad because it shows stability even to the action of acids [5]. The speed of substrate disintegration has a direct influence on technically necessary time for fermentation.

Facilitating contact of anaerobic bacteria with organic substrate is provided by mixing substrate, but intensive mixing should be avoided, as this may lead to emergence of oxygen in the content and cessation of anaerobic fermentation due to the violation of symbiosis of anaerobic acetogenic and methanol bacteria. In the absence of mixing biomass in the reactor, after some time the separation of biomass with formation of layers is observed due to difference in density of particular mineral and organic components, and also due to flotation of particles in gas-flow. At that, most of biomass of anaerobic bacteria is located in the bottom part of the reactor, and the organic part of the substrate is accumulated in the top part of the reactor. The effect of this is that the area of contact of anaerobic bacteria with substrate biomass is limited by the boundary layer of specified parts of the reactor. Floating crust of solid organic substances also blocks the output of biogas. In practice, a compromise is achieved due to slow rotation of stirrers or their operation for a short time.

In the study [6] constructive-technological and microbiological methods of intensification of processes of methane fermentation are emphasized. Preparation of raw materials, mixing, distribution of the process of methane fermentation at the stage [7], maintenance of optimal temperature are assigned to design and technological methods. To microbiological methods - cultivation of new strains of microorganisms, use of additives stimulating oxidation processes, immobilization of microorganisms on the carrier, joint fermentation of organic substrates.

Methods of increasing methanol generation also include the influence of soft thermal pre-treatment (50-120°C) of sediment with low content of organic substances. Results of experiments [8] showed that concentration of soluble organic substances gradually increased with increase of temperature during soft thermal preliminary treatment of excess activated sludge. In addition to the solubilization, the increase in total microbial activity, the increase in the number of methanol and biochemical methane potential was noted.

As an additive that stimulates the fermentation process of active sludge influence of CaO_2 in combination with microwave irradiation was examined [9]. The influence of these factors in CaO_2 adding modes with a dose of 0,1 g/g sediment / microwave processing (480 W, 2 min) allowed to reach an increase of CH_4 output by 80.2% after 16 days of anaerobic fermentation compared to control. The effect is explained by increased activity of hydrolytic and acid-forming enzymes, as well as methanol enzymes, easier solubilization, biodegradation and further intensification of anaerobic fermentation of active sludge. An increase in the dewatering ability of stabilized active sludge is also noted.

At the same time, some researchers [10] draw attention to the fact that not all pretreatment technologies have energy self-sufficiency for implementation in production conditions of treatment plants if they require continuous energy investment. As a general rule, the pretreatment that consumes electricity does not meet the energy demand from biogas production in the same process, although high solubilization or increased biogas production is achieved.

One of the most important factors affecting methane fermentation (biogas release) is the ratio of carbon and nitrogen (C/N) in processed raw materials (Table 1). For effective fermentation, the ratio of COD/N/P in the sludge should be 700/5/1. If the C/N ratio is excessively large, the lack of nitrogen will limit the fermentation process, and if it is too small (less than 20/1), then excess nitrogen in the form of ammonia formed will be toxic to bacteria.

Biofermented substance	***Nitrogen N, %***	***Ratio of carbon and nitrogen C/N***	***Gas production (m^3 per 1 kg of dry substance)***	***Methane content, %***
Animal manure				
Cattle	1.7–1.8	16.6–25.0	0.250–0.340	65
Chicken	3.7–6.3	7.3–9.65	0.310–0.620	60
Horse	2.3	25.0	0.100–0.300	56–60
Porcine	3.8	6.2–12.5	0.340–0.580	65–70
Sheep	3.8	33.0	0.300–0.620	70
Household waste				
Sewage, feces	6.0–7.1	6.0–10.0	0.310–0.740	70
Kitchen	1.9	28.6	0.330–0.500	50–70
Potato skins	1.5	25.0	0.280–0.490	60–75
Cabbage	3.6	12.5		
Tomatoes	3.3	12.5		
Plant dry waste				
Cereal straw	1.0	49.9	0.200–0.300	59
Wheat straw	0.5	100.0–150.0	0.200–0.300	50–60
Corn straw	0.8	50.0	0.380–0.460	59

Table 1: Nitrogen content, carbon-nitrogen ratio, biogas production and methane content for different types of organic substrates [5].

The need to improve the anaerobic fermentation of sewage sludge to obtain methane is due to the low C/N ratio in them and, accordingly, the low efficiency of fermentation, which leads to a relatively small production of CH_4. Consequently, increasing or balancing the low C/N ratio by mixing sewage sludge with other carbon-rich substrates is considered to be a solution that will provide an opportunity to improve the productivity of fermenters, and at the same time solve the problem of handling other organic wastes.

Co-fermentation (co-digestion) of organic substrates involves the processing of several types of waste in one reactor. It is expected that this association will have a positive effect both on the process of anaerobic fermentation itself and on its cost-effectiveness. The effect is achieved by changing quantitative and qualitative parameters - increasing the production of methane and improving stability of the process.

The purpose of the research is to analyse the existing trends of adding organic substrates to sewage sludge to increase the productivity of the methane generation process, as a result of which it is possible to achieve an increase in amount of energy production from alternative fuels (in particular, from biomass), use non-traditional fertilizers and reduce the negative impact on the environment.

The world trends in the co-digestion of sewage sludge and organic waste fraction

As it was indicated, the main co-substrates for improving and increasing the efficiency of the methanization technology of organic waste based on their anaerobic processing are municipal solid waste (MSW) and waste of animal and plant origin (Fig. 2).

The situation regarding MSW management varies in different developed countries and regions. The largest amount of waste is generated by inhabitants of America, mainly the USA, and most of waste here is still taken to landfills (60%). Recycling and composting of waste is most developed in European countries (38%). Thermal treatment of waste is used in countries of Asia and the Pacific region (48%), as well as in Europe, in addition, more than 90% of waste that is burned is used to obtain energy [11].

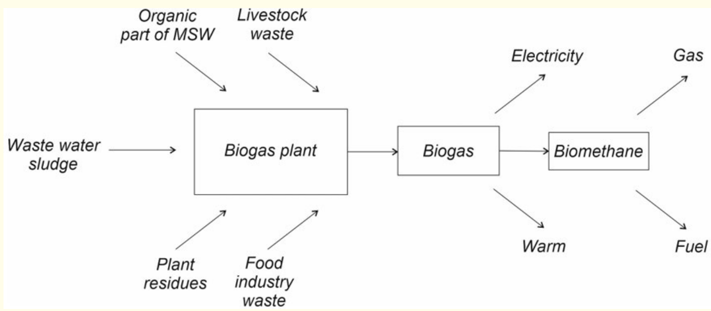

Figure 2: Types of substrates for co-fermentation with sewage sludge.

In Ukraine, in 2020, more than 54 million m^3 of household waste, or more than 10 million tons, was generated, 94% of which was buried in 6,000 garbage dumps and landfills with a total area of almost 9,000 hectares [12]. The number of landfills that are overloaded with waste is 261 units (4.3%), and 868 units of landfills (14%) do not meet sanitary and environmental standards. The need for the construction of new landfills is 318 units.

Due to implementation of separate collection of household waste in 1,725 settlements, the operation of 34 waste sorting lines, 1 waste incineration plant and 3 waste incineration facilities, about 6.3% of household waste was processed and utilized, 1.7% of which was burned, and 4.6% of MSW got into recycling points and waste processing lines [12].

A fact worthy of attention that separate collection, reuse, recycling and energy use of MSW compete with each other for raw primary products but are not mutually exclusive. According to expert assessments, biogas extraction systems have been installed at 26 landfills in Ukraine, and power generation plants with a capacity of 30 MW are in operation. The amount of utilized biogas in 2020 was 64.0 million m^3 (50% methane). The amount of electricity produced in 2020 is 112.3 GWh [11].

In Ukraine, there is no sufficient experience of combined processing of the organic part of MSW with sewage sludge, but there is sufficient experience abroad. At the wastewater treatment plant of a city with a population of 95,000 inhabitants, an 18-month study [13] of the effect of co-fermentation of organic sediments and the organic fraction of solid waste allowed to note a two-fold increase in efficiency of the process without any violations. Biogas production increased from 1,321 to 2,723 m^3/day. The produced energy increased from 4,000 to 8,100 kWh per day. Due to the obtained result, up to 85% of energy demand was covered by own electricity production.

At the same time, the quality of added MSW is important. The practice of collecting and sorting garbage considering its origin and suitability for recycling or secondary use is only developing in Ukraine. However, sorting in production conditions at waste processing enterprises can be done mechanically or depending on the origin of waste.

Research and calculations carried out for anaerobic digestion of waste from an urban sewage treatment plant for the city of Kayseri (Turkey) with a population of 1 million inhabitants [14] showed that about 77% of the plant's electricity needs can be compensated by co-digestion of the plant's primary sediments and mechanically sorted MSW. At the same time, adding the same amount of waste sorted by origin to sewage sludge allows covering almost 100% of the plant's energy needs. Both results are promising considering that fermentation of only primary sludge compensates only 30% of internal energy demand at treatment plants.

The idea of implementation not only low-waste and zero-waste technologies into production in individual technological processes of economic entities, but also the use of waste as secondary raw materials in integrated enterprises, their associations and other branches of national economy is in the plan of complex use of raw substance of food industry [15].

It was noted [16] that in 2010-2016 a downward trend is generally observed in the dynamics of agricultural, forestry and fishery waste. If in 2011 subjects of agriculture, forestry and fisheries produced 12.2 million tons of waste, then in 2013 - 10.3 million tons, in 2014 - 8.45 million tons, in 2016 - 8.72 million tons. That is, in 2016, compared to 2011, the volume of waste generated in agriculture, forestry, and fisheries decreased by 3.5 million tons. However, the amount of waste generated by the food industry remains significant, and once again, the positive global experience of using it deserves attention as co-substrates during the fermentation of sewage sludge.

The work [17] investigated the addition of production waste from fish processing and lawn grass for fermentation together with sewage sludge to determine the optimal mixture that ensures the most efficient production of CH_4. It was found that increasing the concentration of fish waste during co-fermentation with sewage sludge gradually improved the final methane production up to 1.9 times when 75% fish was added. Turf grass improved final sludge methane production only when more than 25% grass was added. Addition of more than 50% grass increased productivity and final production by 1.5 and 1.7 times, respectively. The use of 75% fish waste or lawn grass as a co-substrate with sewage sludge allowed to obtain the maximum final production of methane.

The study of operation of anaerobic reactors of the Tehran waste water treatment plant (WWTP) was carried out in the mono-mode fermentation of sewage sludge and together with floated fat waste from slaughterhouses, bio-waste and cattle manure [18]. The results showed that addition of fats, biowaste and manure to the sludge increased the average amount of biogas produced from 10,524 m^3/day (62.1% CH_4) to 29,161 m^3/day (61.5% CH_4), 30,183 m^3/day (59.5% CH_4) and 32,531 m^3/day (53.8% CH_4), respectively. Also, the output power of the gas engine increased from an average value of 906 kW to approximately 2.5 MW (for the investigated period of operation). In addition, it was found that all three co-digestion processes did not place a new burden on other WWTP equipment used to reduce nitrogen content in WWTP wastewater.

At the same time, the authors in [19] draw attention to the problem of presence of inert impurities in food waste. Other challenges include regulatory uncertainty regarding waste supply fees, challenges related to collection and pre-processing of food waste, the impact of co-digestion on biosolids reuse and biogas utilization, and a lack of design and operational experience. Addressing these bottlenecks requires an interdisciplinary approach to promote co-fermentation of food waste and sewage sludge as one of the key technologies of circular economy.

Plant growing as an agricultural industry generates a large amount of plant waste every year. They are divided into primary formed as a result of harvesting, and secondary formed during its processing at enterprises. Primary waste includes grain straw, as well as corn and sunflower production waste (stalks, sticks, etc.). Secondary waste includes buckwheat and sunflower husks, rice and beet pulp. Part of waste is used for needs of own agriculture (organic fertilizers, animal feed), another part is used in other sectors of economy, and the rest of the biomass is idle. Its potential is often neglected, so it is simply burned in an open space or thrown into a landfill.

Livestock complexes have a problem of formation of a large amount of manure and droppings due to the vital activity of animals. According to the State Statistics Service of Ukraine, as of 2020, there were approximately 13 million livestock in the country. This type of waste is very "picky" about its processing and disposal methods. Its thermal disposal and storage in landfills of MSW has a number of disadvantages: rapid accumulation of landfills, incomplete destruction of combustible waste, toxicity and hygienically dangerous bacteriological composition and formation of carcinogenic compounds.

The advisability of co-fermentation of raw sewage sludge and chicken manure is shown in [20] as such that it can increase the total amount of biogas production, improve the waste treatment process and obtain ecologically clean sludge through the co-fermentation process than separate treatment of each raw substance.

The authors in [21] investigate not only the influence of the mixing ratio of excess sludge with chicken droppings on methane production in thermophilic and mesophilic fermentation modes, but also the influence of co-fermentation on the digestate dehydration process. Compared to anaerobic digestion of excess sludge alone, co-digestion with chicken manure increases methane production by 82.4-123.1 ml/g (mesophilic mode) and 33.9-171.3 ml/g (thermophilic mode), respectively. Also, the research results showed that joint anaerobic fermentation of excess sludge and chicken droppings, provided correct ratio of components of the mixture (1:1.5-2) can ensure a high production of methane and adequate dehydration of the digestate.

During the study of joint fermentation of active sludge and animal manure, an analysis of glucocorticoid degradation was carried out in [22]. These drugs are widely used in medicine and veterinary medicine, consequently, their residues and derivatives are contained in domestic sewage and manure and are now widespread in the aquatic environment and have reached levels that negatively affect humans and aquatic organisms. This has been especially noted in recent years, as glucocorticoid drugs are used extrinsically to treat patients infected with the new coronavirus of 2019 (COVID-19). The research results showed that joint fermentation of activated sludge and chicken manure made it possible to achieve the breakdown of glucocorticoids up to 99% at a 1:1 ratio of components of the mixture at 55°C and an initial pH of 7. At the same time, the volume of processed sludge was reduced by 30% compared to mono-fermentation.

Experimental study of indicators of fermentation of sediments of biological sewage treatment plants in the city of Kharkiv

Technical solutions for the implementation of co-fermentation technologies of organic substrates with the aim of increasing methane generation, improving indicators of treated sediment and reducing the negative impact on the environment can be proposed for municipal wastewater treatment complexes of Ukraine of different productivity. Thus, one of the significant complexes of biological wastewater treatment and processing of sediments in the eastern part of Ukraine are aeration stations of the city of Kharkiv.

The drainage system of the city of Kharkiv is completely separate and decentralized. Wastewater is transported to two biological treatment complexes with the help of pumping stations and main collectors - City sewage treatment plant No. 1 (CSTP No. 1) and City sewage treatment plant No. 2 (CSTP No. 2), which are located in the southern part of the city. The average daily volume of wastewater entering the city's sewage treatment plants in Kharkiv reaches more than 500,000 m^3. And in the summer period, this figure increases by 30%.

In addition to the collection and disposal of wastewater, the task of Municipal Enterprise "Kharkivvodokanal" is to clean it at the CSTP No. 1 and CSTP No. 2 as the final stage of providing water drainage services. Wastewater coming from approximately two-thirds of the city is treated at the CSTP No. 1 (project capacity of CSTP No. 1 - 750,000 m^3/day). Wastewater coming from approximately one third of the city is treated at the CSTP No. 2 (project capacity of CSTP No. 2 - 300,000 m^3/day). The total volume of sediments at biological treatment plants, as a rule, does not exceed 1% of volume of treated effluents, while activated sludge accounts for 60-70%

of the sediments that are formed.

Among the sediments formed at sewage treatment plants, three main types can be distinguished:

- Excess activated sludge discharged from secondary sedimentation tanks;
- A mixture of sediments discharged from primary and secondary settling tanks;
- Sediment from silt sites.

According to the existing technological scheme, sediments produced at the CSTP No. 1 are pumped to the CSTP No. 2, where they are treated together with sediments produced at the CSTP No. 2. To dewater the mixture of raw sludge and excess activated sludge produced at the CSTP No. 1 and CSTP No. 2, sludge sites and a mechanical dewatering workshop are used.

In view of today's requirements, the issue of liquidation of dehydrated sludge after mechanical dewatering, as well as a large amount of sediments accumulated on sludge sites, remains unresolved. The existing situation has a negative impact on surrounding natural environment and worsens the sanitary-epidemiological condition in the area where sewage treatment facilities are located.

In this work, for experimental studies, sediments removed from primary clarifiers and from secondary clarifiers of the biological treatment complex of Kharkiv were used. The dry weight of the sediment samples was 8.0-10.0 g/l, pH - 6.9-7.5, COD - 12,000-14,000 mg/l, sulphate concentration - 189-240 mg/l, total nitrogen - 18-28 mg/l, nitrates - 23-38 mg/l. The selected sediment samples were thickened by centrifugation and stored in a refrigerator at a temperature of 4-6°C.

A chemical study of three types of sediments formed at water treatment plants in the city of Kharkiv was conducted (Table 2). In the table 2, for comparison, similar characteristics of manure as a substrate, which is most often used for fermentation with the production of biogas, are given.

The C/N ratio in investigated excess activated sludge is 4-5, in mixture of primary and secondary sediment - 5-6, in sediment from sludge sites - 6-10, which is much lower than the ratio of 20:1, which limits the negative impact of increased nitrogen content in an organic substrate for methane fermentation.

Indicator	***Concentration in sewage sludge, %***					***Concentration in manure, %***
	***Literary data* [23]**		***Complex of biological treatment of the city of Kharkiv***			
	Sediments from primary settling tanks	***Excess activated sludge***	***Excess activated sludge***	***A mixture of primary and secondary sediment***	***Sediment from sludge sites***	
Humidity	92–96	96–99.2	99	98	89	65
Ashless substance	65–75	70–75	66–74	71–78	50–58	
including proteins	28–32	41; 40–44	38–42	36–40	32–35	
lipids	25–30	25; 18–23	16–20	23–29	22–25	
carbohydrates	14–18	14; 4–7	4–6	10–14	8–10	
C		51.4	40–49	34–39	29–35	43.8
N	5–6	8–10	9–10	7–8	3–6	1.75
P	1.4	3–4	3.0	1.5	1.1	3.05

Table 2: Composition of organic sewage sludge.

It is known that increased content of ammonium nitrogen formed due to high content of nitrogen compounds in the fermentable substrate, suppresses the fourth phase of anaerobic decomposition of organic substrates with the production of biogas - methanogenesis, and does not have an inhibitory effect on previous phases. Based on the mechanism of fermentation of proteins and amino acids, it can be predicted that nitrogen-containing compounds present in sewage sludge will contribute to the microbiological process of formation of nitrogen-containing reduced products that reduce methane output during methanogenesis. In obtained biogas concentration of ammonia will also be significantly higher than during fermentation of traditional carbon-containing substrates - waste from crop production, forestry, woodworking, etc. Thus, effective methanogenesis during fermentation of all investigated sewage sludge requires use of additional organic substrates with a low content of nitrogen compounds (co-fermentation).

Laboratory studies on fermentation of sewage sludge were carried out at a temperature of 25-30°C in a bioreactor (fermenter) with a volume of 1 liter. Based on the peculiarities of chemical and microbiological composition of sewage sludge and experience of operating fermenters, sterilization of media and equipment was not carried out. The entire volume of the reactor was filled with a sludge mixture, and additional air was pushed out of the reactor and purged with inert gases was not carried out. The depth of anaerobicity of medium in the bioreactor was controlled by measuring the redox potential in the fermentable medium. Mixing of sediments in the reactor was carried out using a magnetic stirrer.

The concentration of volatile fatty acids (VFAs) was analysed by the volumetric method after distillation [24]. Propionic, butyric, and valeric acids were detected by thin-layer chromatography on silica gel plates. Total carbohydrates and monosugars, proteins and free amino acids, fatty acids, alcohols, and aldehydes were detected using methods recommended in special literature on general biochemistry and biochemistry of microorganisms [25-27]. pH of liquid media was measured electrometrically using a combined glass electrode, Eh was determined electrometrically (using a platinum electrode, it was measured relative to a chlorine-silver reference electrode) [24]. The proteolytic and amylolytic activity of sludge was determined according to methods described in [25]. Microbiological studies were performed according to [26, 27].

Preliminary alkaline treatment of sewage sludge consisted in bringing the pH of sludge to 12.0 (± 0.1) using a solution of 6 M/l sodium hydroxide, followed by stabilization for about 5 min with stirring. The sample was stored at room temperature (17-24°C) for 12 h [28].

Fermentation of sewage sludge by spontaneous microflora of activated sludge was experimentally studied by analogy with the traditional technology of fermentation of sewage sludge in fermenters. Moreover, as evidenced by data of studies of gas media [28], spontaneous microbiological processes in wastewater led to deep fermentation of organic substrates to the formation of methane above sewage facilities where there was no forced aeration (Table 3).

Compounds	***Concentration in gaseous emissions***
H_2S, mg/m^3	2–100
CH_3-S-CH_3, mg/m^3	(1–4) · 10^{-4}
SO_2, mg/m^3	5–30
NH_3, mg/m^3	0–10
NO_x, mg/m^3	0–5
CO, mg/m^3	4–25
CO_2, volume %	0.1–1.5
CH_4, volume %	0.5–6.0
H_2, mg/m^3	15–100

Table 3: Chemical composition of gas emissions from non-aerated sewage facilities.

It is known that microbiocenosis of activated sludge is a complex consortium, which includes not only methane-producing bacteria, but also microorganisms that actively carry out previous stages of fermentation - disintegration, hydrolysis, acidogenesis and acetogenesis [2, 16-18]. In experimental studies during fermentation of excess activated sludge in contact conditions after reaching the stage of methanogenesis - the formation of methane, the sediment was used as an inoculum for fermentation of a new batch of sediments. Volume of inoculum was 1/10 of the sediment subjected to fermentation.

As is known, fermentation of organic substrates to methane production includes 4 stages (phases) [23, 29]. To determine the duration of the first three stages of mesophilic fermentation of sewage sludge in a liquid medium, the content of proteins, free amino acids, carbohydrates, VFAs, particular VFAs, ethanol, aldehydes and ketones was controlled qualitatively and quantitatively. The end of the first phase of fermentation (disintegration and hydrolysis) was determined by decrease in pH of medium, the detection and increase in the concentration of VFAs, as well as particular VFAs. The end of the second phase (acidogenesis) was determined by detection and increase in the concentration of acetate in liquid medium. The end of the third phase of fermentation (acetogenesis) was determined by stabilization and subsequent decrease of acetate concentration.

Monosugars, proteins and free amino acids are identified among the products of the first stage of fermentation. Among products of the second stage of fermentation, monocarboxylic acids are identified: propionic, butanoic (butyric), pentanoic (valeric). In products of the second stage of fermentation, alcohols and aldehydes were also detected, and Eh was set to -400 mV, which indicated a deep deoxygenation of the medium. Acetic acid and minimal concentrations of other monocarboxylic acids were detected in products of the third stage of fermentation.

Thus, based on obtained data, fermentation took place in a classical way with the formation of products established by other authors during studies of methane production by fermentation of various organic substrates [23, 29].

The established indicators of duration of each of phases of sewage sludge fermentation are presented in the table. 4.

Sludge	***Duration of stages (phases), days***		
	I phase – disintegration (decomposition) of microbial cells and hydrolysis	***II phase - acidogenesis***	***III phase - acetogenesis***
Excess activated sludge	7–9	3–4	4–5
Mixture of primary and secondary sediments	6–8	3–4	3–5

Table 4: Duration of different stages of sewage sludge fermentation.

As can be seen, the first phase - disintegration of microbial cells and hydrolysis of biopolymers - proteins, lipids and carbohydrates - had the longest duration in fermentation of sewage sludge. On the basis of these data, it can be assumed that the process of fermentation of sediments to methane is limited by low hydrolytic activity of sludge.

In experimental studies, separate hydrolytic activities of excess activated sludge (sludge from secondary settling tanks) were determined in relation to proteins and carbohydrates (proteolytic and amylolytic) (Table 5).

Enzyme activity	***Proteolytic activity, (μM tyrosine)·(g of dry substance·min)$^{-1}$***	***Amylolytic activity, (mg of starch)·(g·min)$^{-1}$***
Excess activated sludge	2.5	8
Protein desorbed from activated sludge	11.9	72

Table 5: Hydrolytic activity of microbiocenosis of excess activated sludge.

As can be seen from the table 5, activated sludge has a lower hydrolytic activity than enzyme preparations isolated from the same sludge, as well as than some bacteria, and even more so microscopic fungi. This is caused by presence of inert organic and inorganic mass, dead microorganisms and microorganisms with low hydrolytic activity in sludge biomass.

Based on obtained data, we suggest increasing speed of the first phase of sediment fermentation in several ways:

- Enrichment of inoculated biocenosis with hydrolytic enzyme preparations;
- Enrichment of inoculated biocenosis with microorganisms that have high hydrolytic activity;
- Application of co-fermentation technology;
- Preliminary chemical treatment of sediments - alkaline or acid hydrolysis.

Pre-treatment of sewage sludge using temperature, alkalis and acids significantly accelerates fermentation, as it promotes cell disintegration and hydrolysis of biopolymers. Approbation of this technology during fermentation of sewage sludge in the city of Kharkiv showed positive results (Table 6).

Sludge from sewage treatment plants subjected to fermentation	***Output value pH***	***Duration of I and II phases of fermentation, days***
Excess activated sludge without pretreatment	7.0-7.5	10–13
Excess activated sludge with preliminary alkaline treatment	11.0–11.3	1–2

Table 6: Indicators of anaerobic fermentation of sewage sludge after preliminary alkaline treatment.

According to our research, the optimal pH values for following phases of fermentation of sewage sludge by an auto-selection consortium after disintegration and hydrolysis are:

- For the acidogenesis phase - 4.5-5.5;
- For the phase of acetogenesis of volatile fatty acids (VFAs) - 5.8-6.7;
- For the phase of methanogenesis - 6-8.

Analysis of results of experimental studies and materials of scientific and technical literature allow choosing optimal physicochemical parameters of sewage sludge fermentation biotechnology, which ensure a high rate of biogas generation after preliminary alkaline treatment.

In our research, the composition of microbiocenosis formed in the bioreactor was monitored during fermentation of sewage sludge from the city of Kharkiv (Table 7). It was established the presence of high concentrations of sulfate-reducing bacteria in activated sludge in deep anaerobic conditions. This can be explained by the creation of optimal conditions for development of bacteria of this eco-trophic group: the presence of easily oxidizable organic substrate (VFAs), reducing conditions, anaerobiosis, high concentration of sulphates in the medium. The concentration of sulphates reaches 180-240 mg/dm3 in the wastewater treated at CSTP No. 1 and CSTP No. 2. Sulphate-reducing bacteria during reduction of sulphates form hydrogen sulphide, which can negatively affect further fermentation of such sludge, quality of biogas, and the production of methane: firstly, due to active inhibition by hydrogen sulphide of vital activity of other groups of bacteria, especially methanogens, and secondly, due to their selection of what is necessary for methanogenesis hydrogen, which is formed in the third phase, for autotrophic reduction of sulphates, thirdly, due to an increase in content of hydrogen sulphide in generated biogas (with extremely negative operational consequences for further use).

Microbiocenoses	*Saprophytes*	*Concentration of microorganisms, cells/g dry. substances*				
		sulphate reducing	*thione*	*ammonifying*	*denitrifying*	*nitrifying*
Activated sludge from a secondary sedimentation tank	10^{10}–10^{12}	10^5	10^3	10^{11}	10^6	10^{6}
Activated sludge from a laboratory fermenter	10^7–10^8	10^8–10^9	0–10^2	10^7	10^8	0

Table 7: Characteristics of the microbiocenoses.

It was experimentally established that to reduce the negative impact of this ecological-trophic group on production of a useful product, the concentration of sulphate-reducing bacteria must be maintained at a level of no more than 106 cells/g of sediment.

The main directions of increasing in production of methane during fermentation of a complex organic substrate - sewage sludge, and increasing the economic indicators of the process are:

- An increase in the C/N ratio in the sediment used for fermentation;
- Increasing the speed of all processes (disintegration and hydrolysis, acidogenesis, acetogenesis, methanogenesis) of fermentation;
- Suppression of groups of microorganisms whose metabolism inhibits methanogenesis - sulphate-reducing.

The most promising methods for intensifying the first two stages of fermentation during the processing of sewer sludge are represented by the front processing of alkali. And the complex implementation of indicated areas of improvement of methane fermentation of sewage sludge can be resolved by co-digestion technology.

Perspectives of increasing productivity of methane generation process due to co-digestion of organic waste

There are potentially paid and free resources in Ukraine. Paid raw materials are plant waste which must be processed, collected and harvested in advance. Paid raw materials include such types of substrates as silage corn, sweet sorghum, sugar beet, cereal straw. Since this type of raw material is not profitable for production, it is usually not used as the only substrate, but on the contrary, complements the nutrient function of the substrate for bacteria.

Free raw materials include unpaid substrate or those for which the waste producer has paid for disposal. This type of raw material includes organic fractions of animal waste, food production waste, household waste, organic sludge from sewage treatment plants, as well as organic fractions of MSW landfills.

Therefore, considering the technical possibility, availability and quantity, promising substrates for anaerobic fermentation in Ukraine can be chicken droppings, cow and pig manure, sugar cane pulp and plant residues. Among plant residues, straw and corn stalks have the main potential for biogas production. In Ukraine, in general, higher harvest tend to increase the overall probability of crop residues. However, due to the rational approach to the disposal of this type of waste, special attention is paid to such a product as digestate, because it is suitable for use in the fields, instead of mineral fertilizer.

In [30] it is noted that, despite its high energy capacity, straw as a raw material is not ideal for the operation of biogas plants, since it contains a large amount of non-nitrogenous substances, in particular 33-35% of cellulose, 21-22% of hemicellulose, 18-22% of lignin, 3-5% of proteins and only 4-6% of nitrogen and mineral salts, but if it is prepared in advance, it is possible to reduce fermentation time and increase the production of biogas. The authors suggest grinding the raw substrate (buckwheat, rapeseed, soybean straw and corn stalks) to increase the intensity of methane fermentation.

Analysis of the potential production of biogas in agriculture of Ukraine showed [4] that suppliers of raw materials for biogas plants are approximately 1.14 million cattle, 3.4 million pigs and 118.9 million birds. Up to 2.9 billion m3 of biogas can be obtained from animal manure. However, the fact that the Ukrainian agricultural sector is largely divided into smaller farms and enterprises means that a large part of its availability is, in fact, not used. Even small farms and small biogas plants have problems with profitability and lack of substrate.

According to the latest studies of Bioenergy Association of Ukraine, the energy potential of Ukraine's biomass (24.87 million tons of energy) is 29% of the total supply of primary energy (86.36 million tons of energy in 2020), which is practically equal to the annual import of natural gas into the country [4].

The project of modernization of wastewater treatment plants and sediment treatment facilities in the city of Kharkiv envisages fermentation of sediment mixture in mesophilic mode. Dehydrated sludge after mechanical dewatering of fermented sediments and sludge from sludge sites is expected to be burned in the future.

To solve the set complex task, it is proposed to implement a scheme of separate processing of raw sediment and excess activated sludge and combined thermal utilization of sludge after mechanical dehydration of fermented sludge and compacted activated excess sludge on centrifuges at the stage of sludge treatment and disposal (Fig. 3).

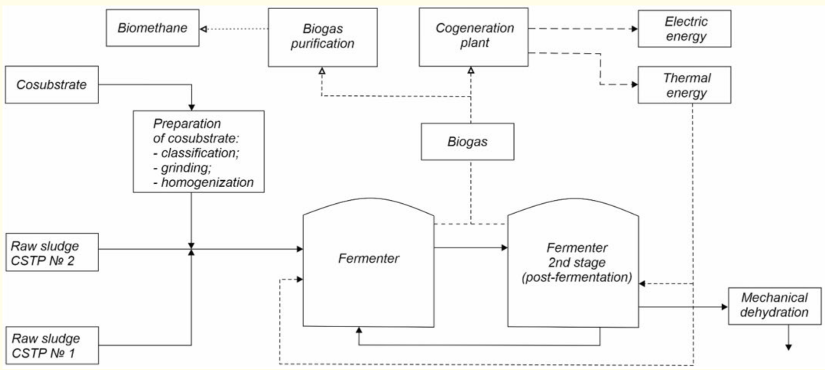

Figure 3: Technological scheme of biogas production by co-fermentation of a mixture of organic waste.

It is proposed to ferment only raw sludge in fermenters, which will allow to increase the specific gas output compared to fermentation of a mixture of raw sludge and excess activated sludge, to refuse the stage of mechanical thickening of excess sludge before fermentation, and to carry out the fermentation process in mesophilic mode, which will significantly reduce costs at this stage of the technological chain.

From the point of view of implementing an effective raw sludge fermentation technology and ensuring the production of biogas with its subsequent use for the station's own needs, it is advisable to add co-substrates to the sludge, which can be used as solid waste, manure from animal husbandry complexes, and chicken droppings. The process can be implemented according to the diagram in Figure 3. The technological parameters of the process, the type and ratio of the used substrates should be established on the basis of theoretical justification, experience of operating similar facilities and laboratory studies.

In order to reduce capital costs, it is proposed not to change the method of mechanical dewatering of sediments during reconstruction of the existing workshop. Dehydrated sludge is suggested to be mixed and sent to the drying and thermal disposal workshop. The heat obtained during burning of part of dried sludge will ensure drying of initial sediment and heating needs of equipment and premises. The rest of dried sludge can be used as low-calorie fuel or nitrogen-phosphorus fertilizer.

Obtained ash (low-toxic product of the fourth-fifth hazard class) can be used in road construction or for reclamation of existing sludge sites.

Implementation of the proposed scheme will allow to fully solve the task - to ensure the guaranteed safe disposal of formed sediments with the production of useful products and gradual reclamation of sludge sites.

Conclusion

Anaerobic fermentation with production of biogas and biomethane is a complex biotechnological process that requires further improvement of technological equipment to ensure the maximum production of biogas and increase economic efficiency of processing organic sewage sludge, plant biomass and manure into organic fertilizers. A promising way to increase productivity of the methane generation process during processing of organic waste is to increase the energy saturation of the organic substrate.

The results of an experimental study of the process of fermentation of sludge from sewage treatment plants in the city of Kharkiv showed that main directions of increasing the production of methane during fermentation of a complex organic substrate of sewage sludge and increasing the economic indicators of the process are: an increase in sludge used for fermentation the C/N ratio; increasing speed of all phases of fermentation, primarily disintegration and hydrolysis through pre-treatment by a chemical method; suppression of sulphate-reducing microorganisms, metabolism of which inhibits methanogenesis.

When considering sewage sludge as the main organic substrate as co-substrates it is advisable to consider use of solid household waste, solid and liquid organic industrial waste, waste of animal and plant origin, forestry complex. The type, amount, phase state, quality composition of organic substrates should be chosen based on productivity of the wastewater treatment complex, their composition, fermentation mode, equipment used, prospects for utilization of fermented mixture and obtained biogas, regional characteristics, the presence of companies supplying substrates, cost and regularity their supply and other factors.

Joint fermentation of sewage sludge, food industry waste, manure and MSW will increase process stability and methane output due to the synergistic effect of a more diverse microbial community. In addition, it is possible to improve properties of processed sludge, which will increase efficiency of using digestate as a high-performance fertilizer for agricultural purposes. At the same time, it will provide an opportunity to resolve environmental problems related to alienation of territories for waste storage and disposal, pollution of the atmosphere and water sources.

The use of obtained biogas and biomethane for production of electrical and thermal energy can provide both own needs of the wastewater treatment complex and the cogeneration plant, and be a source of financial income as a result of the sale of a commercial product.

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