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BIOGAS AND LANDFILL GAS CONVERTING TO GAS MOTOR FUEL THROUGH CLATHRATE HYDRATE*

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Abstract

Every year the amount of municipal solid waste (MSW) generated increases significantly. The main method of disposal of MSW is still their burial at landfills. Landfill gas emissions into the environment cause negative local and global effects. At the same time, landfill gas is an alternative source of heat and power generation. To simulate the processes of anaerobic decomposition of organic matter contained in the landfill body, a lab-scale biogas plant was developed. Municipal sewage sludge (SS), organic fraction of MSW and their mixture were used as substrates for anaerobic digestion. It has been shown that the methane content in the resulting biogas rarely exceeds 60%, which does not allow it to be used as a motor fuel; in addition, the presence of hydrogen sulfide in biogas (0.01-0.06%) negatively affects the resource of internal combustion engines. For additional purification prior to use as a motor fuel, a technical design of the one-stage gas hydrate production process from biogas and landfill gas has been proposed. The unique properties of gas hydrate and its advantages over other methods of purification and storage of biogas and landfill gas confirm the promising nature of the proposed technology.

Keywords: biogas, clathrate hydrate, landfill gas, municipal solid waste, renewable energy

1. Introduction

Every year the amount of municipal solid waste (MSW) generated increases significantly. On average, a person in the process of life produces about two cubic meters of garbage per year - about 400 kg. At present, most of MSW, as well as dewatered municipal sewage sludge (SS), is disposed at landfills, which are often not properly equipped and

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** Corresponding author: email: kovalev_da80@mail.ru operated without compliance or with deviations from the requirements of sanitary-epidemiological and environmental legislation (Izmaylov et al., 2018; Namsaraev et al., 2018). More than a quarter of the generated waste is food waste, about 20% is paper and cardboard and up to 20% wood and other organic matter (OM) - all of this is classified as organic fraction of MSW (OF-MSW) (Namsaraev et al., 2018). In the process of anaerobic decomposition of this fraction in the landfill body, one of the end products is landfill gas, the components of which have a negative impact on human health and the environment, at the same time can be used as raw materials for the production of energy, heat, fuels and substances used in various industries (Smirnova et al., 2012).

Most landfills are large biochemical reactors that are subject to fire, both in the landfill body and on its surface, and are sources of pollution of atmospheric air, soil and ground, surface and ground waters for decades. Landfill gas emissions into the environment cause negative local and global effects. Landfill gas has a depressing effect on the biocenosis, primarily on vegetation due to the displacement of oxygen from the pore space of the soil. With the accumulation of landfill gas in certain concentrations, explosive and fire hazardous situations are created directly at the disposal sites, as well as in buildings and structures located in the immediate vicinity of landfills. Combustion of waste components on the territory of landfills is accompanied by the emission of toxic compounds, which, due to atmospheric mass transfer and migration with surface runoff, enter surface water bodies and groundwater, and also accumulate in ground, bottom sediments and soils (Sadchikov et al., 2016). The migration of landfill gas in the ground and adjacent cavities is dangerous from both a technological and toxicological point of view. Cases of poisoning, often accompanied by fatal outcomes, are observed during the maintenance of utilities located near landfills that are not equipped with systems for collecting and utilizing landfill gas (Sadchikov A.V., 2017). The potential impact of methane, the main component of landfill gas, on global climate change is several tens of times greater than the effect of carbon dioxide, another constituent of landfill gas, therefore collection of CH_4 and CO_2 from landfills and their further disposal is one of the important ways to prevent global warming. The annual resource potential of biogas from landfills in the Moscow region is more than 2 billion m^3. Using the most modern technologies for active degassing of MSW landfills, the average biogas debit from 1 hectare of gas collectors' network is 500 m^3/h (Sadchikov et al., 2016). The approximate composition of landfill gas is shown in Fig, 1 (Sadchikov et al., 2016).

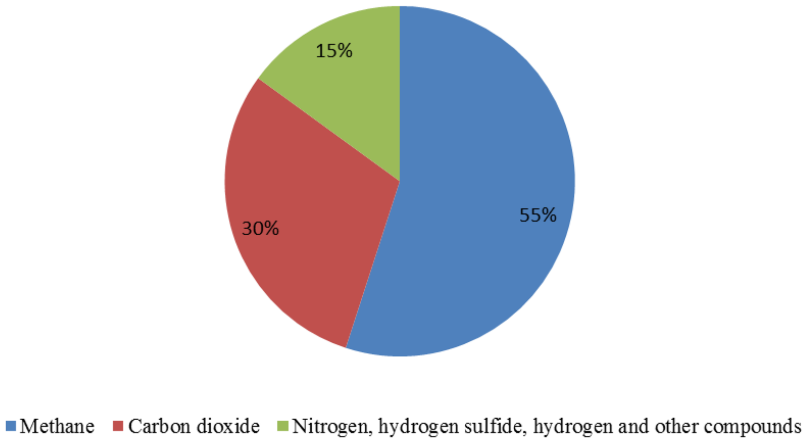


Fig. 1. The approximate composition of landfill gas

Landfill gas is an alternative source for obtaining heat and electricity, which is especially important in the framework of state policy in the field of energy and resource conservation, deserves special attention and is of commercial interest. Currently, about 1500 projects have been implemented in the world for the use of landfill gas for the obtaining of products with high added value (Smirnova et al., 2012).

The main objectives of this study was (1) to simulate the process of anaerobic decomposition of organic matter within the landfill body, (2) to analyze methods and technical solutions for the most efficient and environmentally friendly use of the produced gas, and (3) to describe the process flow diagram of converting landfill gas into gas motor fuel and commercial products.

2. Materials and methods

2.1. Used substrates and inoculum

Municipal sewage sludge (SS), organic fraction of municipal solid waste (OF-MSW) and their mixture were used as substrates for anaerobic digestion.

OF-MSW is represented mainly by paper and food waste. Its composition varies significantly depending on season, quality of waste sorting, etc. (Namsaraev et al., 2018). To eliminate the uncertainty factor and unify the composition, a mixture of cellulose-containing component (low-quality unbleached toilet paper) and easily biodegradable organic matter (SK-8 pig feed) was used as OF-MSW. The SK-8 pig feed consisted mainly of barley, wheat, wheat bran, wheat flour, sunflower meal, malt sprouts, rapeseed cake, etc. The mass content of crude protein was 14.5%, carbohydrates (starch) - 35.5%, crude lipids - 2.3%, crude fiber - 9%, other inert non-degradable organic compounds - 40%. Tap water was added to a OF-MSW to obtain the desired moisture content. The final ratio of toilet paper, SK-8 pig feed and water were 0.2:2:15 on a mass basis.

SS was a mixture of primary and secondary sludge from the Lyubertsy wastewater treatment facilities (Moscow) in a ratio of 1:1 by volume. Portions of SS were taken from wastewater treatment facilities once every 2 weeks and stored at 4°C until use. For a number of experiments where a lower moisture content was required, the SS was dewatered in a centrifuge at 5000 rpm for 5 min. The characteristics of the native and dewatered SS, as well as OF-MSW are presented in table 1.

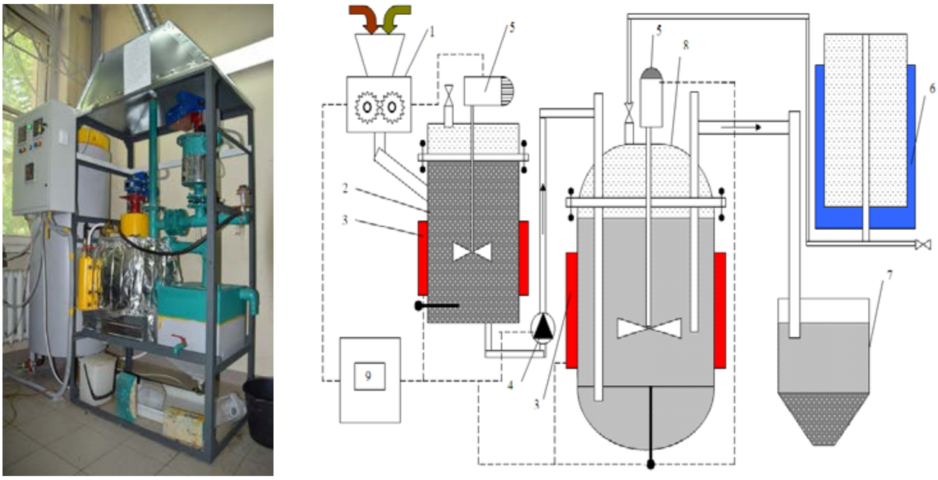
Thermophilically digested SS from the Lyubertsy wastewater treatment facilities (Moscow) was used as an inoculum for the biogas plant.

Table 1. Characteristics of the substrates for anaerobic co-digestion

Parameter	***Unit of measurement***	***Substrate***		
		Native SS	***Dewatered SS***	***OF-MSW***
pH		6.9	6.9	4.8
Moisture content	%	94.7	90.5	88.4
OM	% total solids	63.8	63.4	87.4
Proteins	% OM	35.0	35.0	11.2
Fats	% OM	24.6	24.6	1.8
Carbohydrates	% OM	11.6	11.6	43.1*
Note: * - starch + cellulose				

2.2. Biogas plant for anaerobic co-digestion of SS and OF-MSW

Experiments on anaerobic co-digestion of SS and OF-MSW were carried out on a laboratory biogas plant (Fig. 2, Table 2).



a b

Fig. 2. General view (a) and technological scheme (b) of a laboratory biogas plant: 1- OF-MSW grinder; 2- pretreatment reactor; 3- heater; 4- dosing pump; 5- stirring device; 6- gasholder; 7- effluent settler; 8- digester; 9- control unit.

Table 2. Technical characteristics of the biogas plant

Parameter	**Units**	**Value**
Pretreatment reactor volume	m^3	0.008
Digester volume	m^3	0.05
Gasholder volume	m^3	0.3
Effluent settler volume	m^3	0.08
Pretreatment reactor stirrer speed	rpm	240
Digester stirrer speed	rpm	40
Process (digestion) temperature	ºC	55
Biogas pressure in the gasholder	mm water column	100

It included the following main units: OF-MSW grinder, pretreatment reactor, digester, effluent settler and gasholder. The main units were made of stainless steel. The laboratory biogas plant operated as follows. A mixture of OF-MSW, SS and water was fed into the OF-MSW grinder and then into the pretreatment reactor. Within 30 min, the mixture was homogenized and heated to the working temperature of anaerobic co-digestion (54.9-55.3ºC) in the pretreatment reactor. Then the homogenized mixture was fed into the digester in 10 seconds using a dosing pump. The digester was fed once a day, and the effluent, according to the principle of communicating vessels, was displaced by gravity into the effluent settler. The short-circuiting of the fresh mixture from the digester into the settler during its feeding was less than 3%. The biogas generated during the co-digestion was collected in a gasholder. The volume of the generated biogas was determined by the change in the height of the ascent of the bell of the gasholder. Every day after adding another portion of the substrate, the gasholder was emptied by burning biogas in a gas burner. Stirring in the digester was switched on for 1 minute every 10 minutes. The pretreatment reactor was stirred continuously during the residence time of the mixture of OF-MSW and SS. The biogas composition was determined daily using an Optima 7 Biogas gas analyzer (MRU Instruments, USA).

3. Results and discussion

Data on the composition of biogas obtained as a result of experimental studies lasting 30 days are shown in Fig. 3.

As can be seen from Fig. 3, the methane content in biogas rarely exceeded 60%, which does not allow it to be used as a motor fuel. In addition, the presence of hydrogen sulfide in biogas negatively affects the life of the internal combustion engine, therefore, additional purification of biogas is required.

Various methods and technical solutions are used to dispose of the generated gas:

1. One of the currently widespread methods of disposal of landfill gas in Russia at the moment is flaring.
2. The second most common method is the use of landfill gas for the production of thermal energy - boiler houses, drying plants, thermal waste disposal plants.
3. Electricity generation accounts for the majority of projects for the use of biogas from landfills around the world (Kononovich and Lysukho, 2019). There are two main options for generating electricity near the landfill - using internal combustion engines, gas turbines and steam turbines.
4. Cogeneration - combined heat and power production (CHP); and trigeneration - combined production of heat, electricity and cold in power plants from landfill gas. To carry out the process of co- and trigeneration, a local power plant is required, that is, a cogeneration mini-CHP. This method of utilization of biogas from landfills is currently recognized as the most environmentally and economically efficient in the world.
5. The use of biogas as a vehicle fuel provides significant savings in fuel and energy resources. For fueling vehicles with landfill gas, an additional cleaning system should be installed, after which the resulting gas is called biomethane, a complete analogue of natural gas both in composition and in properties. Today, a network of methane filling stations is actively developing. Because of rising prices for gasoline and diesel, the use of methane becomes more profitable (Sadchikov et al., 2016).

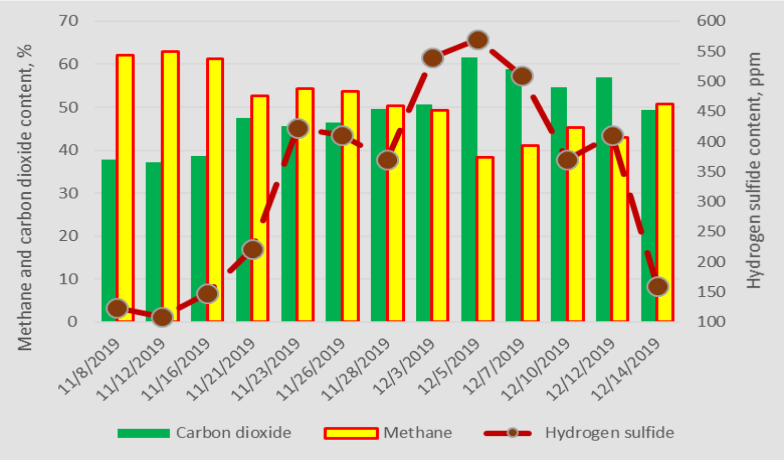


Fig. 3. Composition of biogas

The choice of a specific method for utilizing landfill gas is based on an analysis of the conditions prevailing at a given landfill, and is primarily determined by the presence of demand for energy resources obtained in the process of degassing the landfill.

For the processing of landfill gas and biogas, the authors of this work propose an alternative method for its purification, storage and transportation, for further production of motor fuels and landfill gas components. The proposed method is based on the ability of landfill gas components to form gas hydrates with water under certain temperature and pressure. It should be noted that recently there has been an increased interest in gas hydrates in connection with their possible application in technologies for the separation of gas mixtures (Eslamimanesh et al., 2012), transportation and storage of natural gas (Kumar et al., 2008), storage of CO_2 (Yang et al., 2013), as well as an alternative source of natural energy resources (Boswell and Collett, 2011). Gas hydrate technologies can provide cheaper and safer conditions for transportation and storage of gas compared to the construction of new pipelines and railway systems, gas storage in a compressed state (requiring high pressures (20-25 MPa)) and gas liquefaction (requiring cryogenic temperatures below -160 ºC). The technology proposed includes a one-stage production of gas hydrate from landfill gas and biogas, which is a crystalline solid formed of water and gas.

Fig. 4 shows the process flow diagram of converting landfill gas into gas motor fuel and commercial products. The process is carried out by cooling and compressing the biogas/landfill gas and then mixing it with water. The resulting mixture of gas hydrates is transported to the enterprise for its further processing. When processing a gas hydrate, the gas mixture is separated into components, due to changes in the temperature and pressure conditions in the gas hydrate storage chamber and the properties of the gases included in the mixture.

One cubic meter of methane hydrate with a density of ~ 970 kg/m^3 contains about 164 Nm^3 of methane, which is equivalent to the compression of methane to ~ 20 MPa. High energy consumption (1.7 kWh/kg), as well as stability at atmospheric pressure and a relatively low negative temperature of -29 °C make methane hydrate a cheaper and safer alternative to compressed and liquefied methane when used as a motor fuel.

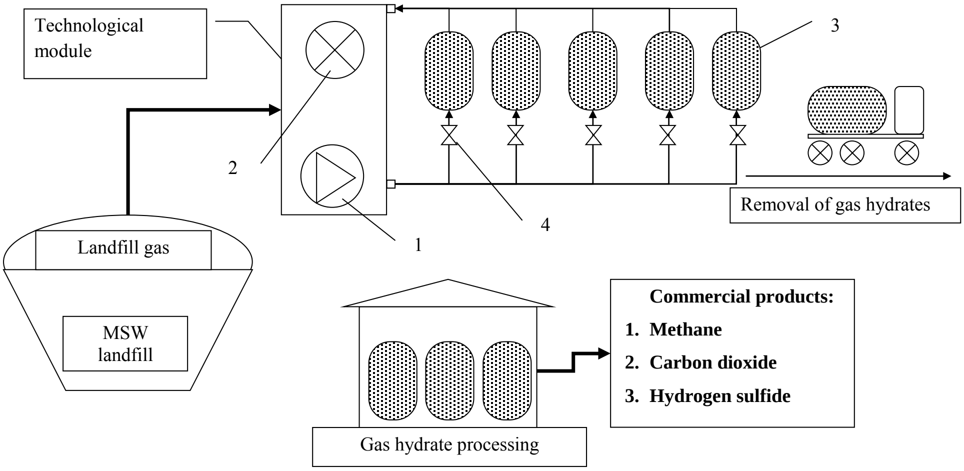


Fig. 4. Process flow diagram of converting landfill gas into gas motor fuel and commercial products: 1- compressor station; 2- heat pump for cooling gas hydrate tanks; 3- transportable gas hydrate tank; 4- fittings

Methane hydrate can be stored in thermally insulated containers, and the required amount of methane can be released in a controlled manner by heating, for example, with atmospheric air. The safety of transportation of methane hydrate is ensured both by its low thermal conductivity and by the effect of self-preservation, which consists in the fact that when methane hydrate decomposes into methane and water, water freezes and forms an ice crust on the surface of the hydrate, which prevents its further intensive decomposition. The use of gas hydrate technology for the extraction of methane from biogas and landfill gas makes it possible to provide vehicle fleets with motor fuel, as well as to implement local gasification of municipal and industrial consumers that do not have a centralized gas supply.

4. Conclusions

The authors of the work carried out an experiment on the anaerobic decomposition of the organic fraction of municipal solid waste and sewage sludge, which are the main organic components of landfill body. It has been shown that the methane content in the resulting biogas rarely exceeds 60%, which does not allow it to be used as a motor fuel; in addition, the presence of hydrogen sulfide in biogas (0.01-0.06%) negatively affects the life of internal combustion engines. The analysis of methods and technical solutions for the most efficient and environmentally friendly utilization of the generated gas was carried out. For additional purification prior to use as a motor fuel, a technical design of the one-stage gas hydrate production process from biogas and landfill gas has been proposed. The unique properties of gas hydrate and its advantages over other methods of purification and storage of biogas and landfill gas confirm the promising nature of the proposed technology.

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