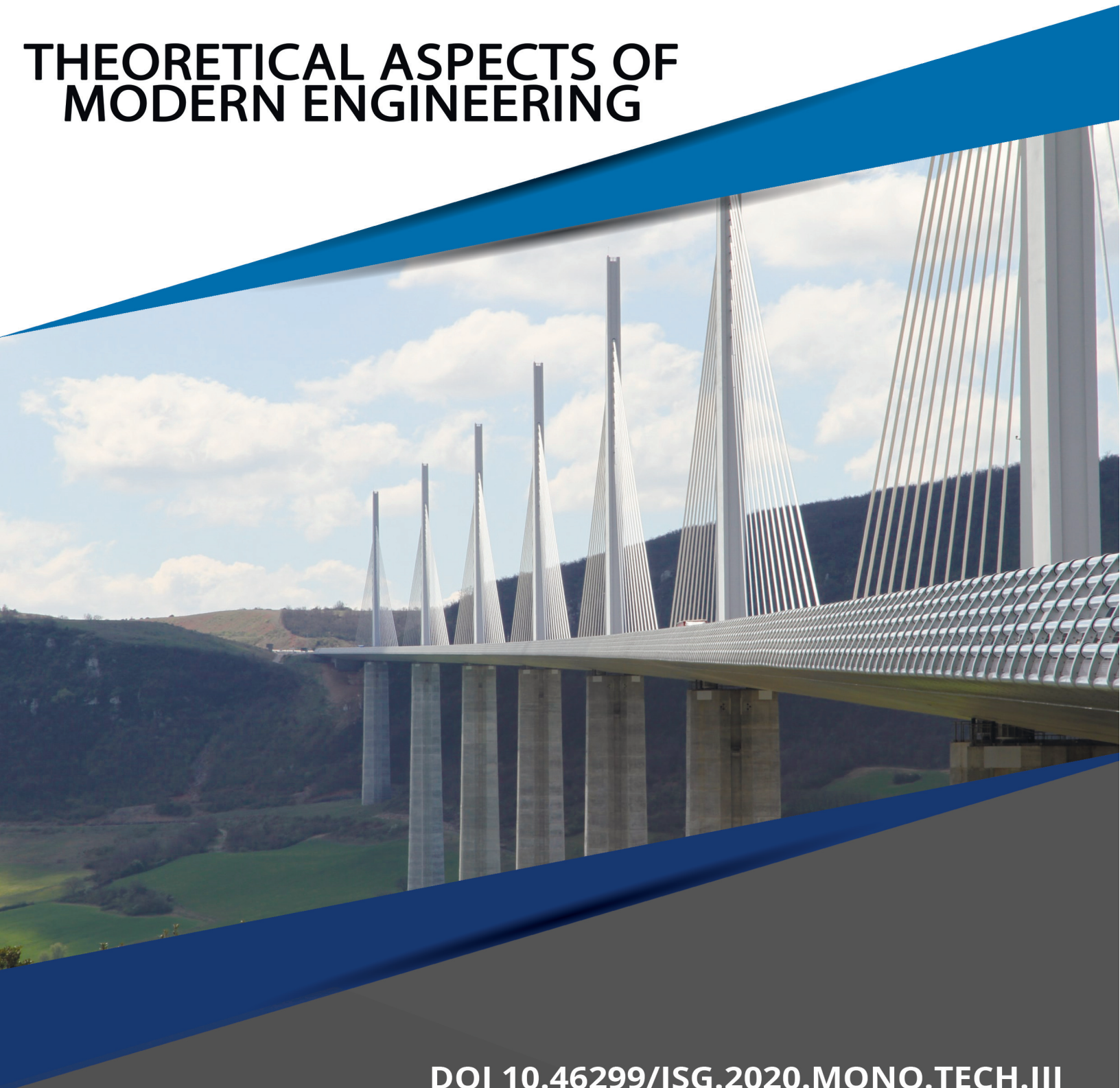


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SECTION 2. CHEMICAL TECHNOLOGY

2.1 Ukrainian prospects for landfill gas production at landfills

Increasing the level of fuel and energy independence is one of the priority goals of the state energy policy of Ukraine. At the same time, there are some negative trends that are observed in the system of traditional energy, which for a number of reasons are related to the problem of providing hydrocarbon fuel and energy resources of the state. This created the preconditions for the need to develop certain segments of alternative energy.

In this situation, the issue of extraction and use of renewable energy sources, one of which is landfill gas (LG), is extremely important for Ukraine. The energy obtained from LG is renewable because it comes from an organic renewable substrate, which attaches even greater importance to gas production in biogas plants.

Consumption of the benefits of civilization is constantly growing, and with it the amount of waste. Colourful packaging, disposable products and much more that is made for general use, invariably turns into scrap. No matter how much you manage to compact the garbage can – you still have to take out the garbage. This means that there is an urgent need to invent new ways of recycling waste.

Municipal solid waste (MSW), which in contrast to solid industrial waste [52-57], is a mixture of organic substances of different origins, is a high-calorie fuel that is not inferior in energy to traditional brown coal [58]. Receiving energy from garbage simultaneously solves the problem of solid waste disposal.

Fuel derived from conventional solid waste is: 1) gaseous (LG, which contains methane); 2) solid; 3) liquid.

At present, waste processing plants are being set up in different countries, equipped with special storage facilities equipped for the proper storage of solid waste in order to obtain LG from them. However, low-calorie gaseous fuels are difficult to transport, and therefore they are usually used directly at the place of extraction for the production of electricity and heat.

Solid fuel from solid waste [59] is a high-calorie fraction consisting of household waste. This type of fuel is widely used as a cheap substitute for combustible minerals and can replace resources such as brown coal, coal, petroleum products, wood.

Liquid fuel is a synthetic diesel fuel that can be used in internal combustion engines. It differs favorably from diesel fuel obtained from oil refining, because it does not contain sulfur, which clogs the engines, which in turn has a negative impact on their durability.

One of the main ways to remove solid waste around the world is to bury it in the surface geological environment. Under these conditions, the waste is subjected to intensive biochemical decomposition with the formation of LG [60-65]. The main components of LG include not only greenhouse gases (methane and carbon dioxide), but also such toxic compounds as carbon monoxide, nitrogen oxides, hydrogen sulfide, sulfur dioxide [66, 67]. Physico-chemical properties of landfill gas are given in table. 1.

In the process of thermal exposure and ignition of waste, carcinogenic compounds are released – benzene, benzopyrene. Emissions of landfill gases entering the environment have negative effects of both local and global geocological nature.

As a result of anaerobic (in the complete absence of oxygen) decomposition of the organic fraction of solid waste from the total amount of methane that enters the atmosphere annually, 40 ... 70% is formed as a result of anthropogenic activity, and 20% of them are landfills. It is estimated that about 200 m³ of LG is formed from one ton of solid waste. Thus the first 15 ... 20 years at decomposition of one ton of MSW up to 7,5 m³ of LG a year are allocated. In the future, the intensity of LG secretion decreases sharply.

Depending on the methane content, LG has a specific heat of combustion in the range from 15 to 25 MJ / m³ (3600 ... 4800 kcal / m³), which corresponds to 1/2 of the heat of combustion of natural gas. The average heat of combustion of LNG is 4200 kcal / m³. The heat of combustion of 1 m³ of LG is equivalent to: 0.8 m³ of natural gas, 0.7 kg of fuel oil or 1.5 kg of firewood.

Table 1.

Physico-chemical properties of landfill gas [66, 67]

Characteristic	Quantitative indicator	Characteristic	Quantitative indicator
Chemical composition, %:		Volumetric heat of combustion, MJ / m ³	18...23
- methane CH ₄	55.1...72.6	Energy consumption, kWh / m ³	6.5
- carbon dioxide CO ₂	10.1...22.2	Explosive concentration in air,%	6...12
- H ₂ O water (at 40°C)	5.12	Ignition temperature, ° C	650...750
- hydrocarbons	0.09...1.2	Critical pressure, MPa	7.5
- nitrogen dioxide	0.6...0.71	Critical temperature, ° C	-2.5
- ammonia NH ₃	0.33...0.35	Normal density, kg / m ³	1.2
- toluene	0.08...0.1	Density relative to air	0.83
- propane	0.06...0.08		
- sulfur dioxide	0.04...0.06		
- chloroethane	0.04...0.06		
- dichloroethane	0.04...0.06		
- total chlorine	0.01...0.06		
- ichlorodifluoromethane	0.02...0.03		
- dean	0.02...0.03		
- isopropylbenzene	0.01		

Statistics on the extraction and potential of LG in different countries are given in table. 2 [68]. In fig. 1 shows the prevalence of LG extraction methods in different countries. As can be seen from Fig. 1, the most common method of LG utilization is electricity generation.

LG is one of the causes of the outbreak of solid waste in landfills and dumps. When the content in the air is 5... 15 methane and 12% oxygen, an explosive mixture is formed. The concentration of methane and other components of LG can be controlled using a gas analyzer, which is considered in detail and described in [69, 70].

Table 2.

Statistics on the extraction and potential of LG in different countries [68]

Country	Volume of LG production, million m ³ / year	Specific volume of LG production, m ³ / person-year	LG potential, million m ³ / year	Specific potential of LG, m ³ / person-year	LG extraction efficiency, %
USA	500	1.723	13000	44.79	3.85
Germany	400	4.872	2050	24.97	19.51
UK	200	3.317	2520	41.80	7.94
Netherlands	50	3.058	560	34.25	8.93
France	40	0.637	874	13.91	4.58
Italy	35	0.583	1040	17.31	3.37
Denmark	5	0.917	105	19.27	4.76

LG also has a negative effect on vegetation, suppressing vegetation in areas adjacent to MSW (the mechanism of action is associated with the saturation of LG in the pore space of the soil and the displacement of oxygen from it).

LG is one of the gases that create a "greenhouse effect" and affect climate change in the Earth as a whole. The United Nations Framework Convention on Climate Change [71] obliges member states to minimize emissions of greenhouse gases such as methane and carbon dioxide (emissions of 1 m³ of methane are detrimental to climate change equivalent to emissions into the atmosphere about 25 m³ of carbon dioxide). In this regard, the reduction of GHG emissions into the atmosphere not only improves the environmental situation around landfills, but also contributes to Ukraine's fulfillment of its international obligations.

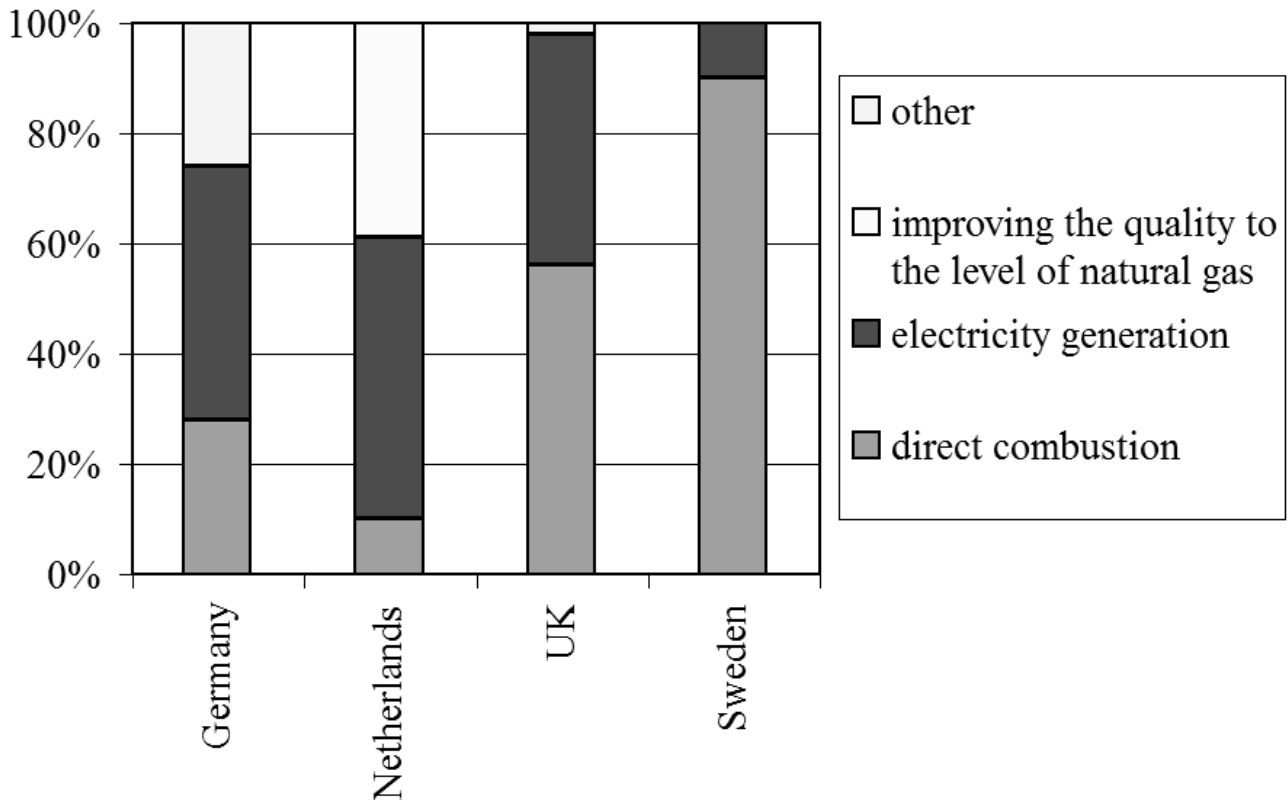


Figure 1. Prevalence of methods of LG extraction in different countries

The need to reduce environmental pollution and save energy makes it more rational to use traditional energy resources, look for other, preferably inexpensive and renewable energy sources, which recently increasingly include solid waste generated in large quantities, and usually do not find application and pollute the environment, are renewable secondary energy resources. Currently, two main areas of energy utilization of solid waste, their incineration and disposal with the production of GHG are intensively developing.

Solid waste incineration requires expensive treatment systems, so landfill is more common worldwide [72]. The main advantage of burial technology is simplicity, relatively low capital and operating costs, and relative safety.

For the energy of developed countries, the use of LGs is not crucial, but this source should not be neglected for both environmental and economic reasons, as evidenced by the experience of many countries. The EU has adopted a directive requiring the collection and disposal of LG from all landfills where biodegradable solid waste has been disposed of in order to minimize harmful effects on the environment and human

health. LG generated in landfills since the early 80's is intensively mined in many countries. Today, the total amount of LG used is approximately 1.2 billion m³ / year, which is equivalent to 429 thousand tons of methane, or 1% of its global emissions.

Currently, about 60 types of biogas technologies are used or developed in the world. The average service life of one well is 15 years, the estimated payback period of the project is from 4 to 5 years.

Let us consider in more detail the process of LG formation and its features. LG occurs due to the decomposition of organic matter by bacteria [73-75]. Different groups of bacteria decompose organic substrates, consisting mainly of water, protein, fat, carbohydrates and minerals into their primary components – carbon dioxide, minerals and water. As a product of metabolism, a mixture of gases is formed, which is called LG. Combustible methane (CH₄) is from 5% to 85% and is the main component of LG, and therefore the main energy-intensive component.

This natural decomposition process is possible only under anaerobic conditions in special biogas plants. The energy released due to the anaerobic process is not lost and due to the activity of methane bacteria it is converted into methane molecules.

The essence of the process of obtaining LG is the decomposition of biomass under the influence of three types of bacteria: hydrolysis, acid-forming, methane-forming.

The formation of LG can be divided into four phases:

1. Hydrolysis phase, during which as a result of bacterial activity, stable substances (proteins, fats and carbohydrates) decompose into simple components (amino acids, glucose, fatty acids).

2. Acid-forming phase. The components obtained during the hydrolysis phase are decomposed by acid-forming bacteria into other organic substances (acetic, propionic acids, alcohols and aldehydes) and inorganic substances H₂, CO₂, N₂, H₂S. This process occurs until the development of bacteria is slowed down by the formed acids.

3. Acetogenic phase, during which acetic acid is produced from the formed acids under the influence of acetogenic bacteria.

4. Methanogenesis, as a result of which acetic acid decomposes into methane, carbon dioxide and water. Hydrogen and carbon dioxide are converted to methane and water.

All the described reactions take place simultaneously, and methane-forming bacteria make much higher demands on the conditions of their existence than acid-forming ones.

All this complex of transformations is carried out by a large number of microorganisms – up to several hundred species. Of these, hydrolytic, fermentation, syntrophic and methane groups are predominant. The qualitative and quantitative composition of microorganisms strongly depends on the composition of fermenting organic substances and the conditions created in the environment.

The composition of LG depends on the content of hydrogen sulfide and other gases, the parameters of the process.

The energy consumption of LG directly depends on the concentration of methane in it, which is a colorless, non-toxic gas that is lighter than air and odorless. Methane combustion produces carbon dioxide and water vapor. With a methane content of more than 60%, LG is considered a very valuable fuel [76].

Thus, the technology of solid waste processing at landfills has the greatest prospects for obtaining and further use of landfill gas because it can be achieved: improving the environmental condition, additional energy benefits, increasing fuel and energy potential and energy independence of Ukraine.