

Analysis of studies of lake sapropel properties

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Summary. Sapropel deposits are widely distributed around the globe. In the Americas area they are adjacent to the Great Lakes region, in Europe sapropel deposits can be spotted in the territory of Scandinavia, France, Switzerland, Germany, Poland, Belarus, Russia and in the northern regions of Ukraine.

Use of sapropel as a fertilizer can enhance high and stable yields of crops. However, despite the proven effectiveness of long-term practical researches in this area, nowadays sapropel is almost not used. One of the reasons - lack of developed processing methods of extraction and processing, including dehydration.

Material properties as an object of interaction with the working bodies, change of their settings in the processing are crucial in the choice of technologies, development, bringing up to the necessary parameters and subsequent use.

Sapropel high humidity (95-98%) is one of the main factor that determines the quality of its properties after the interaction with working bodies. However, in the process of decreasing, in interaction with oxygen, there are significant changes in physical and mechanical properties of sapropel.

Decisive in the direction selection process of lake sapropels' use in the economic sector is their moisture exchange and thermodynamic parameters. The complexity of setting the water apart, if freshly extracted sapropels possess only 15-20% of it, shows their strong water-retaining capacity. The above mentioned phenomenon proves the need for their use as an organic fertilizer during the crops growing, as superficial loss of moisture in the soil creates a new global problem.

On the basis of deep analysis of the sapropels' properties, the authors suggest three areas of freshly extracted lake sapropel application in mixtures with leafy part of the crops: in biogas production with its further use as an organic fertilizer; making a compost mixture of organic origin which physical and mechanical properties are approximate as that of the soil; alternative solid fuels in the form of briquettes.

Key words: water, sapropel, biogas, fuel briquettes, moisture, organics, properties, areas of use.

INTRODUCTION

Sapropel – a fertilizer, which consists of overrotten remnants of aquatic life, which for centuries was deposited on the bottom of ponds with fresh water as

sediment. This substrate is required at the bottom of lakes and rivers, as it plays an important role in their biological systems, purifying water from various harmful impurities. This natural sorbent filter functions with help of bacteria in it and can exist even in the absence of oxygen, in the most polluted water.

Due to the unique conditions of nascence and storage and it has a unique organic matter of composition. It contains a large number of lignin-like humus and many chemical compounds and elements necessary for plant growth. The main components of sapropel are:

- Organics - 40-79%;
- Ash - 2-19%;
- Sodium (N) - 0,6-3,4%;
- Potassium (CaO) - 2,7-33,5%;
- Phosphorus (P2O5) - 0,14-0,27;

This composition confirms the hypothesis about the possibility of sapropel versatile application in various fields of human activity. On the other hand the problem of shortage of fresh water on the planet can be solved only in case of careful attitude to it. Therefore, the release of water of accumulated by thousands years sapropel, will help to create natural reservoirs of fresh water. There is a huge amount of water reservoirs in Ukraine. However, their great concentration is in the river Pripjat zone and its tributaries.

For a long time to cleaning lakes of karstic origin is not paid any attention. That is why the menacing tendency to their extinction becomes irreversible. That problem, to some extent, can be considered a global one. The lack of deep studies on setting properties of lake sapropel does not allow to increase production in the area of lakes and attract investments to solve these problems.

A significant content in the lake sapropel of organic components makes the agricultural sector professionals pay attention on sapropel as a raw material for agricultural production. So, the presented results will be important, especially in the development of this area.

ANALYSIS OF RECENT RESEARCHES AND PUBLICATIONS

The estimated reserves of sapropel in Ukraine make about 65 mln. tons. Their main number is situated in the group of Shatsky Lakes in Volyn region. In Ukraine there is a large number sapropel productive lakes and their share make more than 140 mln. tons, when converted to 60% moisture. [1] This area belongs to one of the most

ecologically clean regions of Ukraine and is provided under the existing amounts of mining for more than 100 years.

Material properties as an object of interaction with the working bodies, change of their settings in the processing are crucial in the choice of technologies, development, bringing up to the necessary parameters and subsequent use. Sapropel high humidity (95-98%) is one of the main factor that determines the quality of its properties after the interaction with working bodies. However, in the process of decreasing, in interaction with oxygen, there are significant changes in physical and mechanical properties of sapropel [2, 3, 4, 5].

In agriculture, the lake sapropel is used as a fertilizer (after freezing the water is separated, then a change in the structure is taking place - the material is transformed into a free-running state. Its particularly effective application is noticed in acidic, light sandy and loamy soils, and if we want to increase the content of humus in soils (dose at grain 30-40 t / ha under vegetables, potatoes and feed roots 60-70 t / ha) [6, 7]. In the case of their local application the doze is decreased by 3-4 times [8, 9, 10]. Lake sapropel in its natural state is a good ingredient to make compost [11].

The use of sapropel as a fertilizer improves the mechanical structure of the soil, shows its moisture absorbing and water-retaining capacity, improves aeration, increases the amount of humus in soil, activates soil processes. Sapropel fertilizer facilitates the mobilization of the soil components, leading to self cleaning of harmful plants, fungi and harmful microorganisms.

In domestic and foreign literature there are many scientific and practical materials for the production and use of organic - mineral fertilizers (OMF). Their production is carried out by various technological schemes with the participation of the various components of both organic and inorganic origin [12].

The technology of their preparation includes the following operations:

- Preparation of components by their granular metric size;
- Dosage, mixing and granulation;
- Drying, separation, packing and storage of fertilizers.

One ton of such fertilizer contains more than 300kg of nitrogen, potassium and phosphate components and about 300 kg of organic matter.

There are many other areas of lake sapropel application in various fields. Practically unstudied remains the possibility of its use as a raw material for the production of alternative energy sources: natural gas, solid fuel material. The main reason for this is the lack of attention of researchers to study the properties of sapropel, which is crucial when used in its natural state.

OBJECTIVE

The purpose of the work is the synthesis of new research results of setting the properties of extracted lake sapropel and outline the areas of its use with regard to changes of water amount in it.

MAIN RESULTS OF THE RESEARCHES

Out of the widely-adopted Reh binder classification, sapropel is referred to colloidal, dispersive, capillary-porous materials with a specific structure and high humidity that is kept by various types of bonds. The presence of colloids cause the problem of lake sapropel dehydration. This free moisture, which can be removed mechanically, is a small part of the colloid total weight. According to experimental studies [13], the equilibrium moisture content for organic sapropel can be determined from the graphic curve Fig. 1, which is a power function. The rest of the moisture is coherent, useful in many areas of agricultural production.

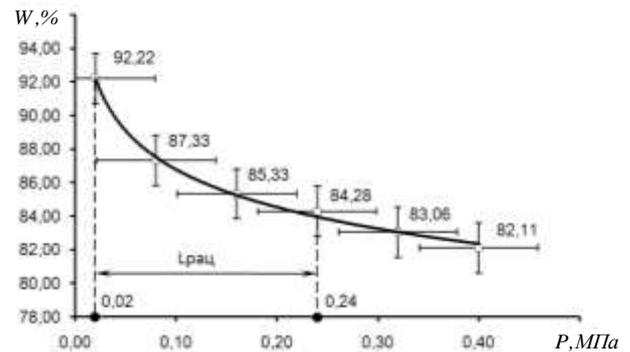


Fig. 1. Dependence of lake sapropel humidity changes *W* of pressure on the sample surface *P*

So, there is about 85-95 per cent of free water in lake sapropel and any mechanical effects associated with the occurrence of landslide efforts on the material lead to changes in its physical state. From capillary - porous body of high humidity, sapropel turns into a pure colloid and is no longer subjected to mechanical dehydration. Consequently, lake sapropel in natural state should be used as a raw material to make compost, biogas with various agricultural materials, as an astringent element in the production of fuel pellets.

If the compost preparation the initial humidity, physical state will not be determinative parameters (Fig. 2). Defining in laying composting collars will be their height as well as the ratio of straw components of crops and sapropel, their rational value should be 1:3.

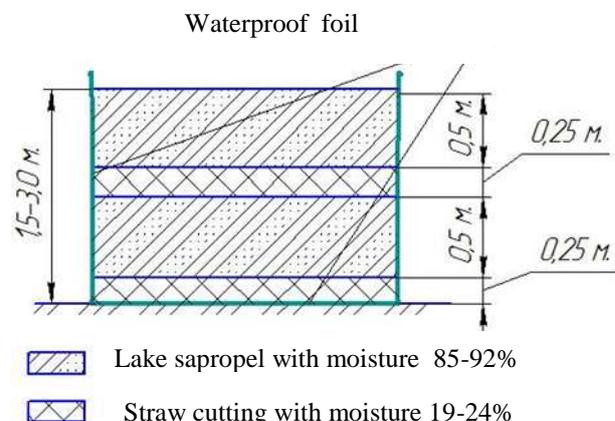


Fig. 2. Defining dimensions of collar in composting

The efficiency of obtained solid organic fertilizers shows up after three months of exposure. Straw components lose their elasticity, are easily destroyed under the influence of mechanical stress, help in making accurate dosing. The obtained results on the impact of the potatoes yield [8] indicate that its growth amounted to 25%. Exposure of compost piles in more than one year results in a homogeneous material similar in appearance to the ground. The application rate of such solid organic fertilizers can be reduced to 80-120 t / ha.

Making pure biogas from lake sapropel is not economically profitable (Fig. 3, 4). For the researches in the laboratory we used two types of lake sapropel, freshly

extracted, pH 8.60 and frosted pH = 8.23. Their dry mass per unit was 4.22% and 11.52% respectively, and dry organic matter 65, 25% and 33.49%. The exit of organic after fermentation amounted to 11.13% and 8.14%. Thus, the results analysis points to promising application of lake sapropel of natural moisture to produce biogas as one of the components. By this the exit of organic of freshly extracted is almost two times higher comparedly to frosted. This phenomenon can also argue about the prospects of using residual product after fermentation as organic fertilizers or organic mineral component of fertilizers.

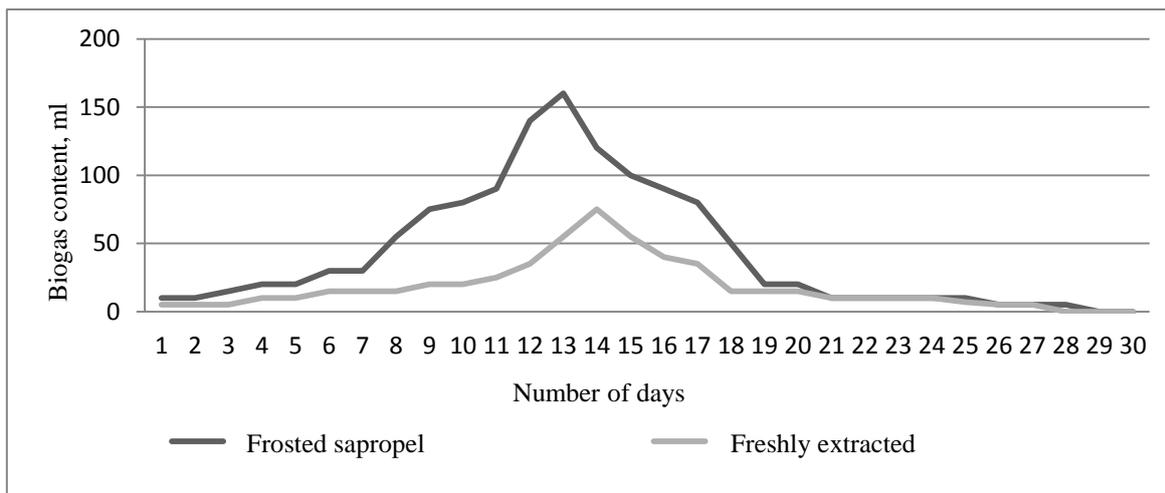


Fig. 3. Biogas emission during fermentation in the laboratory

In its turn, the diagrams' analysis in Figures 3 and 4 allows to conclude that the effect of the maximum allocation of biogas of lake sapropel appears in 11- 15 days for both options. A significant difference in numbers of the variants is explained by the dry mass value, which for the frosted was almost three times higher. However, its widespread use in a production conditions is

questionable because of the complex production technology and the dehydration complexity. Therefore, we believe that more promising for biogas production is freshly extracted lake sapropel of natural moisture and the biogas production facilities should be placed in the zone of extraction.

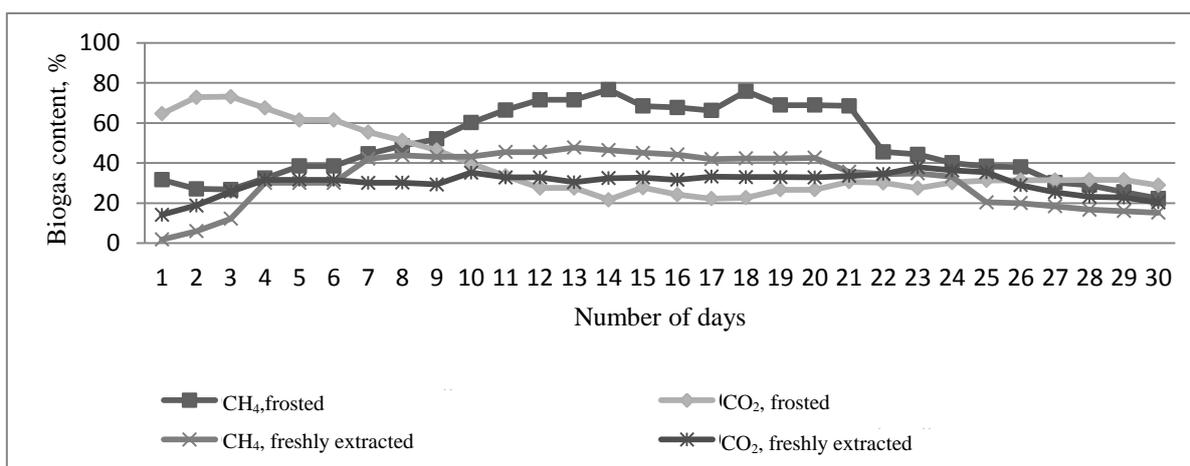


Fig. 4. Biogas allocation distribution during a month

To intensify the process it is important to combine lake sapropel with other wastes of organic origin in agricultural production. Annually in the agricultural enterprises of the country are produced about 45 mln. tons of manure that is equivalent for nutritional value to 62%

of the total production of mineral fertilizers in the country. The country also has large reserves of sapropel, the most valuable raw material for the production of organic and organo-mineral fertilizers. An effective fertilizer production method is to use a mixture of

sapropel + manure. However, this huge potential is used not more than 25 ... 30%, due primarily lack of economic and efficient technologies for the preparation of liquid and semi-liquid wastes of livestock and poultry as an organic fertilizer. The most promising in terms of getting agrochemical (production of fertilizers), environmental (disinfection and deodorization) and energy (production of fuel and electricity) efficiency is a technology processing systems sapropel + manure in anaerobic conditions in special airtight reactors, digesters, made usually of metal. Through the activities of methane making bacteria in an oxygen-free environment at a temperature of 39 ... 40 or 53 ... 55 ° C the fermentation of sapropel and manure mixture process takes place in the reactor to form a combustible gas, the main components of which are methane (60 .. 65%) and carbon dioxide (35 ... 40%). 1 t of manure at humidity of 92% for 10 ... 15 days can produce about 20 m³ of biogas with calorific value 23 ... 25 MJ / m³. Out of this number, about 50% is spent on the support of needed temperature of the digesters, another part of biogas can be used for the needs of the economy. The fermented in the digesters mass is easily digestible by plants and devoid of pathogens and weed seeds, it is a highly concentrated liquid of organic fertilizer containing macro and micronutrients, amino acids and plant hormones that stimulates a plant growth. This fertilizer is used in all types of soil for vegetables, fruit, fodder crops, lawns, flower beds, ornamental shrubs, etc., it is particularly effectively used as a fermented fertilizer for root watering and fertilizing vegetable and other crops (in 3 ... 4 times feeding, but not more than 1 time in ten days), while the yield is increased to 2 ... 3 times.

The process of biogas production from the materials consisting of lake sapropel with different agricultural materials of plant origin remains unexplored. This issue is on the agenda now, because in our country more than 60 percent of the land area is allocated under the grain group, grain in addition to the basic goods - gives a large amount of leaves - stem mass. This material at best is buried in ground and, at worst - burnt.

To the researches of the fuel briquettes production from agricultural materials is paid a little attention. The difficulties of the pellets forming process are in different properties of their constituents, in some moments quite the opposite [14]. Significant efforts are needed to give the pellets a given shape and require the creation of significant pressures and thus significant energy consumption. The efforts reduction on forming the pellets is subject to the application as a binder element the very lake sapropel of natural moisture. It is necessary to establish a number of new power and temperature parameters, taking into account physical and mechanical properties of the basic material – the straw components of agricultural crops.

The use of lake sapropel in these directions and creating the appropriate technical means becomes possible in case of understanding the nature of liaison in the materials. This link explains the moisture exchange and thermodynamic properties. They can be set by use of thermography colorimetric analysis [15, 16] in constant ambient temperature. When drying a sapropel sample in a thermogram mode on the tape of potentiometer KPS - 4 simultaneously the curve of sample temperature with time is recorded (thermogram $T = f(t)$) and the curve of weight

reduction (curve of drying $W = f(t)$) (Fig. 5). In the thermogram of drying the critical points in time and the humidity of the body are marked that correspond to the boundaries periods sequence of moisture removal of body while drying, by different forms of liaisons and their placing it the pores. The porous structure, above all, defines the water-retaining properties of sapropel. The importance of this structure has the material in the processes of heat and mass transfer.

The studies have shown that the dependence of the temperature of sapropel drying time is typical of colloidal capillary-porous materials S - like curve with one straight section between points 4 and 5 and deposited therein critical points that correspond to the limits of different types of moisture during drying [16]. Moisture content of sapropel, which responds to every form of moisture liaisons can be set designing critical points on the curve of mass change over time.

Curves of drying process are divided into sections. By point 1, a weakly coherent moisture evaporation takes place, which does not possess a large liaison energy of the material (after warming the drying curve rapidly falls down). Point 1 responds to the full moisture capacity of the material. From this value to point 3 (can be found graphically) under the influence of temperature of the drying agent the capillary moisture is removed. Moisture content in this critical point corresponds to the maximum hygroscopic moisture of the material and is on the verge (point 3) of free and bound water in the material. As a result of experimental studies we found that sapropel moisture content equals to 1.07 kg / kg and is optimal where the structure of the material remains unchanged. If the moisture is below hygroscopic, then the material undergoes substantial structural changes. One of them is that sapropel becomes insoluble in water and increases its hardness. These structural changes adversely affect the quality of sapropel in its further use. Similar phenomena have been discovered in research with a range of textile materials. We can therefore assume that sapropel is colloidal capillary-porous material and its major structural changes occur during the evaporation of moisture from the hygroscopic micropores.

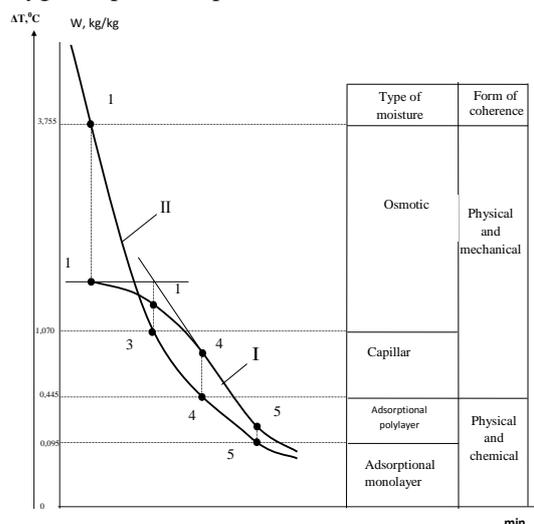


Fig. 5. Scheme of moisture removal sequence of various forms of coherence: I - a typical thermogram for a colloidal capillary-porous body; II - experimental curve of organic sapropel drying

Further drying of organic sapropel is characterized by attenuation of the intensity of dehydration which in turn is accompanied by increased energy costs. It is known that colloidal capillary-porous bodies on the allocation of adsorption-bound moisture must take more energy than the evaporation of free water [17]. Therefore, point 4 characterizes the allocation of moisture adsorption of polylayer, and on point 5 - moisture, which has the highest energy of the material that is moisture adsorption of monolayer. In point 4 shrinkage of the material takes place, which is typical for colloidal capillary-porous bodies. The value of moisture in point 5 allows to calculate the specific surface area of the sapropel sample as follows:

$$S = \frac{N_A \times S_{ef}}{M} \times W_5 \quad ; \quad (1)$$

where: N_A – Avogadro's number;

S_{ef} – the effective area of molecules of adsorbed substance (water);

M – molecular weight of the absorbed substance;

W_5 – moisture content in point 5 (monolayer adsorption moisture).

The calculations showed that for organic type sapropel it makes $350 \text{ m}^2/\text{g}$.

In Table 1. for comparison, the values of specific surfaces of clay materials are displayed (palygorskite, illite, kaolinite). These minerals, as well as sapropel are of colloidal capillary-porous bodies.

Table 1. Specific surfaces of materials

Material	Specific surface, m^2/g
Organic sapropel	350
Palygorskite	340
Illite	136
Kaolinite	88

As shown in the Table 1 the values of the specific surfaces of sapropel and palygorskite are approximately equal. This indicates the presence in these materials a highly developed microporous structure. In sapropels this structure is formed during its formation in the presence of such substances as detritus in it, which is formed by organic and mineral substances. Most of the organic and mineral parts are one. The suspended detritus particles in the water are characterized by a huge total surface. For example, in 1 cm^3 lake water, lake Vyechyer (Belarus), total surface of these particles is 270 m^2 [18].

Thus, based on the results of organic sapropel drying using thermal and energy analysis we established forms of coherence of its moisture and sapropel energy of the material. We have also defined the specific surface area of the material and the specific heat of evaporation for the specified period of moisture content from $22.50 \text{ kg} / \text{kg}$ to $1.07 \text{ kg} / \text{kg}$. The results can be used for method and choice substantiation of optimal process parameters of dehydration of organic sapropel preserving natural properties. Also we have experimentally established that the major structural changes in sapropels take place during evaporation of hygroscopic moisture, it suggests that the material is colloidal and capillary-porous body.

The porous structure defines first of all the water-retaining properties of sapropel. An important role the

structure of the material plays is in the processes of heat and mass transfer. The ability of a material to give moisture to a greater extent depends on the type of coherence that exists between the liquid and solid phases [17]. Weakly bound water or free water removal should cost little energy to overcome the hydraulic resistance during the movement of fluid in the pore space. In that time the bound moisture can be removed from the material by phase transformation with consumption of a large amount of heat energy. Therefore, the content of this or that moisture in sapropels determines a specific application of the method of its removal.

Therefore, the results indicate the possibility of using the combined method of dehydration of lake sapropel, and the presence of free water - the ability of a mechanical action to remove it. Mechanical water spinning due to the presence of free and weakly bound water and sapropel provides cheap exit product and eliminates the material heat treatment. Intensification of spin can be also achieved by use a stepped pressing, during which the material is periodically crushed and mixed. In this case, the violation of filtering surface structure leads to improved conditions of water-yielding capacity.

CONCLUSIONS

The analysis of lake sapropel properties that could be decisive in choosing the direction of their use in the commercial sector, points to the importance and consideration of the moisture exchange and thermodynamic parameters. We also found that water, from which in certain cases it should be released, in the lake sapropels is 15 to 20 percent. So, if we use the lake sapropel in natural state we propose to use it as an ingredient for the production of ly understood process of production of fuel pellets, astringent elemebiogas and compost mixed with leafy mass of crops. Poorly understood remains the process of production of fuel pellets, astringent element of which can also be freshly extracted lake sapropel.

Comparative characteristics of lake sapropel with specific surfaces of other materials clearly indicate their affiliation to the group of capillary - porous solids whose structure contains a considerable amount of organic matter. Powerful moisture-retaining ability of sapropels points to the need for their use as organic fertilizers when growing crops as superficial loss of moisture in the soil creates a new global problem.

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АНАЛИЗ РЕЗУЛЬТАТОВ ИССЛЕДОВАНИЙ СВОЙСТВ ОЗЕРНЫХ САПРОПЕЛЕЙ

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Аннотация. На основе анализа собственных исследований свойств, авторами предлагается три направления применения свежоизятого озерного сапропеля в смесях с листостебельной частью урожая сельскохозяйственных культур: при производстве биогаза, с последующим использованием в качестве органических удобрений; изготовление компостов органического происхождения смеси которых близкие по физико-механическим свойствам к грунтам; альтернативного твердого топлива в виде брикетов.

Ключевые слова: водоем, сапропель, биогаз, топливный брикет, влажность, органика, свойства, направления использования.