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MATHEMATICAL MODEL OF THE PROCESS OF SYNTHESIS OF BIOGAS FROM BLUE-GREEN ALGAE

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Purpose. Based on the analysis of the literature substantiates the relevance of the chosen research areas, namely the production of biogas from algae. The aim of the research is to optimize the synthesis process of biogas using the results of the mathematical models of stimulation of this process. ***Methodology.*** Used methods of acoustic and hydrodynamic cavitation for intensification of processes of energy production, applied principles of mathematical modeling of process of synthesis of biogas from the standpoint of the analysis of chain reactions by methods of physical chemistry. ***Reults.*** Proved viability of the use of cyanobacteria for the production of energy: biodiesel and biogas. Experimental studies aimed at establishing the feasibility of a preliminary preparation of the biomass of cyanobacteria (acoustic and hydrodynamic cavitation) to improve the efficiency of the processes of extraction of lipids and synthesis of biogas. Found that the use of hydrodynamic cavitation allows more than 2-fold increase in the amount of extractable lipids, whereas the influence of acoustic cavitation is negligible. In the case of hydrodynamic cavitation by 30% increases the amount of synthesized biogas. The mathematical model of process of synthesis of biogas from cyanobacteria, the adequacy of which is confirmed by conformity to the experimental data. ***Practical value.*** As a result of identification of the experimental and calculated data values are integrated kinetic constants of the process of synthesis of biogas that can be used to calculate the actual processes. *References 8, no tables, figures 6.*
Key words: cyanobacteria, cavitation, biogas, lipids, adequacy, mathematical modeling.

МАТЕМАТИЧНА МОДЕЛЬ ПРОЦЕСУ СИНТЕЗУ БІОГАЗУ ІЗ СИНЬО-ЗЕЛЕНИХ ВОДОРОСТЕЙ

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Доведена перспективність використання ціанобактерій для виробництва енергоносіїв: біодизелю та біогазу. Проведені експериментальні дослідження з ціллю встановлення доцільності застосування попередньої підготовки біомаси ціанобактерій (акустична та гідродинамічна кавітація) для підвищення ефективності процесів екстрагування ліпідів та синтезу біогазу. Встановлено, що застосування гідродинамічної кавітації дозволяє більш ніж в 2 рази збільшити кількість екстрагованих ліпідів, тоді як вплив акустичної кавітації незначний. У випадку застосування гідродинамічної кавітації на 30% збільшується також об'єм синтезованого біогазу. Розроблена математична модель процесу синтезу біогазу із ціанобактерій, адекватність якої підтверджена відповідністю експериментальним даним. В результаті ідентифікації встановлені значення комплексних кінетичних констант процесу синтезу біогазу, які можуть бути використані для розрахунку реальних процесів.
Ключові слова: ціанобактерії, кавітація, біогаз, ліпіди, адекватність, математичне моделювання.

PROBLEM STATEMENT. The development of new energy sources in terms of depletion of traditional is important for sustainable development of the global community, and for Ukraine, in a strategic reorientation of the energy market, this problem is particularly acute. Prominent in the world belongs to use as an independent energy source or as raw material for production of energy biomass (agricultural or forest waste, energy wood, agricultural crops crops which are raw materials for biodiesel, etc.). But by reducing the acreage of plantations for edible crops often leads to food crises (Latin America, Mexico), which rightly leads the public opposition of the population. In this context, perspective is used as raw material for energy production of algae. The use of such areas does not cause a reduction in cultivated land, so it is to them recently focused attention of scientists from many countries. Prospects of algae for the production of energy involved leading scientists and innovative companies in the world, including project should highlight Seafarm, implemented by the Department of Applied Ecology of the Royal University of Technology (Sweden), the work of the research group of the University of Virginia in Charlottesvle (USA), the multi-year study of a group of scientists from Kremenchuk Mykhailo Ostrohradskyi National University[1 - 3], research installations of Tokyo Gas installation and NEDO (Japan), Seambiotic (Israel), GreenFuel Technologies (USA), and many others [4 - 6]. Microalgae [4]– single-celled "factory" processing of solar energy and carbon dioxide into biofuels. Algae are the fastest-growing plants in the world, they can double their mass several times a day. Contains a record number of oil (80%) and are unique in the plant world on this indicator. Can be used for production of motor fuels, does not differ from traditional. From plants grown on solid ground, they differ in a number of advantages, among which should provide a high yield, ability to grow in the water, not on arable land that could be used for crops other food crops, the ability to absorb a significant amount of industrial carbon dioxide lowest costs of water on growing. Such promising algae biomass for Ukraine are cyanobacteria (blue-green algae), which today due to uncontrolled development in shallow enough sun warmed waters of the Dnieper cascade of artificial reservoirs causes progressive "bloom" of water and create significant environmental threat. The dominant members of these families algae is Microcystis, Phormidium, Aphanizomenon, Anabeana and Oscillatoria. The use of biomass for biogas production not only provides a significant amount of conditioned energy, but also achieve minimization of ecological danger from the consequences of uncontrolled development of cyanobacteria - everify water, aquatic biota destruction, pollution of the atmosphere, hydrosphere and sediment products of biological decomposition of algae [1 - 3] . To implement biogas technology of cyanobacteria along with the problems of collection, concentration, synthesis and utilization of waste biogas biomass is an important development of measures to intensify the process of biodegradable biomass of algae, increasing the completeness of biodegradable, developing a mathematical model to describe the process and allowed to conduct forecasting development. That these problems and devoted study authors, the results of which are reflected in this publication.

EXPERIMENTAL PART AND RESULTS OBTAINED. For research was used cyanobacteria, taken at the Kremenchug reservoir in Svyetlovodsk. Before beginning experiments been prepared, the algae suspension with a dry matter content of 17.1 g/l, which corresponds to the actual concentration of algae in places. At the first stage research determined the content of organic seaweed sample by burning the dried algae in the oven for 550^0C for 15 min. By results of researches the organic portion was 94% of the total weight of algae.

Was investigated two ways of using cyanobacteria for energy:

1. Extraction of lipids, which can be further used for the production of biodiesel.

2. The production of biogas.

Because cyanobacteria have very dense cell membrane, the process of extraction can take place and biodegradable with low intensity. For the destruction of the cell membrane was chosen method of cavitation, in which form zones of high and low pressure, which are destroying cell membranes. In this work, we investigate the influence on the processes of using algae for energy production of two types of cavitation: acoustic and hydrodynamic.

To conduct acoustic cavitation suspension of cyanobacteria was introduced into the ultrasonic reactor (Fig. 1). Ultrasonic vibrations (frequency – 22kHz, power – 35 W, the intensity – 1.65 W/cm3 per unit volume) from the generator UZDN-2T passing-were made using magnetostriction radiator, immersed in the test environment (V = 150 cm3) [4, 5]. Throughout the process through the tested suspension bubbled CO2. The reactor is continuously cooled with running water. Conditions of the ultrasonic treatment: T=298 K, P= 1·105 PA, $\nu_{УЗ}$=22 kHz under the action of gas/UZ.

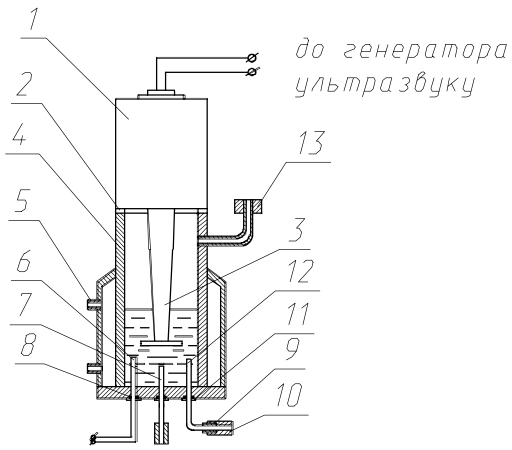

Figure 1 – Scheme of the reactor for processing suspension of cyanobacteria with ultrasound: 1 – magnetostrictor, 2,8,9 – seal, 3 – conductor, 4 – reactor, 5 – fittings for coolant, 6 – thermocouple, 7 – fittings of input gases, 10, 11 – nut, 12 – sampler 13 – gas outlet fittings.

Determination of the effectiveness of treatment, the suspension of cyanobacteria in the field of hydrodynamic cavitation was carried out in the reactor presented in Fig. 2.

As cavitating i body was used three-blade impeller wedge-shaped profile with a sharp front and a blunt rear edge, the speed of the impeller was estimated at 4,000 rev / min. The working capacity of the cavitator poured 1 l of a suspension of cyanobacteria.In further investigated 3 types of suspensions of cyanobacteria:

Sample # 1 without any treatment;

Sample # 2 is processed in rotary catator - mixer, which worked for 10 minutes.

Sample # 3 – treated in an ultrasonic catator who created cavitation field for 15 minutes.

To determine the total lipid content in the collected culture the algae were dried at 80 ^{0}C and were ground in a mortar, then mixed in a separating funnel with 50 ml of hexane and 50 ml of water and were intensively mixed for 10 min. The solid phase of algae and water collected at the bottom of the funnel, and extracted with hexane lipids - in the upper part. Water with algae merged, then extract quantitatively transferred to evaporation cup. After evaporation of hexane from a cup gravimetric determined number of extracted lipids.

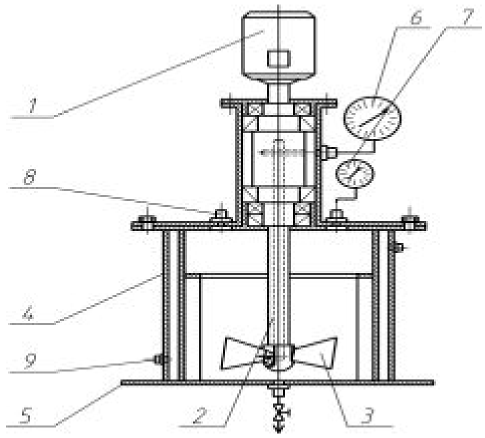

Figure 2 – scheme of the reactor for processing suspension of cyanobacteria in the field of hydrodynamic cavitation: 1-motor; 2-shaft; 3-cavitating body; 4–working volume; 5–stand (frame); 6–tachometer; 7–gauge; 8–samplers; 9– fitting for on-giving fluid.

To determine the maximum amount of lipids, which potentially can be extracted from cyanobacteria studied, conducted hexane extraction of algae suspension (sample №1, №2 and №3). To do this, 60 ml of algae placed in a separating funnel, adding 50 ml of hexane and stirred vigorously for 10 minutes. After settling allocated two phases: the lower, consisting of a mixture of seaweed with water and the high top, which consisted of hexane extracted lipids, bubbles and impurities. The upper phase was washed and quantitatively transferred to evaporation cup. After drying in a water bath cup remained on the surface lipids and gray-green sediment. Lipids re-extracted with hexane and transferred to another evaporator cup. After evaporation of hexane from it, floating on the surface layer of lipids, the amount of which was determined by gravimetric.

The research results are presented in Figure 3.

Studies have shown that the total lipid content in a selected sample of cyanobacteria was 1.27% of the dry weight. With sample №1 managed to extract lipids in an amount corresponding to 0.32% of the dry weight of algae. This result confirms that the cell membranes of raw seaweed is heavily permeable, and use them without processing for energy is difficult. With samples №2 managed to extract 1.01% and about-to №3 - 0,45% lipids. Thus, treatment of cavitation breaks the membrane wall, and leads to more complete extraction.
Especially significant is the effect in the case of hydrodynamic cavitation, because after treatment of the sample extracted manage almost 80% of all available lipids.

For experiments with biogas with the aim of simulating the upper layer of the reservoir, which is a small amount of anaerobic bacteria to intensify the process of anaerobic decomposition, samples №1, №2 and №3 mixed with primary sludge treatment plants, which contain significant amounts of anaerobic bacteria.
To 900 ml each of the samples and added to 50 ml of sludge (dry matter concentration 24.0 g / l organic part was 69.3%) and placed in a separate reactor experimental setup presented in Figure 4 (№1 test reactor 2 , №2 test reactor 3, the sample №3 reactor 4).

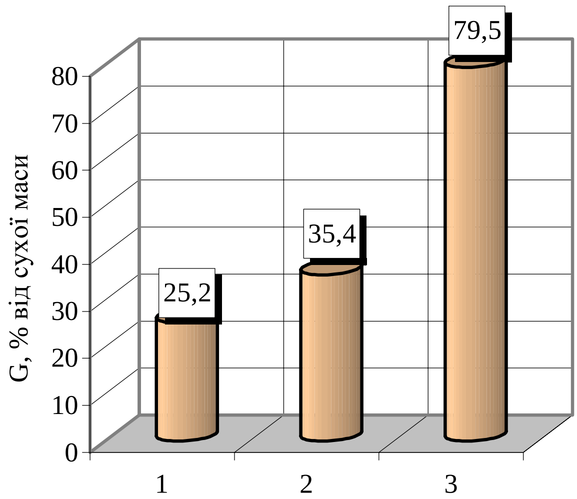

Figure 3 – Dependence degree of cyanobacteria extracted lipids (as a percentage of the total number-bones) pre-treatment of type 1 – no treatment; 2 –treatment in ultrawave catator; 3 – processing in the field of hydrodynamic cavitation.

In order to know which part of the biogas released from silt and algae that was prepared by mixing a zero sample 50 ml sludge with 900 ml of water and placed in reactor 1. The resulting solutions algae had pH=4,57-4,78, due to the early phase of acetogenesis. Optimal for anaerobic decomposition is a pH of 7-7,5, so the pH in the reactors was adjusted to 7.5 by adding small amounts of NaOH. The reactor was sealed closed tube-gas-outlet tubes.

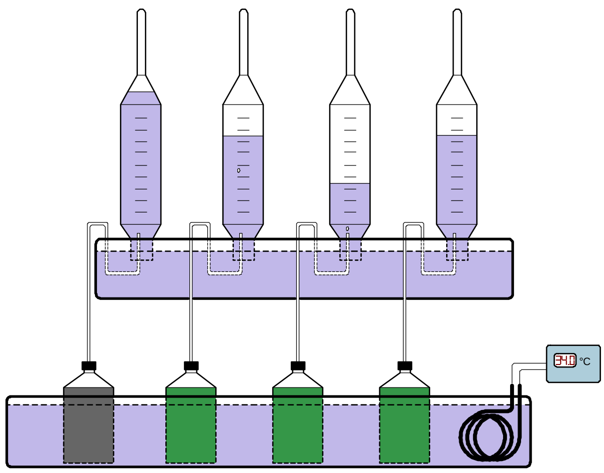

Figure 4 – Experimental installation for research of biogas

Biogas was collected in a graduated flask, which was immersed in water, the pH of the water was maintained below 5. Because at low pH the inorganic carbon is in the form of CO2, it was possible to avoid the formation of carbon dioxide contained in the biogas in the water. The reactor was wrapped in black polythene to prevent the ingress of light and placed in a water bath in which temperature was maintained at 34 °C (mesophilic conditions). The contents of the reactor were stirred for 1 min every 2 days. The research results presented in Figure 5.

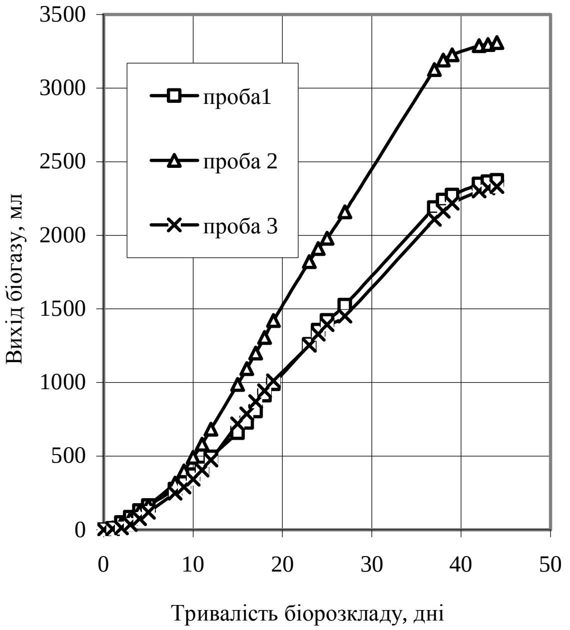

Figure 5 – Kinetics of biodegradation of biomass of cyanobacteria in mesophilic conditions

Of interest is the comparison of the total volume of produced biogas during the studies of the investigated samples. The results of this comparison are presented in Fig.6. For efficiency comparison, conventionally 100% accepted number of biogas, which was extracted from the sample after hydrodynamic cavitation (sample №3).

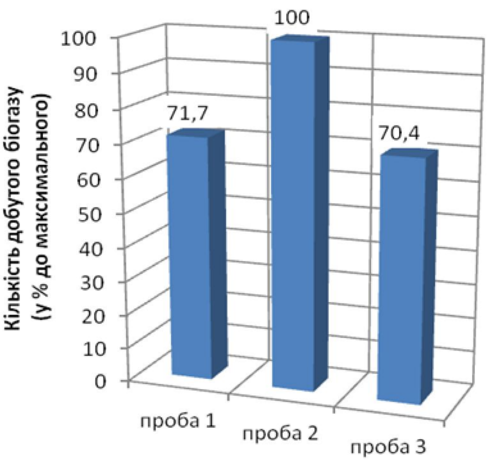

Figure 6 –The dependence of the number of biogas produced from cyanobacteria, from the type of their pre-treatment

As can be seen from Fig.6, as in the case of lipids of cyanobacteria, in the case of extraction of biogas preliminary hydrodynamic cavitation was the most effective.

The process of metagenesis most often present in 3 stages [7]:

Stage 1. Carbon dioxide binds to the carbon carrier with the formation of carboxin (X1-COOH), which is restored to formlogin (X1-CHO).

Stage 2. Passes the transfer formiline group on the second carrier (x2). This leads C1- group in two consecutive reduction reactions to education metylp derivatives (X2-CH3). In the second phase branch anabolic and catabolic and routes.

Stage 3. Metilen groups of the carrier fed to the coenzyme M (Com-SH). In further educated methyl-CoM is recovering, this results in the collapse of the complex and release of methane.

Assuming that the rate-limiting step of the enzymatic reaction is the decay of the enzyme-substrate complex to free enzyme and product, Michaelis and Menten derived an equation describing hyperbolic curve of dependence of the initial velocity against substrate concentration [8]. Dependence is often used to describe the kinetics of enzymatic reactions, however, the complexity of data interpretation with the use of this model is to determine the values of Michaelis constant, which is a part of equation or using the method Layour-Burke [8], or using numerical methods of nonlinear regression for the direct equation of Michaelis-Menten.

In our opinion promising is the description of the synthesis process of biogas from the position analysis of chain reactions by methods of physical chemistry [9], from which the kinetics of the synthesis of biogas from blue-green algae can be represented in the form (Fig.7.).

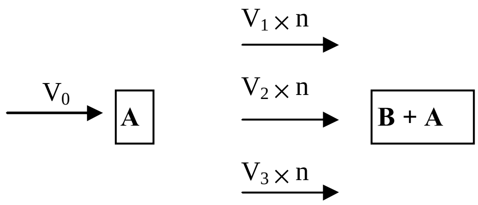

Figure 7 –diagram of the chain of the process of biochemical transformations:

V_0 – the speed of nucleation active sites of synthesis of biogas, A; n – is the concentration of the active centers of anaerobic methane fermentation; V1 – speed constant continue the chain process; V2 – speed constant breakage of chain process; V3 – constant velocity stage of the chain branching process.

In this scheme, $V_1 \times n$ determines the rate of reaction continue the chain process of biochemical transformations, which is equal to the rate of accumulation of product (i.e. the speed of the chain process), V1 depends on the concentration of components in the mixture, which undergoes digestion. $V_2 \times n$ –specifies the rate of chain breakage process. The dependence of V2 on the concentration of other substances is determined by the mechanism of breakage. $V_3 \times n$ – determines the speed stage of the chain branching process.

In accordance with the scheme of the differential equation describing the change in the concentration and accumulation can be written as follows:

$$\frac{dn}{dt} = V_0 + (V_1 + aV_3) \times n - (V_1 + V_2 + V_3) \times n \quad (1)$$

$$V = \frac{dB}{dt} \quad (2)$$

t – is the time from the start of the biochemical process; a is the stechiometric coefficient, and ≥ 2.

Suppose that at time t the values V1, V2, V3 are slightly changed so that to integrate them with a sufficient degree of accuracy to be considered as permanent. This really is true for the implementation of biochemical processes.

Proportional to the concentration of active sites denote:

$$r = V_1 + aV_3; \qquad S = V_1 + V_2 + V_3 \quad (3)$$

r and S for these conditions can be considered as the rate constants of the reactions
pseudo first order, that leads to the regeneration (r) and response (S) active sites.

Let us denote $\varphi = r - s.$ φ is called [9] a constant slew of active sites. Taking into account (3) equation (2) is reduced to the form:

$$\frac{dr}{dt} = V_0 + \varphi \times n \quad (4)$$

After separation of variables in equation (4), integration, exponential and transformations we get

$$n = \frac{V_0}{\varphi}\left[\exp(\varphi \times t) - 1\right] \quad (5)$$

Let us accept the assumption that the yield of biogas in the system Vbio directly proportional to the concentration of active sites of biochemical reactions

$$V_{bio} = \varepsilon \times n \quad (6)$$

ε - the constant of proportionality between the concentration of active sites of biochemical reactions and the yield of biogas.
Taking into account (6) equation (5) takes the form

$$V_{bio} = \Psi \times \phi(t) \quad (7)$$

$$\Psi = \frac{\varepsilon \times V_0}{\varphi}; \quad \phi(t) = \exp(\varphi \times t) - 1 \quad (8)$$

Ψ – complex kinetic constant synthesis of biogas, $\phi(t)$ - a function of time.

Analyzing the type of formulas (7 - 8) can come to the conclusion that in structure they are similar to the formula obtained by simple transformations of the equation Michaels-Menten [8], which once again confirms the subordination of the investigated process are well-known biological laws.

According to equation (7) V_{bio} between and $\phi(t)$ there should be a directly proportional dependence.

Consequently, any analysis of equations (7 – 8) can come to the conclusion that until such time as $t \le \frac{1}{\varphi}$,, the rate of biochemical transformations and the yield of biogas is increasing slowly.

When $t \ge \frac{1}{\varphi}$, the speed of biochemical reactions, and the yield of biogas is increasing exponentially, reaching large values until the complete exhaustion of raw materials in a form accessible to biochemical transformations.

The period of time $t_\varphi = 1/\varphi$ from the beginning of biochemical transformations, by analogy with the kinetics autocatalytic chemical reactions [9], called the induction period.

Thus, the process for chain of biochemical transformations characterized by the presence of 3 periods (Fig.5):

1 – the induction period of active sites of biochemical reactions;

2 – the period of developed process of biochemical transformations;

3 – period of completion of the process of biochemical transformations due to complete exhaustion of raw materials in a form accessible to biochemical transformations.

As can be seen from Fig. 5, the presence of 3 periods is present and kinetic curves for the synthesis of biogas from cyanobacteria. Coordinate transition kinetics with 1 period 2 is determined by the intersection point of line segments tangent to the kinetic curve 1 and 2 periods.

Establishing coordinates tφ for the investigated process was carried out graphically using the data presented in Fig.5.

As a result of graphic constructions it has been established that the kinetics of the formation of biogas in the biomass of cyanobacteria, which were processed in the field of hydrodynamic cavitation tφ1 = 10.9 days; and for the kinetics of the formation of biogas in the biomass of cyanobacteria without treatment and treated with ultrasound tφ2 = 12 days.

With the establishment of values the opportunity to test the adequacy of the developed mathematical model (equation 7) to the real process. The audit was conducted for the process of biodegradation of the sample, which has been in the field of hydrodynamic cavitation and the merged array of samples without treatment and with treatment in the ultrasound field, the kinetic curves which are almost identical. Validation was performed for data that corresponds to the development process of biochemical transformations. For the investigated dependencies consistent with the 19 day of research. Because in the future the process of biochemical transformation superimposed process Carmona process because the costs are capable of fermentation of the material, the use of these data transmission process which falls out of the general concept of his research, inevitably worsened the description of the kinetic curves obtained by the proposed mathematical model. The test results showed that for both investigated the relationship between arrays and describes a straight line, and the determination coefficients of this linear relationship established using the program Microsoft Excel (0,9958 and 0,9954) confirm the linearity of the dependences.

The linearity of the obtained dependences allows to argue about the correctness of the developed mathematical model and provides the ability to define complex values of the kinetic constants of synthesis of biogas, the importance of which for the studied data sets were:

Ψ_1 = 316,25 ml. – for biomass cyanobacteria, about-making in the field of hydrodynamic cavitation.

Ψ_2 = 263,95 ml., for the joint array of samples (without treatment and with treatment in the field of ultrasound). Set the values of the kinetic constants can be used for calculations of real processes.

CONCLUSIONS. A series of experimental studies showed that promising is the production of the collected algae, biodiesel and biogas. Lipid content in the collected culture of blue-green algae is negligible (1,27%), and therefore the extraction method you can remove only a small portion of the energy contained in biomass. The influence of the cavitation field (especially in the case of hydrodynamic cavitation) can significantly increase the efficiency of the extraction of fats.

Experiments on the production of biogas confirmed that pre-treatment cavitation using hydrodynamic cavitation field destroys the cell wall of cyanobacteria, as the production of biogas from algae occurred much faster, and the amount of produced biogas is much higher (approximately 30%). Process kinetics of biodegradation of biomass of cyanobacteria is described by S-shaped curves, indicating a complex chain process of biochemical reactions that accompany the formation of biogas. The mathematical model of the process, the adequacy of which is confirmed by the identification of the theoretical equations to the experimental data. This gave the possibility to define complex values of the kinetic constants of synthesis of biogas.

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МАТЕМАТИЧЕСКАЯ МОДЕЛЬ ПРОЦЕССА СИНТЕЗА БИОГАЗА ИЗ СИНЕ-ЗЕЛЕНЫХ ВОДОРОСЛЕЙ

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Доказана перспективность использования цианобактерий для производства энергоносителей: биодизеля и биогаза. Проведены эксперимен6тальные исследования с целью установления целесообразности применения предварительной подготовки биомассы (акустическая и гидродинамическая кавитация) для увеличения эффективности процессов экстрагирования липидов и синтеза биогаза. Установлено, что применение гидродинамической кавитации позволяет более чем в 2 раза увеличить количество экстрагированных липидов, тогда как влияние акустической кавитации незначительно. В случаи применения гидродинамической кавитации на 30/% увеличивается также количество синтезированного биогаза. Разработана математическая модель процесса синтеза биогаза с цианобактерий, адекватность которой доказана идентификацией полученного уравнения экспериментальным данным. В результате идентификации установлены значения комплексных кинетических констант процесса синтеза биогаза, которые могут быть использованы для расчета реальных процессов.

Ключевые слова:цианобактерии, кавитация, біогаз, липиды, адекватност, математическое моделирование.