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PRODUCTION OF RENEWABLE ENERGY RESOURCES VIA COMPLEX TREATMENT OF CYANOBACTERIA BIOMASS

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Abstract. The process of cyanobacteria complex treatment *via* obtaining of inedible fat, suitable for the production of biodiesel and biogas has been investigated. The prospective application of hydrodynamic cavitation to increase the efficiency of inedible fat extraction and biogas synthesis is shown. A comprehensive strategy for the cyanobacteria use in the energy and agricultural technologies is suggested.

Keywords: cyanobacteria, cavitation, biogas, inedible fat, extraction, strategy.

1. Introduction

Biomass (wastes of wood processing, agricultural products, special planting in forestry and agriculture) occupies a prominent place among the renewable energy sources. So, in Latvia the share of biomass in gross domestic energy consumption is about 28 % (the leader among EU countries), in Sweden – 22 %, Finland – 21 %, Denmark – 17 %, Austria – 16 %, Germany – 8 %. For comparison: in the USA the share of biomass in total energy consumption is 3.9 %, in Ukraine – 1.24 % [1-3].

The most important role of biomass is in the heatand-power engineering sector. Nowadays about 15 % of the total heat energy in EU is produced from biomass. Almost all heat energy from renewable energy sources (99 %) is obtained from biomass and organic wastes. However, in some countries the cultivation and use of plants as a raw material for the production of energy gained such proportions that decreased agricultural production to a critical level and provoked a public protest (Latin America, Mexico, *etc.*). Therefore, the search of application technologies for energy production of such types of biomass, which does not need the reduction of agricultural land areas, is an important task for scientists.

As it was shown by the research data and attempts of practical implementation (Gas and NEDO companies -Japan, GreenFuel Technologies - USA, Seambiotic -Israel), the algae cultivated at special farms or collected from ponds can be such biomass. In Ukraine cyanobacteria (blue-green algae), which pose a threat for environment due to progressive water "blooming", may be such a prospective biomass. Water "blooming", the dominant agents of which in the Dnieper storage ponds are representatives of Microcystis, Phormidium, Aphanizomenon, Anabeana and Oscillatoria genera, is a biological signal of troubles in hydroecosystems. Among numerous mechanical, physical, chemical, biological and ecological methods for preventing mass development of cyanobacteria the latter two methods are the most effective ones, because they can save from the causes and not the consequences of water "blooming" [4]. Concerning the prospects of biomass used for energy production, microalgae are the most promising utilizers of solar energy: maximum efficiency of photosynthesis for them is 20 %.

The search of biodegradation intensification ways and the increase of the share of organic matter in the biomass substrate for biodegradation, which is used for the biogas synthesis, is also the urgent problem. V. Barbash and O. Sklyar [5, 6] found that preliminary preparation (grinding and delignification) of the agricultural wastes used as a raw material is a promising way. During delignification at high temperatures the degradation of lignin lattice, lignin and most of the hemicellulose extraction, as well as splitting of chemical bonds between lignin and hydrocarbon molecules take place. The result is an increase in the mass transfer surface, which becomes available for celluloselytic enzymes of microorganisms. The same situation is observed at substrate grinding on the grinding machine that accelerates the enzymatic hydrolysis and intensifies the process of methane synthesis [7].

The aim of the work is to determine the effect of algae cavitation pretreatment to increase the completeness of getting energy resources (inedible fat and biogas) from them and to intensify the process.

Cyanobacteria extraction and biodegradation are low-intensive processes because bacteria have rather dense cell membrane. We investigated the possibility of these processes intensification *via* destroying the cell membrane by the cavitation method. The areas of high and low pressure (which destroy the cell membrane) are formed during cavitation. We examine two options of algae usage for the energy production of acoustic and hydrodynamic cavitation: i) extraction of fats, which can be further used for the biodiesel production; ii) biogas production.

2. Experimental

For research we used cyanobacteria selected at the Kremenchuk storage pond, Svitlovodsk, Ukraine. The algae suspension was prepared before the experiments. The dry matter content was 17.1 g/l that corresponds to the real concentration of algae in accumulation places.

At the first stage of the research we determined the content of the algae organic matter by burning the dried algae sample in an oven at 823 K for 15 min. According to the investigation results the organic matter was 94 % of the algae total mass.

To determine the total content of fat in the collected culture, algae were dried at 353 K and grinded in a mortar. Grinded algae were mixed in a separating funnel with 50 ml of hexane and 50 ml of water for 10 min. The solid phase of algae and water were collected at the bottom of the funnel, and extracted fat with hexane – in its upper part. Water with algae was poured out and the extract was transferred to an evaporation cup. After hexane evaporation the amount of extracted fat was determined by gravimetry.

For the acoustic cavitation the cyanobacteria suspension was loaded in an ultrasonic reactor. Ultrasonic vibrations (frequency – 22 kHz, capacity – 35 W, intensity – 1.65 W/cm³ per volume unit) of the UZDN-2T generator were transferred through a magnetostrictive transmitter immersed in the investigated medium (V = 150 cm³). Carbon dioxide was bubbled through suspension over the

whole process time. The reactor was continuously cooled by running water. The ultrasonic treatment conditions were: T = 298 K, $P = 1 \cdot 10^5$ Pa, $v_{us} = 22$ kHz.

To determine the treatment efficiency of cyanobacteria suspension in the field of hydrodynamic cavitation the hydrodynamic cavitator was used, where a three-bladed wedge-shaped impeller with sharp front and blunt trailing edges was a cavitation body (revolutions speed was 4000 rev/min). The cavitator was loaded with 1 l of cyanobacteria suspension.

For the experiments concerning biogas production the samples were mixed with primary sludge from the treatment plants, which contains a large amount of anaerobic bacteria. It was done for the purpose of simulating the composition of the upper layer of the pond, where a small amount of anaerobic bacteria are present, to intensify the process of anaerobic decomposition. 50 ml of sludge (dry matter concentration was 24.0 g/l; organic matter was 69.3 %) were added to 900 ml of each sample and the mixtures were placed in the separate reactors of the laboratory plant, the scheme of which is presented in Fig. 1.

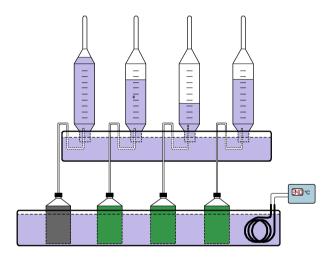


Fig. 1. Laboratory plant for the study of biogas production

In order to know what part of the biogas is released from the sludge and algae, the blank sample was prepared by mixing 50 ml of sludge with 900 ml of water. pH of the prepared algae solutions was 4.57-4.78, as a result of acetogenesis phase beginning. The optimal pH for anaerobic decomposition is within the range of 7–7.5, so we corrected pH to 7.5 in the reactor by adding a small amount of NaOH solution. The reactors were closed by tight plugs with gasescape tubes. The produced biogas was collected in a graduated flask immersed in water, pH of which was maintained below 5. Since at low pH inorganic carbon is in the form of CO₂, it was possible to avoid the dissolving in water of carbon dioxide which is contained in the biogas. The reactors were wrapped in black polyethylene to protect them from light and placed in a water bath with the temperature of 307 K (mesophilic conditions). The contents of the reactors were stirred for 1 min every 2 days. The total time of investigations was 26 days.

3. Results and Discussion

The investigations results of the inedible fat extraction from cyanobacteria show that the total fat content in the sample is 1.27 %. The amount of fat extracted from the sample without pretreatment corresponds to 0.32 % of the algae dry mass, and from the sample after the cavitation treatment – 1.01 %. This result confirms that the cell membranes of untreated algae are hardly permeable, and their use without pretreatment is complicated. The cavitation treatment disrupts the membrane walls and leads to more complete extraction. Such effect is especially significant in the case of hydrodynamic cavitation, because 80 % of the total available fat could be extracted after treatment. The obtained fat may be used for biodiesel production [8].

Kinetics of biogas synthesized from the studied algae is represented in Fig. 2. In the case of activated sludge biodegradation without cyanobacteria, we can assume with high probability that the process of biogas production occurs with a constant speed. In the case of biogas production in the process of cyanobacteria biodegradation (without additional treatment or treated in the field of hydrodynamic/ultrasonic cavitation) the kinetic curves of biogas emission have S-shaped form, that indicates a multi-staged process.

According to data presented by I. Litovchenko *et al.* [9] a metagenesis process can be described by 3 stages:

<u>Stage 1.</u> Carbon dioxide is bonded with a carbon carrier and forms carboxy derivative X1–COOH reduced to formyl derivative X1–CHO.

<u>Stage 2.</u> Formyl group is transferred to other carrier X2. This leads to the formation of methyl derivative X2–CH3 from C1-group *via* two consecutive reducing reactions. At the second stage anabolic and catabolic paths are divided.

<u>Stage 3</u>. Methyl groups transfer from the carrier to the coenzyme M (CoM-SH). Then the formed methyl-CoM is reduced resulting in the complex decomposition and methane release.

Taking into account the above-mentioned mechanism and analyzing our experimental data we consider metagenesis as a chain autocatalytic process for which the extended induction period of biochemical transformations active centers, the period of developed biochemical reactions and the period of metagenesis ending are typical due to the absence of available raw materials for the biogas synthesis.

The research results also show that the preliminary hydrodynamic cavitation was the most effective one. Moreover, the intensity of biogas emission is approximately the same for all samples, while the amount of synthesized biogas is significantly higher (40 %) in the case of cyanobacteria pretreatment in the field of hydrodynamic cavitation.

With the aim of funding utilization ways for waste cyanobacteria biomass the dynamics of quantitative germination of peas and wheat was studied by using biomass as the organic fertilizer [10]. The experimental results (which are confirmed by the studies of Daphnia survival in aqueous solutions of substrate with different concentrations [11]) show that dilution of the waste substrate with the ratio of 1:200 for wheat and 1:100 for peas is the optimum for cyanobacteria waste bioculture as the organic fertilizer.

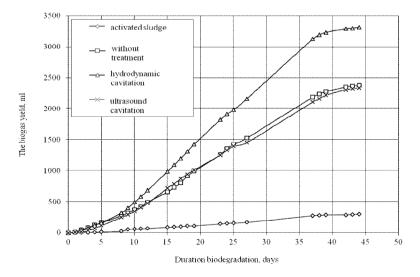


Fig. 2. Biodegradation kinetics of activated sludge and biomass of cyanobacteria under mesophilic conditions

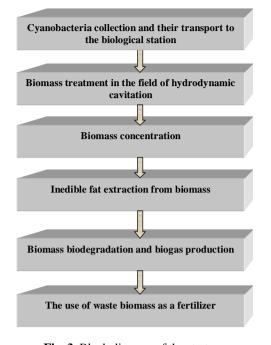


Fig. 3. Block diagram of the strategy using cyanobacteria in energy and agricultural technologies

On the basis of the conducted researches we developed a rational strategy for the cyanobacteria use in the energy and agricultural technologies. The block diagram of the developed strategy is presented in Fig. 3. In accordance with Fig. 3 a promising technology for producing energy resources from cyanobacteria is a complex processing which consists of the following stages:

1. The collection of cyanobacteria and their transport to the biological station, where it undergoes further treatment.

2. Cavitation treatment in a hydrodynamic cavitation field.

3. Extraction of fats by hexane followed by the production of biodiesel.

4. Anaerobic decomposition of biomass residues and biogas production.

5. Centrifugation of waste biomass and its use as a fertilizer.

4. Conclusions

Utilization of cyanobacteria for the production of biodiesel and biogas is a promising way. The fat content in the collected culture of blue-green algae is insignificant (1.27 %). Therefore, using the extraction method it is

possible to extract only a small part of the energy present in biomass. The influence of the cavitation field (especially in the case of hydrodynamic cavitation) allows to significantly increase the efficiency of fats extraction. Biogas production experiments confirmed that cavitation pretreatment using hydrodynamic cavitation field destroys the cyanobacteria cell walls because the biogas from such algae is produced much faster. The waste biomass obtained after the synthesis of renewable resources can be used as an organic fertilizer. So the developed complex strategy for the cyanobacteria use is a rational one. It consists of the collection of cyanobacteria \Rightarrow treatment in the field of hydrodynamic cavitation \Rightarrow inedible fat extraction \Rightarrow biogas synthesis \Rightarrow use of waste biomass as the organic fertilizer.

References

[1] http://www.iea.org/stats/index.asp.

[2] http://ec.europa.eu/energy/observatory/statistics/statistics_en.htm.

[3] Energetychnyi Balans Ukrainy za 2011. Express-vypusk 08/4-16/290 ot 20.12.2012, www.ukrstat.gov.ua.

[4] Nikiforov V., Degtyar S. and Shmandiy E.: Mashinostroenie i Bezopasnost Zhyznedeyatelnosti: Mezhvuz. sbornik, 2008, **5**, 51.

[5] Barbash V., Pymakov S., Tembus I. and Klik M.: Visnyk Nats. Techn. Univ. Ukrainy "KPI", 2010, **6**, 97.

[6] Sklyar O. and Sklyar R.: Nauk. Visnyk Tavrijskyi Derg. Agrotechn. Univ., 2014, 1, 3.

[7] Nesterov A., Suslenkov B. and Starovoitov G.: Prikl. Biokhim. i Microbiol., 1973, **9**, 873.

[8] Mata T., Martins A. and Caetano S.: Renewable and Sustainable Energy Rev., 2010, **14**, 217.

[9] Litovchenko I., Makarenko K. and Struchalyna T.: Problemy i Perspektivy Anaerobnoi Microbiologicheskoi Conversii Aminokislot v Biogas. Ilim, Frunze 1990.

[10] Nikiforov V., Kozlovska T. and Avramenko A.:Ecologichna Bezpeka, 2010, 9, 67.

[11] Krainykova N. (Ed.): Metodicheskoe Rukovodstvo po Biotestirivaniyu Vody. VNIIVO, Kharkov 1991.

ОТРИМАННЯ ВІДНОВЛЮВАЛЬНИХ ЕНЕРГОНОСІЇВ ВНАСЛІДОК КОМПЛЕКСНОГО ПЕРЕРОБЛЕННЯ БІОМАСИ ЦІАНОБАКТЕРІЙ

Анотація. Досліджено процес комплексного перероблення ціанобактерій через отримання технічного жиру, придатного для виробництва біодизеля, та біогазу. Показано перспективність застосування гідродинамічної кавітації для збільшення ефективності екстрагування технічного жиру та синтезу біогазу. Запропонована комплексна стратегія використання ціанобактерій у енергетичних та сільськогосподарських технологіях.

Ключові слова: ціанобактерії, кавітація, біогаз, технічний жир, екстрагування, стратегія.