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QUALITATIVE AND QUANTITATIVE CHARACTERISTICS OF BIOGAS OF CYANEA ORGANIC MASS

Sergy Digtiar

Kremenchuk Mykhailo Ostrohradskyi National University, faculty of Natural Sciences, Department of Biotechnology and Human Health, 39600, Pershotravneva str, 20, Kremenchuk, Ukraine.

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Abstract. The article discusses the results of studies of the methane production from cyan biomass based on the data obtained in the course of a laboratory experiments. The yield of biogas was calculated from the substrate per unit volume, and its energy properties were determined. Experimental data indicates the feasibility and economic viability of this biotechnology.

Key words: cyanobacteria, algal bloom, biogas, methanogenesis, heat of combustion.

Introduction

The problem of so-called “flowering” of water bodies caused by the intensive development of photosynthetic microorganisms in particular cyanobacteria becomes more acute in the cascade of the Dnieper reservoirs from year to year. This is facilitated by a complex of factors, the most significant of which are the changes in the hydrological regime of the river due to construction of reservoirs cascade and formation of the optimal conditions for the growth of phytoplankton organic mass. Researches show [1, 2, 3] and the bulk of the excess biomass is necessary for the type of blue-green algae *Microcystis aeruginosa*. Emissions of algotoxins and mass extinction of cyan followed by oxidation processes in the water volume can cause large-scale aquatic mortality [4].

A radical solution to this environmental problem requires a comprehensive approach and global hydro-technical activities over large areas and therefore significant capital expenditures, which now seems hardly a feasible project. However, the negative cyanea impact on the river ecosystem can be substantially reduced by the mechanical extraction of biomass from the reservoir and its further processing.

Achieving a balance between environmental and economic aspects of the problem is possible due to full utilization of the organic matter recovered from hydro-ecosystems. To collect and concentrate the substrate on an industrial scale, special concentration columns are located in the areas of maximum natural thickening of cyanea biomass (Fig. 1).

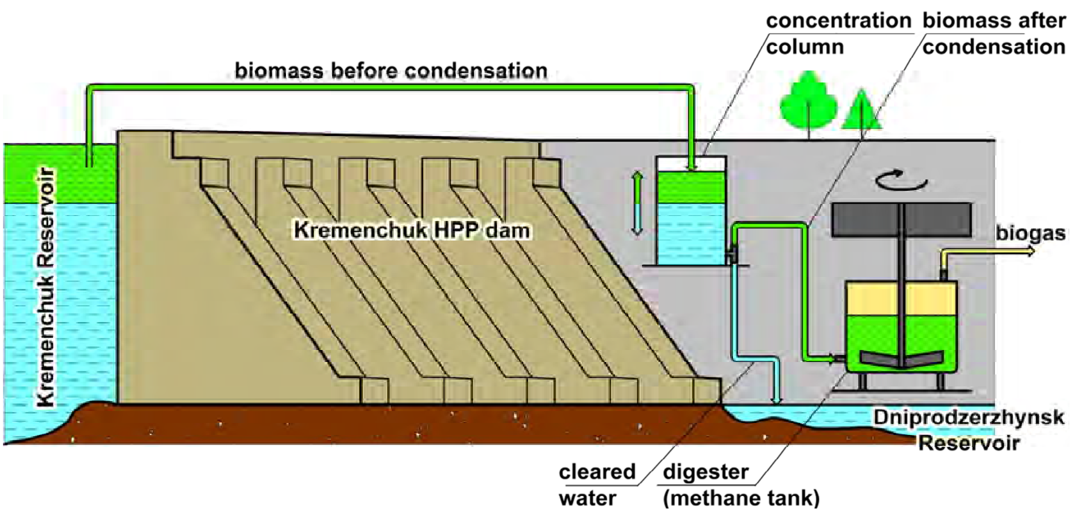

Fig. 1. The circuit arrangement of processing units of industrial installations for the production of biogas

Biomethanogenesis is the process of obtaining the gas mixture, the main component of which is methane, can be considered among the possible ways of cyano bioconversion as the most promising possibility. The substrate spent in the process of methanogenesis can be recognized as a sufficient one since the series of substances concentration used in various fields of economy reaches the values that lead to the economic feasibility of their industrial extraction. In addition, the waste biomass is an effective fertilizer, ready for the use in agriculture and forestry.

Classical technology for biogas producing from organic wastes of agrogene origin is based on the symbiotic interaction of three groups of microorganisms. At one of its stages the process of biosynthesis of a gases mixture by methanobacteria with prevalence of methane (more than a half of the volume) and impurities of other gases in the presence of which methanogens are developed (H_2 and CO_2) or repressed (O_2). *Methanobacterium formicicum* and *Methanospirillum hungati* species dominate in the process of methanogenesis [5].

Effective use of this technology by applying cyanea biomass as a substrate requires a number of research results of which are discussed in this article.

Material and methods

To study the properties of the organic cyan matter in the upper Dniprodzerzhynsk reservoir in the city of Kremenchug there was selected about 10 kgs of aqueous concentrate. Species composition and the number of cells in the selected substrate were determined by hemocytometer (Goryaev's camera), light microscope Ningbo Shengheng XS – 3330 with a video attachment "micro med" and a computer program for the "ISCapture" image processing.To accomplish this, a drop of cyanea cells from the condensation was placed in the center of a chamber and covered with special cover glass, carefully lapping at the edges of the chamber until Newton rings appear. In this case, the thickness of the liquid layer in the chamber above the grid is corresponded to 0.1 mm, and the volume of the chamber is approximately 1 mm^3. Each small square limits the amount of fluid in the 1/4000 mm^3.

Counting of cells in the hemocytometer began after 3–5 minutes after its filling when the cells settled and located in the same plane. After this, calculation was made in 20 small squares moving on them diagonally. To achieve the results with sufficient reliability of the test, 3 or 4 samples were taken from organisms suspension for mounting a camera.

Microscopy of samples was performed at a 160 times magnification and showed that the concentration of the *Microcystis aeruginosa* has exceeded 1 million. cl./cm^3 (Fig. 2).

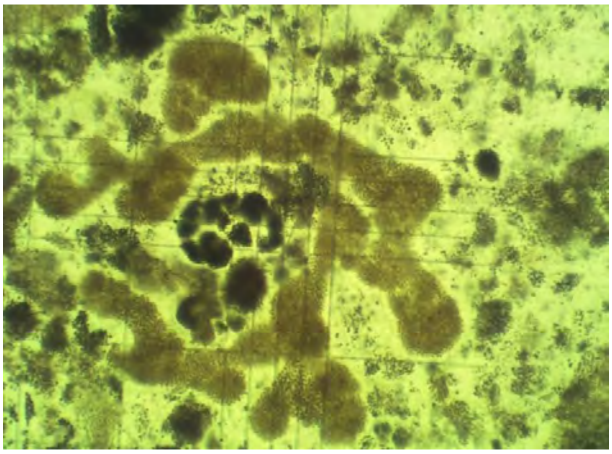

Fig. 2. Photomicrograph of *Microcystis aeruginosa* cells in hemocytometer (Goryaev's camera) (×160)

To obtain dry residue, liquid concentrate was exhibited for 96 hours at average daily temperature of 28 ºC. Drying was carried out in shallow flat-bottomed cuvettes with the volume from 0.5 to 1.5 dm^3. As a result, dry samples with the average weight of 18 g from 1 dm^3 of biomass were obtained and that allows to attribute the reservoir site, where samples were taken, to the fifth class of flowering (hyper-flowering) [6].

To determine the mineral content in the dry mass, three 10 g samples have been burn in a muffle furnace ПМ–8 at 800 °C on 40 minutes. After complete combustion of organic matter, the weight of the test portions was 1.7 g, 2.0 g and 2.0 g respectively (with average of 19 % of the dry mass).

The chemical composition of the gas mixture obtained during the experiment, as well as its density and calorific value were determined using a gas chromatograph Crystal–2000M [7].

The research of quantitative measures of fermentation dynamics was carried out by measuring the amount of emitted gas per time unit. In addition, the mechanism of methane fermentation "launch" and the effect of fermentation rate temperature are researched.

The changes in the biogas volume during the inoculation of fresh cyanea mass with and without the substrate were determined. The reserch has shown that fermentation is successfully held at the temperature in the range of 20–30 °C. In this case, 1.2 m^3 of biogas is extracted from 1.0 m^3 of substrate per week. The fermentation process ends average in a month.

At the same time, the analysis showed the absence of heavy metals and other contaminants in the substrate. This makes it possible to classify the remainder as an organic fertilizer of wide application range.

Extracted biogas contains 85 % of methane (Table 1).

Table 1

The chemical composition of biogas (by Nykyforov V. V.)

gas	volume, %
methane	75–85
carbon dioxide	10–20
carbon monoxide	1
hydrogen	1

Results. An experimental installation for methanogenesis process simulation at industrial conditions for the first time was assembled and tested in the Department of Natural Sciences of Bioenergy laboratory [8] and seven years later modeled and put into operation in the Department of Biotechnology and Human Health laboratory at Kremenchuk Mykhailo Ostrohradskyi National University [9]. The experiment was conducted in a dry-air electric thermostat TC-80M at 30 °C.

During the experiment there were used two samples of cyan biomass ($V = 0.5$ dm^3) selected from Dniprodzerzhynsk reservoir (nearby the "Neptune" pool) in September, 2015. Based on the data from a number of studies [10, 11], in which determined the effectiveness of applying pre-processed cyanobacteria biomass by using hydromechanical methods, one of the samples has been previously subjected to a process of mechanical cavitation for 7.5 minutes.

The emission of the first volume of biogas, which was collected in the relevant measuring cylinders by means of "water gate", was recorded in a day after the start of the experiment. The formation of biogas from the substrate, which was not carried to cavitation process is marked on the chart with a dark color, and from the sample after cavitation marked with a lighter one (Fig. 3).

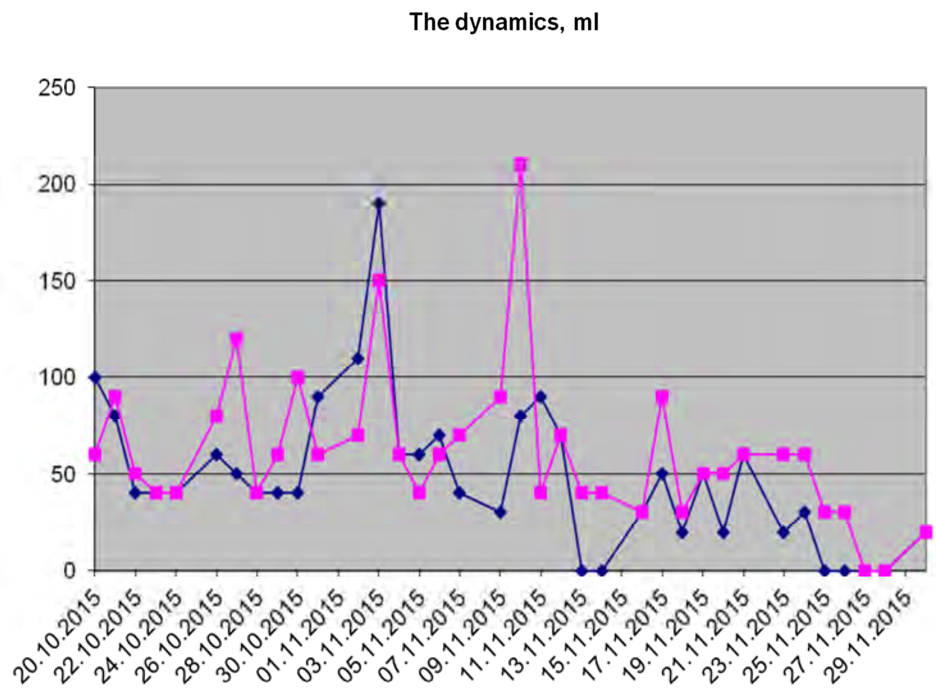

Fig. 3. Chart of laboratory productivity of biogas plants (the 0Y-axis describes the volume of biogas, cm^3)

As a result, during the whole experiment while gas released from 1 dm^3 of non-cavitated substrate an 1.72 dm^3 of biogas mixture was obtained (on 37 days), and from the same volume but cavitated substrate respectively 2.19 dm^3 (42 days) – an increase of 21.5 %. These samples were analyzed by a gas chromatograph Crystal–2000M and chemical composition of the gas mixture as well as its density and the calorific value have been defined basing on that analysis. Qualitative and quantitative characteristics of gas mixture formed in case of the cyanobacteria organic matter bioconversion, regardless of it has been subjected to pre-cavitation or not did not differ fundamentally.

Absorption analysis of biogas samples showed the presence of arithmetic mean amounts of methane (CH_4) and hydrogen (H_2) – 71.33 %, carbon dioxide (CO_2) – 20.35 %, nitrogen (N_2) – 6.45 %, oxygen (O_2) – 0.42 %, hydrogen sulfide (H_2S) – trace (0.01 %), carbon monoxide (CO) – 0.18 %, as well as other gases – 1.26 % (Table 2). The gas density was 0.915 – 0.925 kg/m^3 with a calorific value of Q = 5100 – 5200 kJ/m^3, which are in its parameters close to natural gas (propane-butane mixture).

Table 2

The chemical composition of biogas (%) obtained from the cyanogen during November, 2015

№	date	CH_4+H_2	CO_2	N_2	O_2	CO	H_2S	other
1	02.11	70,10	20,05	8,15	0,36	0,15	0,04	1,15
2	03.11	72,00	19,07	7,05	0,49	0,22	–	1,17
3	04.11	71,75	20,77	6,75	0,73	–	–	–
4	05.11	71,90	20,00	7,23	0,43	0,22	–	0,22
5	06.11	70,14	22,04	7,34	0,34	0,11	0,03	–
6	07.11	71,15	21,05	7,30	0,33	0,12	–	0,05
7	09.11	73,09	20,14	6,13	–	0,54	–	0,10
8	10.11	72,05	19,05	7,02	0,03	0,02	0,09	1,74
9	11.11	70,30	21,05	7,25	0,80	0,60	–	–
10	12.11	71,11	20,01	6,30	0,55	–	–	2,03
11	13.11	73,00	19,11	5,98	0,30	0,29	–	1,32
12	14.11	71,15	20,05	5,41	0,18	0,10	–	3,11
13	16.11	71,56	20,28	6,02	0,42	0,16	–	1,56
14	17.11	71,74	19,95	7,31	0,59	0,27	–	0,14
15	18.11	70,25	20,21	5,47	0,85	0,15	0,07	3,00
16	19.11	72,77	19,18	6,12	0,27	0,13	–	1,53
17	20.11	70,26	21,09	6,54	0,21	0,23	–	1,67
18	21.11	72,05	19,54	7,00	0,48	0,25	–	0,68
19	23.11	69,78	22,87	5,97	0,35	–	–	1,03
20	24.11	67,99	24,14	6,18	0,30	0,18	–	1,21
21	25.11	72,54	19,91	5,11	0,41	0,09	–	1,94
22	26.11	70,97	20,10	7,00	0,43	0,11	–	1,39
23	27.11	73,25	18,88	5,01	0,55	–	–	2,31
24	28.11	72,14	19,14	6,05	0,61	0,21	–	1,85
25	30.11	70,23	21,13	5,55	0,40	0,24	0,05	2,40
$\Sigma_{aver.}$	**–**	**71,33**	**20,35**	**6,45**	**0,42**	**0,18**	**0,01**	**1,26**

Conclusions

Experimental data indicates the feasibility and economic viability of using cyanea organic mass extracted from flowering spots in the water of the Dnieper reservoirs for industrial production of biogas, followed by the application of the waste substrate as a balanced organic and mineral fertilizers in forestry and agriculture. Research results generally confirm the earlier calculations of average yield of biogas per week in amount of about 0.7 dm^3 per 1 dm^3 of concentrated substrate at the optimum temperature of 30 °C [12] and the data on the prospects of the biological substrate pre-treatment in a cavitation field as the preparatory process for its further bioconversion [13].

Experiments on the production of biogas confirmed that cavitation pre-treatment by using hydrodynamic cavitation field, 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 accompanies the formation of biogas.

Obtaining certain biologically active substances used in pharmaceutical and cosmetic from phytoplankton biomass can also be perspective.

Thus, we can estimate the ability of using cyanobacteria to obtain biogas in Kremenchuk reservoir with water surface area of 2250 km^2. By collecting seston in “flowering” spots in the amount up to 50 kg/m^3 [15] in the water volume of 828 million m^3 (depth up to 2 m; 18.4 % of the reservoir area) its biomass will be 4.14×10^7 tons during the growing season. Subjecting the biomass to fermentation in the process of methane “fermentation” it’s possible to receive up to 28.98 million m^3 of biogas (≈18.837 million m^3 of methane), which is equivalent to 20000 tons of oil, or 17000 tons of diesel fuel.

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