Decarbonizing gas emissions from petrochemical production using microalgae

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Abstract. Thermal and catalytic processes of purification of hydrocarbon raw materials, which are produced by oil refineries and petrochemical enterprises, make a significant contribution to the increase in greenhouse gas emissions. Exhaust gases of thermal and catalytic processes containing a mixture of inert gases and C_1-C_5 hydrocarbons are sent for flaring. Industrial enterprises, especially petrochemical ones, emit a large amount of other greenhouse gases besides CO_2. This study was executed in order to study the absorption of blow-off gases obtained during petrochemical production by marine microalgae Isochrysis galbana and Chlorella microalgae. In each experiment conducted as part of this study, microalgae underwent two successive growth phases: the preparation phase and the cultivation phase. The studies were conducted at various temperatures and pressures. Exhaust and blow-off gases of the existing industrial production of isoprene were selected for laboratory experiments, so the composition of the gas changed significantly between tests. The microalgae showed the highest absorption capacity under the condition of 32 °C and high gas pressure. Microalgae Isochrysis galbana and Chlorella microalgae showed the ability to absorb gases C_1–C_5 with an efficiency of 75.0%. The obtained research results can be used in the complex cleaning of biological treatment facilities.

1 Introduction

In accordance with the Decree on the National Development Goals of the Russian Federation for the period up to 2030 and for the future up to 2036 dated May 7, 2024 [1] p.5. Establish the following targets and tasks, the fulfillment of which characterizes the achievement of the national goal "Environmental well-being": b) gradual halving by 2036 of emissions of dangerous pollutants that have the greatest negative impact on the environment and human health in cities with high and very high levels of atmospheric air pollution.

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At the same time, laws on the reduction and complete cessation of greenhouse gas emissions into the atmosphere are in force [2].

The Intergovernmental Panel on Climate Change (IPCC) has forecasted that by the year 2100, the concentration of CO_2 in the atmosphere will reach 570 parts per million, resulting in an average temperature increase of 1.7-1.9 degrees Celsius. Full information in the IPCC's and others [3-6].

These matters must be tackled comprehensively. Currently, biological treatment plants (BTPs). The composition of the sludge changes under the influence of harmful substances, leading to the mutagenesis of organisms. Natural selection results in the emergence of new strains that can utilize any, even toxic, substances as a source of carbon. To completely eliminate harmful substances, both anaerobic and aerobic conditions are employed in the cultivation of sludge, which leads to the secondary production of gases such as CO2, H2S, NOx, and CH_4 in BTPs. These secondary gases are greenhouse gases, and their emissions must be reduced to zero by 2050, as they contribute to global warming and have a significant impact on the global ecosystem. [7].

At large enterprises, greenhouse gas emissions occur not only at BTP. Significantly more gases are released during fuel combustion and technological processes. It is logical to combine all greenhouse gas flows together and dispose of them in the most cost-effective way. Such an effective way is the natural process of carbon dioxide absorption by plants during photosynthesis. At the same time, it is known that among the many plants, microalgae - green microalgae or chlorophytes have unique advantages. They have the highest possible growth rate (about 10-50 times faster than terrestrial plants), ease of cultivation and relatively low cultivation costs [8].

By using CO_2 to produce microalgae biomass, sustainable CO_2 removal can be achieved. The use of CO_2 from industrial flue gases has been documented in several studies, even when unfiltered gas from coal platforms was used [9, 10].

Consequently, microalgae are considered as the main candidates for biological fixation of CO_2 [11, 12].

The enzyme was discovered in the algae Chlorella variabilis and is referred to as fatty acid photodecarboxylase (FAP), and it works in combination with the cofactor flavin adenine dinucleotide (FAD). The team found that the FAP enzyme does its job by combining the biocatalytic and photoreceptor properties of flavin to catalyze fatty acids through radical chemistry. As a result, the removal of carboxyl groups from fatty acids leads to the formation of alkanes [13].

Methanotrophs are the only microorganisms that can oxidize methane, thanks to their unique enzyme methane monooxygenase. They use methane as their sole source of carbon and energy. Methanotrophs consume up to 80% of biogenic methane, which is of great interest due to their ability to offset methane emissions [14, 15]. Methanotrophs convert methane into carbon dioxide and water, producing intermediate metabolites such as methanol, formaldehyde, and formate. The initial step in methane oxidation is catalyzed by a complex enzyme system called methane monooxygenase (MMO). This enzyme exists in two forms: membrane-bound (pMMO) and soluble (sMMO), which is located in the cytoplasm. The membrane-bound form of methanmonooxygenase is present in all known methanotrophs, except for bacteria of the genus Methylocella, which produce a high proportion of copper (> 2.5 mmol/g cells) in the membrane form of the enzyme, with a low proportion of sMMO [20]. The incorporation of formaldehyde into the metabolic processes of methanotrophs is a crucial aspect that requires careful examination. This process occurs in various biochemical cycles, depending on the type of methanotroph [16]. In type I methanotrophs, formaldehyde is assimilated through the ribulose monophosphate pathway (RMF). In type II methanotrophs, it is incorporated into the serine pathway. A group of methanotrophs, known as group X, falls into a separate category. These organisms not only

utilize the RMF pathway but also employ the Calvin cycle for formaldehyde assimilation. [14, 15].

The research conducted by [17] explored the capacity of microalgae (Isochrysis galbana, Chlorella vulgaris) to absorb gases emitted during the production of isoprene, encompassing both inorganic gases and methane-based gases in the C_1-C_5 range.

Isochrysis galbana is a marine microalgae [18, 19].

Chlorella vulgaris is a fresh water microalgae [20, 21].

The ambient temperature has a significant effect on the productivity of microalgae biomass. It is generally recognized that the optimal temperature ranges from 20 to 30 degrees for most types of microalgae. The temperature between 22 °C and 35 °C was favorable for the growth of microalgae Chlorella vulgaris can grow in the temperature range of 25-30 °C, as well as in extreme conditions (30-35 °C) [22].

An increase in temperature increases the productivity of biomass to a certain extent, while with a further increase in temperature, a stress symptom appears that suppresses growth [23].

Another way to enhance the growth of microalgae is to increase pressure, since more CO_2 can be dissolved at higher partial pressures [24].

The direct effect of changes in CO_2 pressure on important raw materials for growing microalgae has not been well studied. Studies have been devoted to changes in the lipid composition of specific species of microalgae (Isochrysis galbana and Tetraselmis suecica) in response to ocean acidification [25, 26]. The results of the effect of high CO_2 pressure on the fatty acid content in Chlorella vulgaris cells are presented [27].

Industrial enterprises, especially petrochemical ones, emit a large amount of other greenhouse gases besides CO_2. It is important to study the effect of CO_2 pressure in a mixture with hydrocarbon gases on the photosynthesis process of microalgae in order to predict the optimal regime for both the absorption of greenhouse gases and the release of oxygen.

As an example, to assess the possibility of creating a bioreactor, a study was conducted on the absorption of greenhouse gases generated during the production of isoprene by marine microalgae Isochrysis galbana, as well as freshwater microalgae Chlorella vulgaris, depending on the temperature and pressure of the gas flow. The study was conducted in 2024 at Ufa State Petroleum Technical University in Ufa, Republic of Bashkortostan, Russia. During the synthesis of isoprene by two-stage dehydrogenation of isopentane, waste gases such as light hydrocarbons C_1–C_5 and gases CO, CO_2, N_2, O_2 - gas waste are formed.

Since the gas waste from the production of isoprene is not used in the technological process, the gases are sent to the furnace for combustion. Then the combustion products of the exhaust gas and furnace gas (gas waste) are released into the atmosphere. Expert estimates on the calculation of CO_2 emissions from gas waste in the production of isoprene are not presented in the literature. But according to rough estimates, carbon dioxide emissions alone range from 10,000 to 15,000 tons per year [17].

2 Materials and methods

The gas waste from the production of isoprene was taken from the installation into rubber chambers. Before the experiment, the gas composition was analyzed on a chromatograph, and the weight and volume of the rubber chamber were also measured.

The analysis of the proportion of non-hydrocarbon gases (H_2, N_2, O_2, CO, CO_2) and methane in waste gas was conducted using the absolute calibration method on the LHM-8MD gas chromatograph. The gas chromatograph is equipped with a flame ionization detector, a chromatograph control unit, and a chromatographic information processing unit. The chromatographic column is 2 meters in length and has an internal diameter of 3-4 mm.

The column is filled with molecular sieves zeolites NaX (fraction 0.25-0.5 mm) that have been calcined at a temperature of 300°C.

The analysis of the mass fraction of C_2–C_5 and other experimental conditions are similar [17].

Gas samples from bioreactors were taken every 96 hours. The biomass concentration (g of dry chlorella per dm^3) of microalgae cells was measured by weighing on analytical scales with an accuracy of 0.0001 g before and after each stage of the study. The preparation of the dry residue was carried out by pre-filtering a sample of 100 cm^3 of a suspension of phytoplankton through a Blue Ribbon filter, evaporation and drying at 105 ± 2 °C for 2 hours to a constant weight [28]. The thermobaric conditions of the experiment are presented in Table 1.

Table 1 – Thermobaric conditions of the experiment

Microalgae	Pressure, atm	Temperature, ^{0}C	
Isochrysis galbana	3.94–5.50	22	32
	1.60–2.83	22	32
Chlorella vulgaris	3.78–5.39	22	32
	1.80–3.24	22	32

3 Results and discussion

Since the experiment period was four days (Tables 2 and 3), the ionic composition did not undergo significant changes, while the hydrogen index shifted to the acidic environment by 1 pH unit in the aqueous medium of Chlorella vulgaris and by 0.23 pH units in the aqueous medium of Isochrysis galbana.

Table 2 – Characteristics of the aquatic environment containing Chlorella vulgaris strains

	pH	Ca^{2+}	PO_4^{3-}	NO_3^-	Cl^-	SiO_3^{2-}	HCO_3^-	Dry residue
		mg-eq/L	мг/дм^3					wt.%
The initial composition								
Chlorella vulgaris	6.12	1.86	230.4	2917.5	14.56	1.01	0	0.80
After the experiment 22 °C with high pressure								
Chlorella vulgaris	5.34	1.82	206.2	3279.5	14.56	1.01	72.8	0.67
After the experiment 22 °C with low pressure								
Chlorella vulgaris	5.90	2.23	210.0	3135.4	14.56	1.01	10.9	1.24
After the experiment 32 °C with high pressure								
Chlorella vulgaris	5.13	1.92	210.03	2003.55	14.83	1.01	11.9	0.69
After the experiment 32 °C with low pressure								
Chlorella vulgaris	5.67	1.82	393.7	1855.92	29.10	1.01	16.4	1.01

Table 3 – Characteristics of the aquatic environment containing Isochrysis galbana strains

	pH	Ca^{2+}	PO_4^{3-}	NO_3^-	Cl^-	SiO_3^{2-}	HCO_3^-	Dry residue
		mg-eq/L	mg/L					wt.%
The initial composition								
Isochrysis galbana	7.20	19.24	4.05	34.45	20606.0	0.64	0	4.07
After the experiment 22 °C with high pressure								
Isochrysis galbana	7.36	19.64	2.54	7.66	19514.23	0.64	0.21	4.30
After the experiment 22 °C with low pressure								
Isochrysis galbana	6.97	21.73	2.95	64.82	17111.36	0.64	16.2	3.02
After the experiment 32 °C with high pressure								
Isochrysis galbana	7.35	18.22	2.32	–	24373.79	0.64	1.5	6.34
After the experiment 32 °C with low pressure								
Isochrysis galbana	7.69	18.03	1.69	–	20772.29	0.64	3.8	4.20

The decrease in the level of the hydrogen index after the experiment is associated with both the absorption of carbon dioxide and the formation of bicarbonate ions.

The content of the components of the gas waste does not have a constant composition and the results of the purified gas obtained in each series of experiments have different end results for the same component. In this connection, the assessment of absorption efficiency is presented as the difference of the final concentration minus the initial one related to the initial concentration, expressed as a percentage. Accordingly, for gas components that had a decrease in concentration after absorption by microalgae, the result had negative values, and vice versa, a positive efficiency result in the case of an increase in the final concentration.

In experiments for the conditions of holding bioreactors of both types of microalgae at 22 °C with high and low pressure, different vector results of bioabsorption of gas waste and oxygen release were obtained. The results of absorption of methane hydrocarbons have low efficiency, significantly below 100%. In the aggregate of the obtained results of this series of experiments, there is no reproducibility of the nature of gas absorption by Isochrysis galbana and Chlorella vulgaris.

The microalgae showed the highest absorption capacity under the condition of 32 °C and high gas pressure. The results obtained showed stability and reproducibility for four days. The absorption of methane and hydrocarbons ΣC_2-C_5 by microalgae Isochrysis galbana averaged ≈75%, the absorption of methane by microalgae Chlorella vulgaris also averaged ≈75%, the absorption of hydrocarbons ΣC_2-C_5 86% (figure 1, 2). CO_2 uptake by microalgae Isochrysis galbana was 27%, by microalgae Chlorella vulgaris 21%. Probably, the process of assimilation of methane hydrocarbons by the microalgae under consideration takes place in priority order and through the stage of carbon dioxide formation. The high absorption of hydrocarbon gases leads to a greater release of oxygen than under other experimental conditions.

For experimental conditions, at low pressure of injection of gas waste into aquatic microalgae environments, low absorption of carbon dioxide leads to the release of a small amount of oxygen.

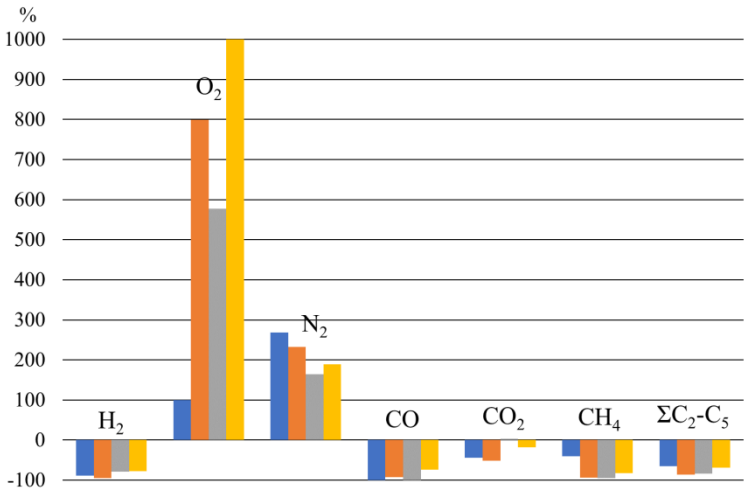

Fig. 1 – Isochrysis galbana high pressure, 32 degrees

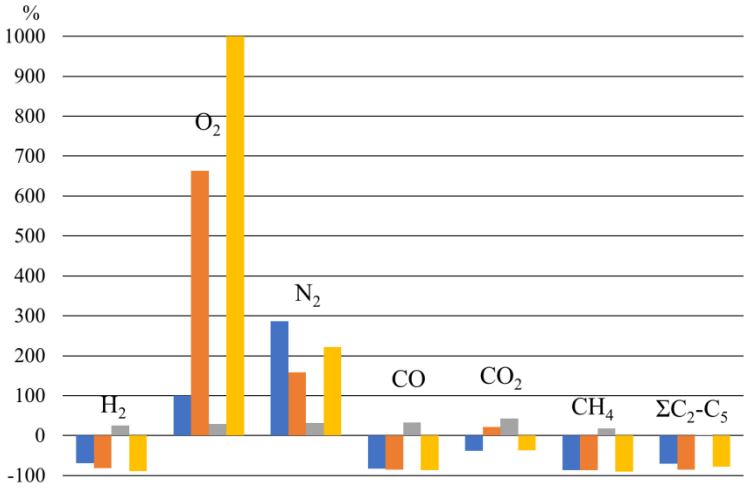

Fig. 2 – Chlorella vulgaris high pressure, 32 degrees

One common pattern for all conditions of the Isochrysis galbana and Chlorella vulgaris experiment was a decrease in the hydrogen content in the purified gas.

On the one hand, the genus of green microalgae Chlorella belongs to a few oxygenic phototrophic organisms that have active hydrogenases. Hydrogenase catalyzes the reversible oxidation reaction of molecular hydrogen. Also, hydrogen photogenesis is facilitated by mineral starvation, the lack of macronutrients is one of the main natural stress factors stimulating hydrogen biosynthesis, which was excluded in the experimental conditions.

On the other hand, hydrogenase is highly sensitive to molecular oxygen and requires anaerobic conditions for functional activity. In green microalgae, molecular oxygen inhibits hydrogenase activity due to disruption of the enzyme maturation process, as well as oxidative destruction of the catalytic center [29, 30].

In conditions of oxygen deficiency, protons play the role of an alternative electron

acceptor in green microalgae. But since an increase in oxygen content occurred during the experiment, oxygen generation inhibited hydrogenase activity accordingly.

4 Conclusions

A long-cultivated culture of green algae is polluted by bacteria and fungi. Gradually, as a result of the adaptation of the microflora to the conditions and nutrient medium, the creation of symbiotic agglomerates of the microbiota – active sludge occurs. Even without the identification and identification of strains in the active sludge, its absorption capacity can indicate the presence of certain microorganisms in it. Based on the results obtained, it can be argued that another stage is needed for BTP – the stage of purification from greenhouse gases using the process of photosynthesis by microalgae, nitrogen fixation and methane oxidation by bacteria and fungi. The use of the third degree of purification at the BTP will allow both wastewater and flue, process and other gases to be cleaned at one BTP installation. In this case, gases can be used for effective bubbling and mixing of sludge in the aerobic BTP circuit. The sealing of the BTP and the supply of all gas waste - technological, blow-off and flue gases together with activated sludge released during the life process, will minimize (to zero) greenhouse gas emissions at industrial enterprises.

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