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Comparative Evaluation of Pyrolysis and Hydrothermal Liquefaction for Obtaining Biofuel from a Sustainable Consortium of Microalgae *Arthrospira platensis* with Heterotrophic Bacteria

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Abstract: This article presents a comparative evaluation of pyrolysis and hydrothermal liquefaction (HTL) for obtaining biofuel from microalgal biomass (MAB). The research was carried out using biomass of a stable microalgae-bacteria consortium based on *Arthrospira platensis*. *A. platensis* was chosen because of its simple cultivation and harvesting. Pyrolysis was carried out at temperatures of 300, 400, 500, and 600 °C with a constant rate of temperature change of 10 °C/min; HTL was carried out at temperatures of 270, 300, and 330 °C. The bio-oil yield obtained by HTL (38.8–45.7%) was significantly higher than that of pyrolysis (up to 21.9%). At the same time, the bio-coal yields using both technologies were almost the same—about 27%. Biochar (bio-coal) can be considered as an alternative strategy for CO_2 absorption and subsequent storage since it is 90% geologically stabilized carbon.

Keywords: biomass; microalgae; bio-oil; hydrothermal liquefaction; pyrolysis

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1. Introduction

Currently, energy and fuel producers, both those based on fossil fuels and those on renewable energy sources, face the problem of obtaining a product which is not only competitive but also obtained with minimal carbon dioxide emissions. Moreover, this requirement applies to the process of fuel and energy manufacturing, and its use. Increasingly, major players in traditional energetics (mining and generating companies) are solving this problem by implementing large-scale projects for capturing and dumping CO_2 emissions. Thus, despite the well-known economic difficulties in the world due to the coronavirus pandemic, in May 2020, in Paris, the largest companies—namely Equinor, Shell, and Total—agreed on investments in the 'Northern Lights' project for the construction and operation of a carbon dioxide storage facility on the Norwegian continental shelf [1]. Stabilization and further reduction of CO_2 emissions can be implemented by various methods, including through the development of renewable energy. Moreover, the leading role in this process can be taken by the bioenergy industries, through the production of biofuel from biomass of various origins. This process is characterized by zero net CO_2 emissions. This kind of technology seems to be the link between today's energetics, which is based on organic fuels, and the subsequent transition to renewable energy sources.

Microalgae biomass (MAB), as a renewable non-traditional non-food resource, is a budding raw material for the manufacturing of third and fourth generation biofuels, since

it has higher productivity and at the same time does not compete with food and feed. The microscopic dimensions, relatively simple structure, and habitation in liquid media make MAB photosynthesis efficiency theoretically higher (up to 12.6%) compared to land plants [2]. The cultivation of MA in artificial ponds for energy purposes does not violate the natural conservation of organic matter in the biosphere, and algal farms can be considered absorbers of anthropogenic CO_2 by converting it into high-density energy. This allows CO_2 sequestration to be taken into account when assessing the energy efficiency of biofuel production from MAB. Among the existing strategies for long-term capture and storage of CO_2, algal technologies are considered, such as: (1) burial of the grown biomass of algae in geological formations; (2) burial of fractions extracted from the biomass of algae, with high carbon content, such as lipids, etc.; (3) transformation of MAB by hydrothermal liquefaction (HTL) technology, as a result of which 55% of biomass carbon is converted into biochar with a content of up to 90% of carbon, which is subject to burial for a long period [3].

One of the main advantages of HTL and pyrolysis technology is that not only lipids but also proteins and carbohydrates contribute to bio-oil, thus increasing the total yield of a more efficient energetic product [4]. The application of HTL technology, unlike pyrolysis, makes it possible to transform wet biomass into fuel, which is especially valuable in the processing of MAB that grows in an aqueous medium. Nonetheless, firstly, the HTL process still requires drying for a concentrated feed-in stream of around 20 wt.% dry basis; secondly, converting the whole of the algal biomass components (lipids, carbohydrates, proteins, etc.) may not be a cost-effective method for fuel production, due to the severe operating conditions and relatively high O and N content in the oil [5].

Despite the huge successes of recent years, the introduction of the production of algae biomass and fuel from it remains a difficult task because of the high uncompetitive price of the produced biofuel [6,7]. Therefore, it remains relevant to enhance the competitiveness of technologies for the conversion of algae biomass conversion into biofuels and to increase the range of useful products of such conversion [8–10]. One of the costly stages of biofuel production is growing microalgae biomass and separating it from the aquatic environment. In this study, a strain of *Arthrospira platensis rsemsu Bios* was used with a cheap open cultivation technology and a simple method of biomass collection due to the increased buoyancy of this strain acquired during long-term cultivation and selection. At the same time, the concentration of carbon-containing components in this MAB is not a record. The transformation of the grown *A. platensis* by pyrolysis and HTL technologies has been studied.

This research was carried out using a microalgae-bacteria consortium based on *A. platensis*. Microalgae by their nature are primary producers and synthesize organic matter necessary for heterotrophic bacteria. Bacteria in consortiums increase the availability of nutrients for MA and stimulate their growth, development, and the destruction of the cell wall during conversion, enhancing flocculation, etc. In the case of *A. platensis*, attachment of bacteria to the cell surface occurs with the formation of a mucous membrane around trichomes, higher concentration of nutrients compared to the environment. Studies have established that associations between microalgae and bacteria are species-specific. All this expands the biotechnological possibilities of biofuel production from MAB [11].

Prokaryotic microalgae (cyanobacteria) *A. platensis* is one of the most studied sources of renewable raw materials for food, feed additives, and biofuels [12]. As a raw material for the production of biofuels, both *A. platensis* biomass and biomass based on stable consortia of arthrospira with other microorganisms are grown. At the same time, various types of biofuel can be obtained from this raw material: biodiesel by transesterification of neutral lipids, bio-oil, and biochar by pyrolysis and hydrothermal liquefaction technologies, etc. [10,12–14]. *A. platensis* is grown using simple and cheap methods and its biochemical composition is characterized by high liability to changes in the external environment, which are stressors and promote targeted biosynthesis of target products [15]. These algae, in terms of biomass productivity and content of neutral lipids, significantly exceed those of traditional agricultural land plants [16].

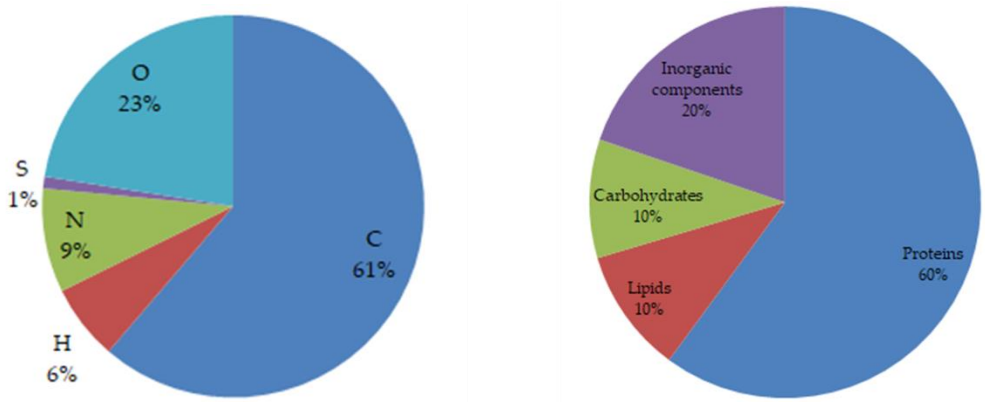
2. Materials and Methods

Arthrospira platensis is a prokaryotic microalgae/cyanobacteria commercially known as spirulina. As noted in [17], this algae can be used to study growing biomass technologies for transformation into biofuels. The microalgae-bacteria consortium based on *A. platensis* was used as the object of the experiments in the present work. The identification of the phylogenetic position of this culture has been carried out by biomolecular methods showing that the original culture was isolated in the north of Lake Chad. The culture of the alga is represented by straight trichomes, which were transformed from the originally spiral forms due to natural morphological variability when cultivated in laboratory conditions for thirty years. The culture was periodically reseeded by the passage method and maintained in open cultivators with a volume of 500 L with surface mixing. As a result of collecting the biomass that floated to the surface and using it as seed material during successive passages, an *A. platensis Bios* strain with increased buoyancy was obtained, which greatly simplifies the collection of biomass. The separation of biomass from culture is possible with sieves by the gravimetric method. DNA was isolated from this strain, sequencing was performed, and the nucleotide sequence was registered in the GenBank (Bethesda, MD, USA) NCBI database: *A. platensis Bios* (GenBank accession number KU855375). Zarruk's nutrient medium was used as a nutrient medium, illumination was 25 ± 3 μE/(m^2 s), and temperature T = 21 ± 2 °C [18]. Heterotrophic bacteria in the microalgae-bacteria consortium were identified as representatives of the genera *Pseudomonas* and *Bacillus* [19].

Figure 1a,b shows the characteristics of experimental MA *A. platensis rsemsu Bios*: the element composition (obtained by VARIO EL III Element Analyzer for a dry ash-free state; the oxygen content is determined by subtraction), the biochemical composition obtained by the known techniques [20–22]. The moisture content of the dry biomass sample was 3%. Ash content, obtained by Simultaneous Thermal Analyzer SDT Q600, was 5.1 wt%. Lower heating value (LHV) was determined according to the Mendeleev formula for solid fuels as follows:

$$Q = 4.18 \cdot 10^{-3}(81C + 300H + 26(S - O)) \quad (1)$$

where C, H, S, O are the chemical elements that make up the biomass of microalgae in terms of the dry ash-free state, wt.%, and amounted to 25.04 MJ/kg.



(**a**) (**b**)

Figure 1. Elemental composition (**a**) and biochemical composition, wt.% (**b**) of the feedstock (*A. platensis rsemsu Bios*).

Microalgae pyrolysis was carried out with the experimental setup described in [23]. Pyrolysis of microalgae biomass was carried out in the absence of oxygen, in pure nitrogen (grade 6.0). The mass of microalgae subjected to pyrolysis in each experiment was 15 g (in terms of dry weight). For the pyrolysis of biomass, it is necessary to maintain the temperature within the range of 400–600 °C (in some cases, not lower than 800 °C). Therefore, in the experiments, the microalgae biomass was heated from room temperature to 1000 °C at a constant rate of 10 °C/min. The composition of gases was determined by sampling at

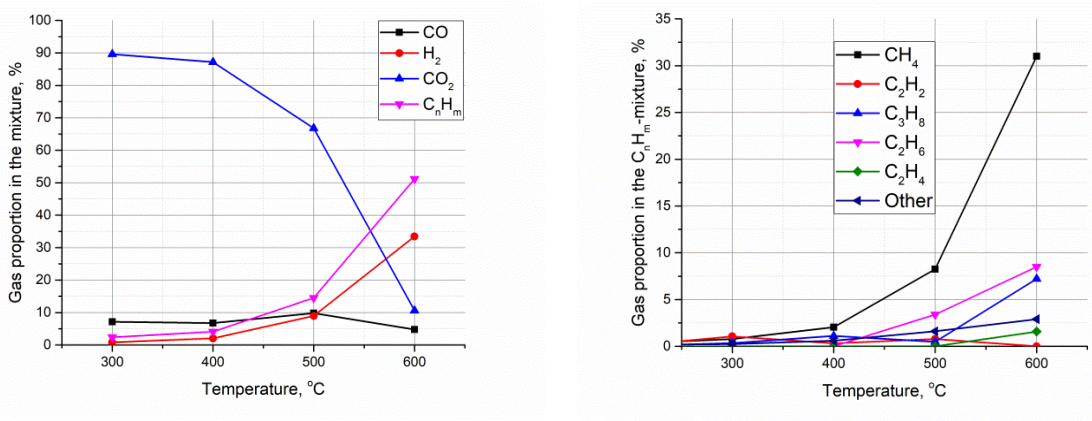
temperatures of 300 °C, 400 °C, 500 °C, and 600 °C, followed by chromatographic analysis (Chromatek Crystal 5000.1 chromatograph). The setup for the hydrothermal liquefaction process is described in [24,25]. Hydrothermal processing experiments were performed at a laboratory reactor-autoclave (volume of 0.9 L, maximum operating pressure 30 MPa, temperature—500 °C). The reactor was loaded with 650 g of wet microalgae biomass (a mixture of 500 g of distilled water and 150 g of dried microalgae). The reactor was sealed and purged with nitrogen, and after that it was heated up to a temperature of 270, 300, or 330 °C. Then, upon reactor cooling, the condensed products of hydrothermal liquefaction were removed in a separate container.

3. Results and Discussion

Biomass pyrolysis products are non-condensable pyrolysis gases, pyrolysis liquid (bio-oil), and biochar. Non-condensable gases (carbon dioxide, carbon monoxide, hydrogen, and methane) are formed during pyrolysis due to the primary decomposition of microalgae biomass and the secondary decomposition of vapors. Condensable gases, consisting of heavier molecules, condense upon cooling and form bio-oil. The pyrolysis products of *A. platensis Bios* biomass at 600 °C were as follows:

- Non-condensable pyrolysis gases in the amount of 76.7 wt.% of the original dry weight of the sample;
- Pyrolysis liquid (bio-oil)—about 21.9 wt.%.;
- Residual semi-coke (biochar)—about 27 wt.% of the original dry weight of the sample.

Non-condensable pyrolysis gases concentration at 300 °C, 400 °C, 500 °C, and 600 °C can be seen in Figure 2a. At temperatures below 550 °C, CO_2 makes up the main part of the gas mixture; in the temperature range from 300 °C to 600 °C, the concentration of CO_2 drops from 90 to 10 wt.%. At the same time, the amount of high-calorie non-condensable combustible gases (carbon monoxide, methane, hydrogen) increases. As a result, the LHV of the gas mixture as a whole increases.



(**a**) (**b**)

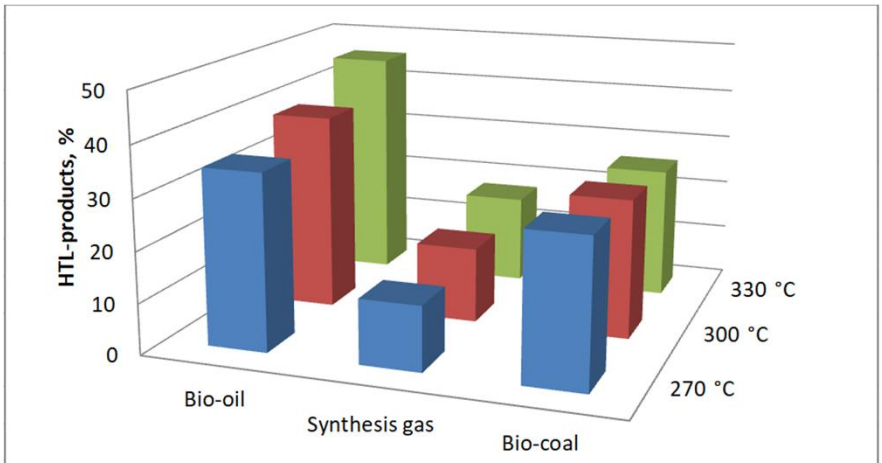
Figure 2. Dependence of the composition of non-condensable pyrolysis gases (**a**) and hydrocarbon gas mixture (CnHm) (**b**) on the feedstock heating temperature.

The composition and amount of hydrocarbon gases at different process temperatures are shown in Figure 2b. With a general increase in the content of these gases throughout the process of pyrolysis of raw materials, methane is characterized by the highest content.

By the change in the gas component content, the total calorific value of pyrolysis gases changed. As the temperature rises to 600 °C, the total share of hydrocarbon gases and hydrogen in the total volume of non-condensable gases increases to 73%. As a result, the lower heating value of non-condensable pyrolysis gases formed at T = 400 °C was 1.8 MJ/Nm^3, at T = 500 °C—5.15 MJ/Nm^3, T = 600 °C—15.3 MJ/Nm^3. Thus, the growth was more than 7-fold.

The obtained dependence of the composition of non-condensable pyrolysis gases on temperature shows that the amount of combustible gas components does not reach its maximum value at 600 °C (Figure 2b). Therefore, the results presented are lower estimates of the content of high-calorie gases such as hydrogen, methane, etc. in the resulting pyrolysis products. In addition, it should be expected that, in addition to the process temperature, the yield and composition of the resulting gases depend on the biochemical composition of microalgae, the residence time of the biomass in the chamber, etc.

HTL of biomass *A. platensis rsemsu Bios* has been performed at temperatures: 270 °C, 300 °C, and 330 °C (Figure 3). The average values of bio-oil yield by HTL conversion of biomass with an increase in temperature have comprised 34.6%, 38.8%, and 45.7%, respectively, and for bio-coal, 28.7%, 27.4%, and 26.0%, respectively.



	Bio-oil	Synthesis gas	Bio-coal
270 °C	34.6	12.7	28.7
300 °C	38.8	14.8	27.4
330 °C	45.7	17.5	26

Figure 3. Products of biomass conversion by HTL of *A. platensis* at 270 °C, 300 °C and 330 °C.

As can be seen from the Figure 3, the yield of bio-coal/bio-char during HTL of *Arthrospira* is significantly high (from 26.0 to 28.7%), depending on the process temperature, so this technology of converting MAB into biofuel could be also viewed as a method of storing CO_2 in the form of bio-char.

4. Conclusions

Conversion of microalgae-bacteria consortium based on *A. platensis rsemsu Bios* into biofuels by pyrolysis and HTL technologies was carried out. HTL was carried out at temperatures of 270, 300, and 330 °C; pyrolysis was carried out at temperatures of 300, 400, 500 and 600 °C with the rate of temperature change constant at 10 °C/min. Comparative evaluation of pyrolysis and HTL technologies for obtaining energy products from grown MAB showed that the bio-oil yield obtained by HTL technology (38.8–45.7%) was significantly higher than that obtained by pyrolysis technology (21.9%). At the same time, the bio-coal yields using both technologies were almost the same—about 27%. It can be seen from the experimental results that at the same process temperatures (300 °C), the amount of non-condensable gases formed under pyrolysis and hydrothermal liquefaction is comparable. Thus, HTL technology is somewhat preferable in terms of obtained energy product composition. Since the same strain of microalgae was used in the pyrolysis and hydrothermal liquefaction experiments, the biomass production cost must not be taken into account when comparing the technology advantages. An additional significant HTL advantage is the need to concentrate the biomass (at least up to 20 wt%), but not dry, as in the preparation of biomass for pyrolysis. As shown earlier [4], with hydrothermal

liquefaction of microalgae biomass, a relatively high thermodynamic efficiency can be achieved by optimizing the heat engineering scheme of the setup. Comparative thermodynamic estimates of energy costs during hydrothermal liquefaction and drying of microalgae biomass have shown that recuperation under HTL allows for a reduction of the thermal energy cost by at least 35%.

Author Contributions: N.I.C., S.V.K. and O.M.L. designed the study; A.V.G. and M.S.V. wrote the introduction section; N.I.C., A.V.G. and O.M.L. performed analyses of the samples; S.V.K., A.V.G. and O.M.L. carried out the experiments; S.V.K., M.S.V. and V.K. analyzed the results and wrote the rest of the manuscript; N.I.C., S.V.K. supervised the study and edited the manuscript. All authors have read and agreed to the published version of the manuscript.

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Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Conflicts of Interest: The authors declare no conflict of interest.

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