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Review

Industrial CO_2 Capture by Algae: A Review and Recent Advances

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Abstract: The problem of global warming and the emission of greenhouse gases is already directly affecting the world's energy. In the future, the impact of CO_2 emissions on the world economy will constantly grow. In this paper, we review the available literature sources on the benefits of using algae cultivation for CO_2 capture to decrease CO_2 emission. CO_2 emission accounts for about 77% of all greenhouse gases, and the calculation of greenhouse gas emissions is 56% of all CO_2 imports. As a result of the study of various types of algae, it was concluded that *Chlorella* sp. is the best at capturing CO_2. Various methods of cultivating microalgae were also considered and it was found that vertical tubular bioreactors are emerging. Moreover, for energy purposes, thermochemical methods for processing algae that absorb CO_2 from flue gases were considered. Of all five types of thermochemical processes for producing synthesis gas, the most preferred method is the method of supercritical gasification of algae. In addition, attention is paid to the drying and flocculation of biofuels. Several different experiments were also reviewed on the use of flue gases through the cultivation of algae biomass. Based on this literature review, it can be concluded that microalgae are a third generation biofuel. With the absorption of greenhouse gases, the growth of microalgae cultures is accelerated. When a large mass of microalgae appears, it can be used for energy purposes. In the results, we present a plan for further studies of microalgae cultivation, a thermodynamic analysis of gasification and pyrolysis, and a comparison of the results with other biofuels and other algae cultures.

Keywords: algae; CO_2 capture; thermochemical regeneration; algae cultivation; gasification; pyrolysis

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1. Introduction

The development of civilization is directly related to the increase in energy consumption. Since the beginning of the industrial revolution, more and more energy has been consumed by humanity. And as energy consumption grows, so does the output of greenhouse gases. From the mid-18th century to the early 21st century, carbon dioxide emissions increased from 3 metric tons to 8230 tons, respectively, according to the Carbon Dioxide Information Analysis Center.

One of the first important attempts to limit CO_2 emissions was the Kyoto Protocol of '97. Its essence was that all its participants should reduce the level of greenhouse gas emissions to below 5% of the 1990 level [1]. The effect of the Kyoto Protocol has been studied in many works [2–4]. When the Kyoto Protocol ended, it was replaced by the Paris Agreement.

The Paris Agreement was formally implemented on 4 November 2016. Its main goal is the same as that of the aforementioned Kyoto agreement—to maintain the average global temperature. In the long term, the outcome of the Paris Agreement will be climate change mitigation [5].

In a decade, the topic of decarbonizing the energy sector has come to the fore. For example, EU countries want to abandon hydrocarbon fuels by 2030. Furthermore, many large oil and gas companies have stopped investing in the exploration of new oil and gas fields and switched to the development of alternative energy sources. Therefore, there is a request for another type of fuel—biofuel. Previously, biofuels first and second were well studied. Generation first biofuels are waste of sugar, starch, vegetable oil, animal fat [6]. Biofuel of the second generation differs from the first generation in the use of non-food parts of plants—stems and husks [7]. However, there is also a relatively new, much less studied biofuel of the third generation—biomass of micro and macroalgae, since algae can accumulate lipids, capture CO_2 [8], thereby utilizing greenhouse gases.

After thermochemical regeneration, some types of algae have a calorific value at the level of peat or wood. The purpose of this work is a detailed review of algae cultivation and a review of the results of thermochemical algae regeneration. In addition, this review has another purpose—to determine the optimal conditions for the cultivation of algae and the further thermal regeneration of these algae. Considered are such optimal conditions for the cultivation of algae as flocculation, drying, pH level, lighting. Thermochemical regeneration of algae is not only a renewable alternative energy source, but also a good carbon dioxide trap. The capture of carbon dioxide by algae can have a direct impact on the environment because the consumption of traditional fuel will decrease, and, consequently, harmful emissions will decrease. Thus, macro and microalgae are a method of dealing not only with the consequences of environmental pollution, but with that which causes it.

2. The Impact of Greenhouse Gases on the Environmental Situation in the World

Continuous climate change is driven by rising emissions of carbon dioxide, the main component of greenhouse gases. The sources of carbon dioxide emissions include fossil fuels (oil, coal, peat, gas) and waste (animal husbandry, agriculture [9]). Atmospheric concentrations of N_2O, CH_4, and CO_2 have increased by 20%, 150%, and 40% since 1750, respectively [10]. Parts of gas emissions in various energy-intensive industries [10] are shown in Table 1.

Table 1. Parts of gas emissions in various energy-intensive industries.

%	NO_X	SO_2	SO_3	CO	SPM	CO_2	CH_4	N_2O
Domesticated	6.6	7.0	8.6	0.9	1.8	25	7.3	4.2
Industry	9.3	22.2	32.1	0.4	2.8	16.6	4.1	2.6
Transport	48.4	28.7	30.6	96.8	86.8	23.4	79.7	47.9
agriculture	3.9	5.4	3.2	0.2	4.7	2.6	1.4	40.4
Oil refineries	NA	NA	NA	NA	NA	3.2	0.7	0.4
Power plants	31.8	36.7	25.5	1.7	3.9	29.1	6.7	4.4

The problem of global warming and greenhouse gases is already directly affecting world energy and production. In the future, the impact of CO_2 emissions will only grow. Many researchers are engaged in the description of solutions to the problem of greenhouse gases (GHG) [11–14]. Moreover, in 2013, the Intended Nationally Determined Contributions (INDC) Agreement was signed in Paris. This agreement states that it is necessary to reduce the global temperature by 2 °C in the 21st century. The main negative effects of climate change due to GHG emissions on the planet are presented in Table 2.

If we compare the CO_2 emissions of the countries of the world economies for 2016 and 2019, we can see a directing a slight decrease in carbon dioxide emissions. For example, the share of CO_2 emissions from China in 2019 was 28.8% of the total emissions compared to 29.3% in 2016. These data allow us to conclude that more developed countries have already embarked on the path of capturing CO_2 to preserve the climate. However, at the moment, the methods of capturing CO_2 have been scarcely researched, despite the existence of a wide range of publications on this topic.

Table 2. Climate threats due to greenhouse gases.

No.	Brief Description of Threats	Reference
1	Continuous increase in the temperature of planet Earth	[10]
2	Melting glaciers (Himalayan glaciers have melted by 21% in the last 40 years)	[3]
3	Radiation exposure	[11]
4	Changes in the composition of the atmosphere	[11]
5	Sea level rise	[12]
6	Violation of the agricultural system	[12]
7	Increased flood risk	[13]

3. Capture and Sequestration of Carbon Dioxide by Microalgae

Previously, a lot of research was devoted to the capture of carbon dioxide. Now, scientists from all over the world are actively offering a completely different approach—not only to capture CO_2 but also to immediately use it for energy reproduction. This approach to solving the greenhouse problem is very relevant because of the high cost and complexity of technologies for capturing CO_2 emissions, the same CO_2 storage facilities also need to be maintained, and they uselessly occupy a considerable area. Thus, the reproduction of biofuels together with the capture of carbon dioxide is an elegant and high-potential solution to the problem of global warming. CO_2 accounts for 77% of all greenhouse gases. Thus, despite the content of nitrogen oxides, hydrocarbons, and sulfur dioxide in greenhouse gases, it is necessary to capture CO_2. Therefore, if you defeat uncontrolled mass emissions of CO_2, you can also defeat a whole host of environmental problems, such as the drying up of natural freshwater, disruption of food chains, and the extinction of entire animal species, and so on.

Carbon dioxide is a stable and inert compound, so increasing the value of biofixed carbon dioxide is a major challenge. There is a detailed and in-depth review on this topic [15]. The authors of this review considered a range of technologies to increase the value of carbon dioxide, such as mineralization of carbon dioxide as an inorganic carbonate or supercritical carbon dioxide as a solvent.

The purpose of the study of the authors [16] is to analyze the impact of carbon dioxide on the environment and to justify the use of CO_2 in the reproduction of biofuels. By their nature, greenhouse gases in some quantities are vital for organic existence on Earth, as they absorb the thermal radiation of the Earth and reflect it. That is, greenhouse gases help to maintain a normal temperature for all living things on the planet. However, excessive amounts of greenhouse gases are already having a disastrous effect on our organic world, and their resulting amount must be reduced and constantly monitored. In addition to maintaining the number of greenhouse gases at an acceptable level, it is necessary to reduce the consumption of fossil irreplaceable natural resources, as this is also an urgent need for the survival of future generations of the planet.

In the works of researchers [16–18], it was noted that the combustion of traditional fuel brings 56% of all CO_2 emissions into the atmosphere. Carbon capture and sequestration technology are some of the most widely used methods need to be reduced the influence of CO_2 emissions in the world. Carbon dioxide is captured directly from the carbon source and transported to storage.

Storage facilities must ensure safe storage of CO_2 for hundreds of thousands of years, without dumping it into the atmosphere. Speaking about this method in more detail, the stages of CO_2 capture should be distinguished: separation of the gas phase, dissolution into liquid, absorption into a solid. When dissolved in a liquid, carbon dioxide is absorbed by a special liquid solvent, then this medium is heated until CO_2 is released and the cycle is repeated. Absorption into a solid is an adsorption process performed by decreasing pressure and increasing temperature. Capturing CO_2 before direct fuel combustion is possible only when using a thermochemical gasification process.

According to Rahman, Farahiyah Abdul, et al. [16], CO_2 capture before combustion is more economical than after combustion. One of the problems of CO_2 biofixation and safekeeping technology is also an insufficiently studied base from the political side. There is not enough research on the exact costs of capturing and general rules for storing CO_2. Countries need to cooperate on these issues, and this is not happening properly at the moment. Therefore, the method of long-term storage of CO_2 cannot be preferable and it must be useful to utilize it in biofuels. According to the authors, there are very few studies on the simultaneous capture of CO_2 and the production of microalgae at present, although according to the authors, this is a promising area of modern science. Microalgae can actively absorb CO_2 from the exhaust gases for photosynthesis and self-reproduction.

In Alami, Abdul Hai, et al. [19] presented a deep research and understanding on the use of algae as traps for CO_2 from flue gases. The quality of such systems depends on many factors considered by the authors. In general, algae are resistant to external influences, so pure carbon dioxide for their high-quality cultivation may not be used. This means that flue gases are perfect as a source of carbon dioxide for micro and macroalgae. Under the right growing conditions, the degree of carbon dioxide capture by algae can reach 99%, and the slow supply of exhaust gases causes an increase in the growth rate of cultured organisms. Of the flue gases, only CO_2 is necessary for the growth of algae; however, it is necessary to take into account that, in addition to carbon dioxide, flue gases contain at least 140 different chemical compounds [17], which can affect the culture and the environment as a whole. For example, sulfur oxide is toxic to algae. The atmosphere contains a small amount of CO_2, so the method of saturating the environment with outgoing gases remains more relevant. The growth ratio for most microalgae to the CO_2 introduced to them is about 1/10.

Bhola, V., et al. [20] claim that microalgae can biofix carbon dioxide 50 times more than plants. Algae can generate an average of about 280 tons of already dry biomass per 1 ha per year, provided that solar energy is available 9% of the time. These microalgae can absorb about 513 tons of carbon dioxide during their growth. Given the composition of the flue gases, namely the carbon dioxide content of 3–30%, the most important task is the correct selection of algae that can withstand and absorb such high concentrations of CO_2. However, if it is not possible to cultivate exactly CO_2-resistant algae, then it is necessary to constantly maintain the optimal pH level. Under these conditions, the crop will be able to multiply and effectively deal with CO_2 emissions by absorbing them. Moreover, when choosing algae, you should give preference to species that are resistant to NO_X and SO_X, because they form acids when interacting with water, which is destructive to most crops. It is worth noting that, according to studies, when cultivating algae in natural conditions (pond and sunlight), a pond with a volume of 4000 m^3 can absorb about 2200 tons of CO_2/year.

The authors of the study [20] experimentally studied the degree of CO_2 capture, crop growth, and the kinetic velocity coefficient of algae such as *Chlorella Vulgaris* and *Nannochloropsis gaditana*. The authors found that algae of the types *Chlorella*, *Scenedesmus*, *Spirulina*, *Nannochloropsis*, and *Chlorococcum* are characterized not only by large and active growth but also by high tolerance to environmental conditions and CO_2 concentrations. Scientists claim that 1 kg of dry biomass accounts for 1.88 of carbon dioxide absorbed. However, such a rough assumption is not true, and each of the genera of algae must be studied separately by experimental measurement.

The objectives of Adamczyk, Michal et al.'s work are to assess CO_2 biofixing and the study of the growth rate of algae *Chlorella Vulgaris* and *Nannochloropsis gaditana* were carried out. *Chlorella Vulgaris* figure is green microalgae, 2–10 microns in size, spherical in shape, living in freshwater. *Nannochloropsis* is a cylindrical and spherical microalga that lives in saltwater. The diameter of *Nannochloropsis* cells is 3–4 microns. The cultivation was carried out under the artificial conditions of a bioreactor. The capacity of the bioreactor was 15 L. Additionally, the biomass was cultivated in plastic bottles with a volume of 1.5 L. The pH level in the bioreactor was maintained at 7, the temperature was 25 °C, the lighting period was 8 h, the CO_2 concentration was 4 and 8%, and the gas consumption was 100 L/h. The incubation time of microorganisms is 15 days. *Chlorella* was grown in a 15 L bioreactor, in another *Nannochloropsis* bioreactor. The results of cultivation, in this case, can be compared, because the conditions for the penetration of light and the area of contact were the same for both algae. Artificial lighting, which was used in parallel with daylight, was more than twice the intensity of daylight.

According to the results of the experiment with a concentration of CO_2 of 4% in the middle of the experiment, an extreme concentration of biomass can be observed. On the last day of the experiment, the level of biomass concentration was equal to the level of the first day. This statement is true for both types of algae. Other results showed the use of 8% carbon dioxide. *Chlorella Vulgaris* performed worse than *Nannochloropsis gaditana*. The concentration of *Nannochloropsis gaditana* for all the days of the experiment changed from 0.24 g/L to 4.0 g/L. This is a very high result. According to fixation, *Nannochloropsis gaditana* also showed a higher result, in comparison with *Chlorella Vulgaris*. Trapping was determined by two methods: the first-simplified and generally accepted, the second complex and more accurate. According to two methods, the fixation index of *Nannochloropsis gaditana* exceeded the biofixation of *Chlorella Vulgaris* by about two times. During the 9 days of the experiment, the density of microalgae cells increased more than 7–10-fold. According to the results of the kinetic analysis of the daily growth of crops, we can say that the authors obtained a growth rate coefficient of 0.5–0.4 per day.

The (Figure 1) shows algae *Chlorella* sp. in bulbs.

Figure 1. Algae *Chlorella* sp. in bulbs [21].

It is also worth mentioning the experimental study [22] of the efficiency of CO_2 capture by microalgae of the *Scenedesmus obliquus* type in an artificial photobioreactor. The results showed that the saturation of CO_2 in an amount per volume of 384.9 kg/m^3/day, or in a percentage concentration of 15% CO_2, ensures optimal CO_2 capture and crop survival. To meet these capture targets, the maximum biomass output was 0.36 kg/m^3/day, the CO_2 conversion rate was 0.44 kg CO_2/m^3/day, and the oxygen release rate was 0.33 kg CO_2/m^3/day. Under these conditions, the maximum efficiency of CO_2 removal reached 30.76%. From a general point of view, the results obtained can be described as the potential for commercial use of such biofuels. However, Scenedesmus obliquus is not the most popular species for its cultivation for energy purposes compared to other algae species.

In addition, biofixation of greenhouse carbon dioxide by algae of the species *Scenedesmus obliquus* and *Spirulina* sp. was studied in detail at a temperature of 30 °C in a tubular bioreactor [23]. In the absence of carbon dioxide, microalgae showed low survival after the fifth day of the experiment. If we talk about the results before the death of crops, the best results from this sample were presented by microalgae of the species *Spirulina* sp. For the cultivation of these microalgae, a carbon-free environment was initially maintained, so that the microorganisms became more tolerant to carbon dioxide, they were slowly assimilated with CO_2 for 7 days. The light period in a tubular bioreactor with columns was

12 h. Without CO_2, the biomass concentration of both microalgae increased until day 5, and then there was a specific extinction of the crops. Furthermore, the experiment was carried out with 6% and 12% carbon dioxide in microalgae runs; its duration was 21 days. The cultivation performance values of *Spirulina* sp. were still significantly higher than those of *Scenedesmus obliquus*. Thus, the species *Spirulina* sp. can be called suitable for cultivation to capture CO_2.

The results of the analysis [24] on the amount of carbon dioxide absorbed under different conditions of various microalgae are presented below. From Table 3, we can conclude that *Chlorella* sp. best copes with carbon dioxide capture.

Table 3. Comparison of the main results of the experiment.

Type of Algae	Biomass Productivity, mg/Ld	CO_2 Content, mg/Ld	Temperature, °C	The Capture CO_2, mg/Ld
Nannochloris sp.	350	15	25	658
Nannochloropsis sp.	300	15	25	564
Chlorella sp.	950	50	35	1790
Chlorella sp.	700	20	40	1316
Chlorella sp.	386	50	25	725
Chlorella sp.	1000	15	25	1880
Chlorella sp.	500	50	25	940
Chlorogleopsis sp.	40	5	50	20.45
Hot spring algae	266.7	15	50	501.3
Chlorocuccum littorale	44	50	22	82

As already mentioned, the degree of carbon dioxide capture by algae directly depends on the environment. In [25], the authors investigated the absorption of CO_2 by microalgae, their productivity when cultured in a photobioreactor with bubble columns. For algae production for carbon dioxide biofix and further energy use to become part of everyday world practice, it is necessary to obtain a positive energy balance of this system. Thus, there is a clear understanding of the need to build artificial bioreactors that can both efficiently use lighting and minimize energy costs. The results of the laboratory study report that this kind of bioreactor design has a high potential in obtaining biofuel from algae. However, the results obtained after conducting experiments using the same bioreactor tell us that comparing alternative technologies without significant optimization can be unreliable.

4. Micro and Macro Algae—Rationale for the Use of Algae to Capture Carbon Dioxide

The importance of the cultivation of algae in various fields, including in the field of energy, is very high [26–31]. Algae as a reserve type of renewable fuel are considered thanks to the rapid growth of algae and the ability of algae to store lipids [32]. Kumar, B. Ramesh, et al. [33] shows not only the potential of this type of energy but also the natural insurmountable limitations of such a type of fuel as organic algae. Table 4 shows the results of the Proximate and ultimate analysis of various types of algae.

The energy potential of algae microalgae is very high, since it does not require complex expensive conditions for keeping and growing algae, and the compensation of non-renewable fuel is effective. If we talk about macroalgae, then the cultivation of such crops, on the one hand, is not too difficult a task. Their cultivation can take place in their natural environment—on the seashore, where there is a lot of sun. However, here you can face the problem of seasonality. Cultivation of macroalgae in the cold, low-sun period is a technical problem. In addition, for the introduction of this type of energy as a commercial project, it is necessary to increase the discounted profitability of the project and reduce the cost of yeast and strains of viable bacteria.

Table 4. Proximate and ultimate analyses of algae (ad, wt%).

	Proximate Analysis (wt.%)				Ultimate Analysis (wt.%)					
	Moisture	Volatile	Fixed Carbon	Ash	C	H	O	N	S	
Nannochloropsis	-	-	-	-	43.3	6.0	25.1	6.4	0.5	[34]
Chlorella	-	72.9	18.4	8.7	51.9	7.1	30.5	9.6	0.9	[35]
Chlorella	-	12.36	72.3	15.1	85.7	2.1	7.5	4.3	0.4	[35]
Algae	7.53	75.59	10.91	5.97	42.3	10.84	23.84	9.26	0.27	[36]
Chlorella	6.18	85.85	2.66	5.31	38.98	6.46	48.25	0.51	0.16	[37]
Spirulina	4.47	84.54	5.85	5.14	36.29	6.15	45.35	0.68	0.15	[37]
Chlorella original	-	-	-	4.89	47.93	7.31	31.13	9.27	-	[38]
Chlorella after extraction	-	-	-	4.37	47.35	7.08	31.00	9.69	-	[38]
Chorda filum	13.1	52.2	24.9	11.61	39.1	4.7	37.2	1.4	1.6	[39]
Fucus serratus	11.4	45.5	24.2	23.4	33.5	4.8	34.4	2.4	1.3	[39]
Gracilaria gracilis	5.9	53.1	10.9	36.0	31.5	5.9	17.5	2.9	2.0	[39]
Enteromorpha clathrata	10.1	57.9	10.7	21.2	32.7	4.9	24.7	4.4	2.0	[39]

There are various ways to grow algae; two common options are bioreactors and open water. The selected algae need to create conditions close to ideal for their cultivation. Each type of microalgae has its conditions. According to studies [40–42], such algae as *Spirulina* and *Dunaliella* grow best in open water bodies. *Prokaryotic* and *eukaryotic* algae, which are most often grown in a reservoir, include *Nannochloropsis* sp., *Chlorella* sp., *Tetraselmis* sp., *Arthrospira platensis*, *Dunaliella salina*, *Scenedesmus* sp., *Haematococcus pluvialis.*, *Anractenaba* sp.

In [32], the authors write that the cultivation of microalgae from seawater is more preferable to freshwater. The main reason is the acute shortage of drinking water in the world. However, the cultivation of algae in saltwater involves some difficulties—insufficient levels of nitrogen and phosphate, which are responsible for the production of algae. Thus, the problem of commercializing the bioenergy of algae arises, since the solution of the problem of phosphate and nitrogen content requires significant economic costs. The study was carried out for the Indian subcontinent, where the climate is favorable for the active growth of various types of microalgae. Strain samples were isolated from salt seawater and standing salt baths.

Mathimani et al. [32] investigated a total of 56 different strains of microalgae and cyanobacteria from different coastal regions in India. Microorganisms such as *C. vulgaris* showed the highest lipid content results—up to 22.2%. However, samples of this type of microorganism showed too wide a range of lipid percentages from 9.2% to 22.2%. Picochlorum showed the most consistently high results for the lipid component from 15.9% to 16.9%. Cyanobacteria showed a lower lipid content than microalgae. Various types of cyanobacteria contain between 2.3% and 10.2% lipids. The study further focused on the development of lower nitrogen and phosphorus combinations to make it possible to lower the cost of industrial-scale microalgae growing and make it profitable for business. As a result, the microalgae *vulgaris BDUG 91771* with a high content of $NaNO_3$, K_2HPO_4, corrected by HNHP, was found to have an increased weight of 0.2 g/L when the culture with LNLP corrections showed 0.06 g/L dry weight. If you pay attention to the percentage of lipids, you can see a different picture. Microalgae contain 22.3% lipids with corrections for HNHP, and 27.4% with corrections under LNLP conditions, which is 5% higher. In addition, the models constructed by the authors are highly determinate for objects—0.9902 and 0.987 for $NaNO_3$ and K_2HPO_4, respectively, which means that the models can be trusted and these are suitable for interpolation and extrapolation to dry weight and lipid content.

In a study [32], Mathimani et al. reported that the most suitable microalgae for cultivation, for the reproduction of biodiesel, is *C. vulgaris.* In addition, these authors published the results of a study that seeks to review the problems associated with the cultivation and collection of microalgae that are cultivated for biofuel reproduction [43]. The authors considered marine microalgae such as *Chlorella BDUG 91771* grown in an open pond in a semi-continuous mode. They successfully cultivated a 5 kL microorganism in an open pond. The control and measurement experiment lasted for 51 days. As a result, according to the presented figures, with a maximum optical density of 683 nm and the dry weight of *C. vulgaris BDUG 91771* was 0.21–0.149 g/L. Furthermore, every 2 days, biomass was collected for 2 kL, which corresponded to 50% of all microalgae. The remaining 50% of the culture was added to the seawater environment, which contains $NaNO_3$, K_2HPO_4. Thus, a working volume of the medium of up to 4 kL was obtained at a seeding depth of 30 cm. Then the dry weight and optical densities were 0.04 g/L and 0.09, respectively. A high volume of microalgae growth is achieved through a large number of harvests. In addition, the authors noted that the samples that were grown in laboratory conditions have a low survival rate in an open pond. The doubling time of the cultured microorganisms was approximately 37–40 h, which is higher than the cultivation of freshwater algae. Thus, it can be concluded that the quality of biomass for biodiesel is significantly influenced by the biomass content with limited sedimentation.

Among other things, it should be mentioned again that, according to recent studies, 1.88 kg of carbon dioxide is absorbed per 1 kg of biomass already produced [19,20]. The rate and quality of algae growth are strongly under influence the pH level. The optimum pH diapason for successful cultivation is 7–9. The pH is controlled directly by the CO_2 concentration. Temperature is an equally important factor in algal productivity. It should be kept at 20–30 °C. Temperature is a very important factor, since going beyond the highest optimal value by only 2 degrees can lead to a complete loss of the crop.

Now, microalgae already have an extensive history of cultivation. For the production of bio-oil, algae have some advantages, which will be discussed below. However, the complexity and cost of cultivating them outweigh the benefits of using microalgae as an energy source. Therefore, in addition to the main factors for the successful cultivation of biomass, such as light, temperature, and pH, the natural habitat of algae must also be taken into account if they are planned to be cultivated in open natural ponds.

5. Algae Cultivation Methods

The most common method for cultivating microalgae, which is also used on an industrial scale, is an open pond. Such an artificial pond should have a shallow depth of 0.3–0.5 m and be large in area for the growth of micro cultures [44]. Moreover, to mix the medium, introducing various nutrients, etc., such a pond must be equipped with a rotating impeller. In ponds for growing algae, it is necessary to maintain chemical and biological environmental conditions appropriate for the growth of crops, therefore, as necessary they are saturated with the required macronutrients for nutrition. In [45], the authors propose palm oil mill effluent as a nutrient medium for cultivating algae. In a study by Prakash Bhuyar, Sathyavathi Sundararaju et al., the following conclusion was obtained—the most effective conditions for the cultivation of *Chlorella* sp. are a carbon dioxide concentration of 10.9% and a light intensity of 9963.8 lux. In this paper, the authors study the growth rate of seaweeds, the content of lipids, and chlorophyll in a medium with different urea content [46]. The authors of the study found that the lower the urea content in the nutrient medium, the higher the production of low-weight lipids and vice versa.

Carbon dioxide, without which algae will not grow and multiply, enters the pond, usually through the atmosphere through a physical process of diffusion. This cultivation method is more in demand than others due to its relative simplicity and low cost, but it has some disadvantages. For example, it is necessary to provide unlimited access to water it is difficult to remove biomass. Since the conditions of such a pond are inherently natural, it is not uncommon for the environment or crops to become infected with parasites or infections [47–50]. Therefore, choosing an artificial open pond is good for Mexico, some European countries, such as Italy or Spain, and several US states, such as California.

One of the implemented ways of organizing an open pond is a source that looks like a racetrack. The authors of [47] spoke in detail about the implementation of such a pond in life. This is not just one large pond, it is a system of a narrow and shallow enclosed pond. The water in such a pond is constantly moving, thanks to the paddle wheel, a “snake” like a racing car on the track (Figure 2). Pond channels can be produced from a wide variety of products from concrete to soil. The grown microalgae enter the impeller as if from the rear, and the impeller captures the biomass [51–55].

Figure 2. Conventional algal raceway pond [56].

The second way of cultivating microalgae is bioreactors (Figure 3). Bioreactors come in many different types. These differ in the type of design and, in general, all bioreactors are closed, isolated systems, which exclude the ingress of infections and parasites into the environment [57].

Figure 3. Green Wall Panel photo-bioreactors [58].

Special artificial conditions help to grow a specific type of algae or to select certain types of microorganisms. The earliest photobioreactors consisted of plastic bags [58] and had a number of maintenance and operational problems [57,59–62]. Furthermore, tubular vertical and horizontal bioreactors appeared which can now often be found in laboratory conditions. Special compressors now perform good mixing and aeration, which was difficult to carry out in outdated bioreactors, in tubular systems [63–66]. The disadvantages of a tubular horizontal bioreactor are the difficulty of accurate temperature control due to the adhesion of microalgae to the tube walls and low mass transfer. Therefore, predominantly vertical tubular bioreactors are commonly used. Vertical tubular bioreactors are equipped with bubble columns or split cylinders [67–70]. The last specific method of algae cultivation, which is not suitable for all crops, is dark systems [60,61]. Such crops are called heterotrophic, and they obtain carbon from glucose or acetate. *Chlorella* was successfully cultivated in dark systems as early as 1980. Growing conditions are not overly specific;

it is necessary to maintain the pH from 6.1 to 6.5 and the concentration of nitrogen and phosphorus in a quantitative ratio of 9:1.25. The advantage of this method is the good productivity of high-concentration biomass up to 100 dm^3/L.

6. Using Micro and Macroalgae as an Energy Resource

Algae are the fastest-growing plants on the planet. Algae's ability to capture carbon makes them a promising biofuel. By maintaining precise growing conditions, which will be mentioned below, biofuels can be obtained from algae. The use of algae as a biofuel product has been reviewed many times in many studies [71–77]. For example, Mathimani, Thangavel et al. [78] investigated various types of thermochemical treatment of algae for energy and industrial purposes. Plouviez, Maxence et al. [75] point out some advantages of using microalgae, macroalgae, and cyanobacteria as energy fuel. The (Figure 4) demonstrate the main advantages of using algae as bio-oil. Equally of particular importance are experiments conducted with different types of algae about their lipid profile. The authors of this study experimentally found that, among the algae from the coast of Kuantan, *Nannochloropsis* sp. are the most suitable for biodiesel production. In addition, freshwater macroalgae *Rhizoclonium* sp. [79] were studied as an energy source in the form of biodiesel. The authors were able to optimize the biodiesel production process and obtain 6.044 g of macroalgae oil with ultrasonic treatment. In addition, there are studies on the production of bioethanol from the mass of macroalgae [80]. In this study, fermentation was applied by the method of two-way separate hydrolysis and fermentation. As a result, this study was able to confirm that macroalgae are excellent for bioethanol production.

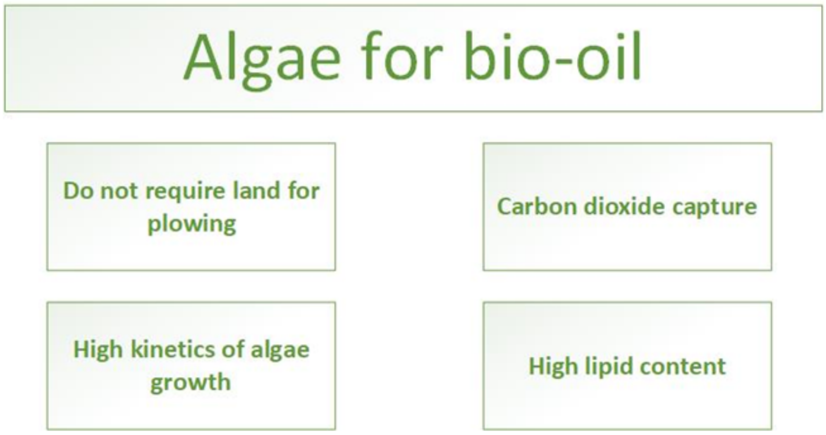

Figure 4. Advantages of producing bio-oil from algae.

Biofuels are a alternative source of unconventional energy in the world. The advantages of biofuels, besides being renewable, are sulfur-free and biodegradable. Biofuels are a low viscosity energy source with a high flash point. Thus, algae biofuels are a promising energy source. It is possible to obtain biofuel from algae during thermochemical treatment.

Thermochemical treatment of algae in comparison with other types of biofuels has the following advantages: high lipid content, which cannot be said about terrestrial crops; no competition with first generation biofuels (agricultural products) due to intensive growth; high absorption of CO_2. Thermochemical processes include five types: pyrolysis, hydrolysis, carbonation, hydrothermal liquefaction, direct combustion. According to Mathimani, Thangavel et al. [78], hydrothermal liquefaction is the most optimal method for producing liquid fuels. The Table 5 shows the composition of microalgae combustion products at a temperature of 500 °C for 30 min.

Table 5. The composition of the combustion products of algae at 500 °C for 30 min [81].

Sample	NaOH (M)	Ni/ Al_2O_3	H_2 (mol%)	CO (mol%)	CO_2 (mol%)	Methane (mol%)	C_2–C_4 (mol%)	C_V (MJ/m^3)
Spirulina	–	–	21.1	4.26	36.2	21.2	16.9	27.9
Spirulina	1.67	–	60.5	–	–	21.9	14.6	31.3
Spirulina	1.67	Yes	59.0	–	–	26.5	14.5	34.0
Spirulina	–	Yes	23.5	0.97	37.9	21.6	16.1	26.3
Saccharina	–	–	24.8	4.23	50.2	12.0	8.74	17.3
Saccharina	1.67	–	68.8	–	–	23.3	7.94	25.2
Saccharina	1.67	Yes	61.8	–	–	28.7	9.53	27.6
Saccharina	–	Yes	26.0	1.85	51.2	14.8	6.23	13.7
Chlorella	–	–	18.3	5.28	45.0	17.1	14.3	22.8
Chlorella	1.67	–	57.3	–	–	25.9	16.8	33.3
Chlorella	1.67	Yes	52.6	–	–	27.6	19.7	35.6
Chlorella	–	Yes	24.5	0.45	34.6	22.7	17.7	28.2

Recently, the practice of reducing carbon dioxide emissions by saturating microalgae with flue gases has begun worldwide. Of all the five types of thermochemical treatment for the production of gas fuel—synthesis gas, supercritical gasification is the most preferable. The calorific value of biofuel, its volume, and quality are directly influenced by the choice of the type of algae. When gasification takes place at high temperatures, it becomes possible to obtain thermal and electrical energy by, for example, their combined generation. Gasification can be carried out in two ways—with less intensive drying (conventional gasification), with intensive drying (supercritical gasification). According to earlier studies, an increase in the calorific value of synthesis gas requires joint gasification of microalgae and, for example, wood. In addition, it has been found that supercritical gasification is most suitable for microalgae in terms of energy production. Supercritical gasification *Nannochloropsis* sp. at a temperature of 450–500 °C and 24 MPa gives synthesis gas with a composition of 32% H_2, 30% CO_2, and 30% CH4. You can also process microalgae using the carbonization method—obtaining solid fuels at temperatures from 280 °C and above. Then with the help of the obtained solid fuel, it is possible to generate both thermal and electrical energy.

In addition, it must be mentioned that the beneficial effect on the processes of thermochemical regeneration of carbon dioxide. Authors Parvez, Ashak Mahmud, et al. studies [82] reported that carbon dioxide has a beneficial effect on the pyrolysis and gasification processes in terms of controlling the H_2 output. Using carbon dioxide as a raw material also lowers the net yield of carbon dioxide and so provides serious ecological advantages. With all the positive aspects, the use of carbon dioxide during thermochemical conversion is limited because of the endothermic character of the gasification reactions. This limitation can lead to high-energy costs. Advanced carbon biofix and sequestration gasification technology allows up to 90% CO_2 to be permanently stored [82].

In addition, one of the processes of thermochemical conversion is pyrolysis—the process of decomposition of biomass in an environment without an oxidizing agent. Pyrolysis leads to the formation of char, oil, and gas [83]. The pyrolysis process can take place at temperatures of 400–700 °C, and the gasification process at temperatures over 900 °C. In addition, mention should be made of the thermochemical processing of algae for the production of biochar, a solid product obtained by pyrolysis of biomass in the atmosphere with complete or partial removal of oxygen [84–89]. The main task of obtaining biochar of good quality and in large quantities is to determine the optimal reaction temperature.

7. Algae Gasification

An alternative method to conventional combustion of biofuels, eliminating the main disadvantages of direct combustion of biomass, is gasification to obtain synthesis gas. The gasification process includes several stages that are carried out in one technical unit: drying (removal of moisture from biomass), thermal decomposition of dry biomass, oxidation of vapor–gas mixture components, and heat release during pyrolysis, synthesis gas evolution—gasification itself. Biofuel gasification is conducted by heating biofuel to a temperature of 1100...1300 °C and higher in an environment with a limited oxidant content [90–93]. During gasification, reactions occur both with the release of heat and with its absorption; therefore, to maintain the process, the autothermal condition must be provided, in which the total heat effect of all reactions will be zero. Next, we will consider experimental studies of the process of gasification of microalgae biomass.

In [94], the authors studied the properties of microalgae *Nannochloropsis* sp. during biofuel gasification. Gasification takes place in supercritical water, that is, the pressure and temperature of the water exceed its critical point 647 K, 22.1 MPa. This gasification results in the formation of heating gas. Traditional gasification technology is not suitable in this case since microalgae are inherently high-moisture biomass. There is a need for moisture evaporation for the appearance of dry raw materials. Gasification of microalgae in water with supercritical parameters allows avoidance of the stage of evaporation and drying of wet fuel [38,95–97]. The positive aspect of this method is that part of the energy that is spent on reaching supercritical water parameters can be captured and returned to the cycle [98–100].

Guan, Qingqing et al. [101] carried out some experiments with the microalga *Nannochloropsis* sp. Small bioreactors were used as a place of cultivation for the convenience of extracting experimental products in various phase states. The experiment was conducted in this way: the biomass of *Nannochloropsis* sp. in an amount of 0.24 g was immersed in a bioreactor with fresh water with a volume of 0.67 cm^3. The dry weight of the algae immersed in the reactor had a solids content of 18%. Instead of air in the bioreactor, the authors of the study used a helium medium. The bioreactors were placed in a fluidized bed of alumina particles, but the valve had to be left on the surface due to supercritical conditions. A pressure of 24 MPa was maintained at 500 °C. The reactors remained in the layer of aluminum oxide particles for several minutes, after which they reached the surface, that is, the reaction proceeded extremely quickly. For the first time, the authors gave the exact organic composition as the reaction proceeded. During the experiment, it was found that the degree of loading of algae in the reactor does not significantly affect the yield of carbon or methane. In addition, the study showed that the composition of the released gas does not depend on the density of the water. However, in previous studies, the density of water influenced the mole fractions of carbon monoxide and hydrogen because of its effect on the reaction velocity of water gas conversion due to the use of quartz reactors. At the same time, the research results describe the influence of water denseness on carbon yield. The higher the authors recorded the value of the density of water, the higher the level of carbon yield. The same thing happens with the energy that was extracted from the resulting gas.

Moreover, Guan, Qingqing et al. [101], mentioned above, investigated supercritical gasification of microalgae *Nannochloropsis* sp. using catalysts. In this study, the authors used two homogeneous catalysts for sodium and potassium hydroxide and two heterogeneous catalysts—ruthenium catalyst and palladium black. The gaseous volatiles yield was the highest with the use of four catalysts. The best results were shown by an experiment using a ruthenium catalyst. The Ru/C catalyst enhances the yield of volatiles from biomass even at lower temperatures. Previously, it was not possible to gasify a compound that arose because of thermal reactions of gasification of microalgae—ethylbenzene. All four catalysts coped with the task of decomposition and yield of ethylbenzene. In addition, it should be noted that the catalysts work only up to three times of use, inclusive; with subsequent uses, they are not active. By spectroscopic study, a poisonous substance for ruthenium catalysts, sulfur, was found, thus it can be concluded that it is sulfur that deactivates Ru/C. Therefore, if sulfur is present in the algae, the use of a ruthenium catalyst is not recommended.

Furthermore, it is necessary to highlight the effect of CO_2 on thermochemical gasification, since the cultivation of algae presupposes the saturation of the biomass with CO_2. This effect was investigated by the method of thermogravimetric analysis–gas chromatography [102], i.e., the emission of gases H_2, CO_2, CO, and CH_4 was assessed in their quantitative ratio depending on the temperature. Increases in S/C and CO_2/C have been recorded at temperatures above 700 °C. The release of hydrogen was observed at temperatures above 450 °C; however, a decrease in hydrogen was observed at 700 °C and above. A decrease in aggressive ash content and carbonization was observed in the presence of CO_2. The experiments were carried out on a combustion gasification test facility at the Catalysis Laboratory at Columbia University. Furthermore, the authors prepared samples of bark, needles, and grass by drilling, grinding, and drying. The sample weights varied from 16 to 110 mg. Rapid weight loss was observed at temperatures of 300–400 °C. The carbonization of the remaining mass took place in the further gasification process. Oxygen, which contributed to the high-temperature combustion, was introduced along with the steam. Substances with a low content of lignin polymer indicated a high mass residue.

The research goal is Butterman, Heidi C., and Marco J. Castaldi [102] was the determination of the optimal ratio of the operating mode and the ratio of CO_2/C. The overall result of biomass gasification is synthesis gas with different ratios of hydrogen and carbon dioxide. As has been said many times earlier, such synthesis gas can be used in the future for the combined generation of heat and electricity. Most often, the air is used for gasification, since it is a more accessible and cheaper medium, but the use of oxygen increases the quality, that is, the calorific value of synthesis gas [103–108].

In a study by Butterman, Heidi C., and Marco J. Castaldi [102] pure oxygen obtained after air purification was used for gasification. In this work, three gasification modes were compared: direct heat supply when there is an external heat source for the gasifier, indirect heating in the presence of an external heat source for synthesis gas as a fuel, and indirect heating with an external heat source of biomass as fuel.

During direct heating with the added CO_2, the H_2/CO of the synthesis gas product decreased [102]. In general, it has been found that steam demand increases with the addition of CO_2. With the addition of heat-synthesis gas, its consumption increases with the addition of CO_2; however, with a high O_2/C ratio, the increased consumption of synthesis gas is required even slightly more since O_2 also takes part in the production of additional CO_2 during the reaction. However, under all conditions, the addition of oxygen reduces the consumption of synthesis gas, since more biomass is burned. It is also clearly seen in this experiment that the added CO_2 favorably influences the results of gasification in any of the modes proposed by the authors. According to Butterman, Heidi C., and Marco J. Castaldi [102] of the three investigated gasification modes, the most effective is the mode using an external heat source such as biomass, since it is the most environmentally friendly and thermodynamically efficient.

8. Algae Pyrolysis

The pyrolysis process involves the thermal decomposition of organic compounds with a lack of oxygen. As mentioned, early pyrolysis is high-temperature and low-temperature. Pyrolysis up to 900 °C is considered low-temperature and, when it is carried out on biomass, solid fuels are predominantly obtained [109–115]. When sublimated at high temperatures, the final product will mainly gas. In terms of the course of the process, the more energy is received, the more freedom of connection the molecules have. In addition, the more freedom, the lighter the substance, since the distances between the molecules increase. Next, we will consider some experimental studies of pyrolysis on microalgae biomass.

Belotti, Gianluca et al. [116] researched the method of fast pyrolysis on algae of the *Chlorella* type. The fast pyrolysis method is potential due to the increased bio-oil yield. The work describes in detail the stages and content of the experiment with *Chlorella*. In short, BG-11 and BG-11* media with no sodium nitrate salt were used for cultivation. The cultivation took place in an artificial bioreactor with a volume of 5 L at a room temperature of 25 °C. The period of light irradiation was 12 h a day. The number of cells grown during the experiment was found by fixing the parameters of the optical density of the medium at a wavelength of 686 nm. *Chlorella Vulgaris* was collected using a centrifuge, dried in a hermetically sealed vacuum, and the dried biomass was ground to a size of 100–150 μm. Pyrolysis was performed in a different temperature between 400 and 700 °C with steps of 100 °C. The vapors formed after pyrolysis were cooled to 40 °C. Under these conditions, slow pyrolysis proceeded. Fast pyrolysis was carried out under conditions of constant contact between the particles of microalgae and the walls of the reactor, which made it possible to increase the heating rate up to values characteristic of such a thermochemical process. Furthermore, with the help of a centrifuge, the authors obtained bio-oil by separating from it the aqueous fraction—bio-oil. As a result, the concentration of *Chlorella Vulgaris* cultured in BG-11 medium will reach 1.7 g/L after 250 h. After drying, the grown culture will be 17% lipids. However, algae cultured in an environment without sodium nitrate showed much better results in terms of lipid content per unit of dry weight. Highest biomass content was reached after 200 h, and the percentage of lipids per dry weight was 28%, which is 9% more than in the BG-11 medium. As a result, the authors using nitrogen starvation of microalgae have shown that this increases the lipid content to 68% of the biofuel mass and increases the bio-oil yield.

Grierson, Scott et al. [117] selected six kinds of algae *Tetraselmis chui*, *Chlorella like*, *Chlorella vulgaris*, *Chaetocerous muelleri*, *Dunaliella tertiolecta*, and *Synechococcus* and studied their thermal conversion during slow pyrolysis. The choice of algae was due to their use in the world by humans, resistance to various environmental conditions, high lipid content in dry matter. Thus, already actively cultivated species of algae were selected for production, energy, growing animal feed, etc. The algae were cultivated in an artificial environment by enriching the saturated air with carbon dioxide—about 2%.

After performing standard slow pyrolysis, the dried processed biomass was subjected to thermal analysis using the method of computer thermal analysis. All volatiles were analyzed with a gas chromatograph. As a result of the analysis of the results, all types of algae showed a low-temperature endothermic peak in the range from 140 to 220 °C. The second endothermic peak occurred at 250–350 °C; these peaks are associated with the active release of carbon dioxide. The released CO_2 was from 10 to 18% of the total mass already at 500 °C, depending on the studied culture of microalgae. As a result, the calorific value of each of the considered crops was also analyzed.

Grierson, Scott et al. [117] found that *C. vulgaris* has the highest calorific value at 4.8 MJ/kg, and the lowest in *C. muelleri* at 1.2 MJ/kg. Moreover, the results of the study showed that an growth in temperature from 500 to 550 °C will lead to an increase in calorific value by about 1.0 MJ/kg. As a result of the experiment on the percentage of solid, liquid, and gaseous products, *C. vulgaris* is predominant over other microalgae if gas is needed (25%). If solid is needed, then *D. tertiolecta* is the most preferred 63%, and for liquid biofuels, it is better to use T. chui—43%. Furthermore, the pyrolysis of microalgae of the species *Scenedesmus* sp. was considered [110]. Harman-Ware, Anne E., et al. [118] experimented with a temperature of 480 °C and a pressure of 1 atm. The cultivation of this species of algae took place in the natural environment of an open pond. The authors dried 76 L of microalgae at 60 °C for 24 h. After drying, the moisture content of the algae was 2.9%. After grinding, the size of the biomass fractions was 2 mm. The pyrolysis was spent according to the following criteria: temperature 480 °C, pressure 1 atm, stay of steam 2 s, and total operating time 120 min. After passing the high-temperature cyclone in the bioreactor, the biomass passed through four condensers in succession, where the bio-oil was collected. The original product *Scenedesmus* sp. characterized by several parameters. The volatiles content was 59.7% by weight of the product, the moisture content was 2.9%, the fixed carbon was 2.1%, and the ash content was 35.2%. The combustible mass of microalgae consists of C 32.1%, H 4.8%, N 5.3%, O 22.1%, S 0.5%. This high ash content has a considerable influence on quality of biofuels [115,119–122]. The content of proteins and lipids in the feedstock was 27.8% and 11.5%, respectively. This lipid content suggests that *Scenedesmus* sp. is not the best type of microalgae for pyrolysis, since there are species with a lipid content of up to 26%.

Furthermore, the authors considered the study of nonisothermal pyrolysis of algae of the species *Porphyra tenera* using spectrometry [123]. Kim, Young-Min, et al. write that the inorganic metals contained in the *Porphyra tenera* algae act as a catalyst for the pyrolysis process. Such a high advantage over other algae, which do not contain a sufficient amount of inorganic metals, immediately has a significant drawback—a high degree of slag formation during combustion. The purchased biomass samples were subjected to grinding using liquid nitrogen cryo-milling. The authors obtained fractions less than 500 μm in size. The authors gave the full composition of the working mass of the feedstock. From the features of the working mass, it can be noted that *Porphyra tenera* has a high ash content, nitrogen, and sulfur—8.43%, 7.32%, 1.98%, respectively.

Most of the decomposition of microalgae took place in the temperature range 200–500 °C. After pyrolysis, about 30% of the mass of the feedstock remained in the form of a solid residue; this is because of the high ash content of algae and the high content of fixed coal. The average heat of combustion during pyrolysis of *P. tenera* was 224.1 kJ/mol. The minimum enthalpy of biofuel was 165.1 kJ/mol, and the maximum one was 368.4 kJ/mol. The maximum heat of combustion of *Porphyra tenera* is due to the decomposition of proteins in the high-temperature region of the reaction.

In addition, attention should be paid to the formation of carbon dioxide and water during pyrolysis in low and medium temperature zones [124–128]. The authors explain their formation by reactions of dehydration and decarboxylation of algal components. Lipids decomposed in algae result in the creation of glycerol and hexadecanoic acid. The release of many combustion products is easily explained by the thermal effect on carbohydrates, lipids, and proteins that are contained in *Porphyra tenera.* However, when analyzing a detailed chromatogram, there are also difficult to explain components, such as hexadecanenitrile, hexadecanamide, 5,10-diethoxy-2,3,7, 8-tetrahydro-1H, 6H-dipyrrolo [1,2-a:1′,2′-d] pyrazine. The reasons for the appearance of these compounds require separate study. However, it can be assumed that this is the result of a reaction with intermediate components of pyrolysis. As a result of separate consideration of the reaction in different temperature ranges, the authors were able to detect the products of intermolecular reactions between biopolymers in *Porphyra tenera* algae.

In the block diagram below (Figure 5), you can see the scheme for the preparation and further beneficial use of biomass.

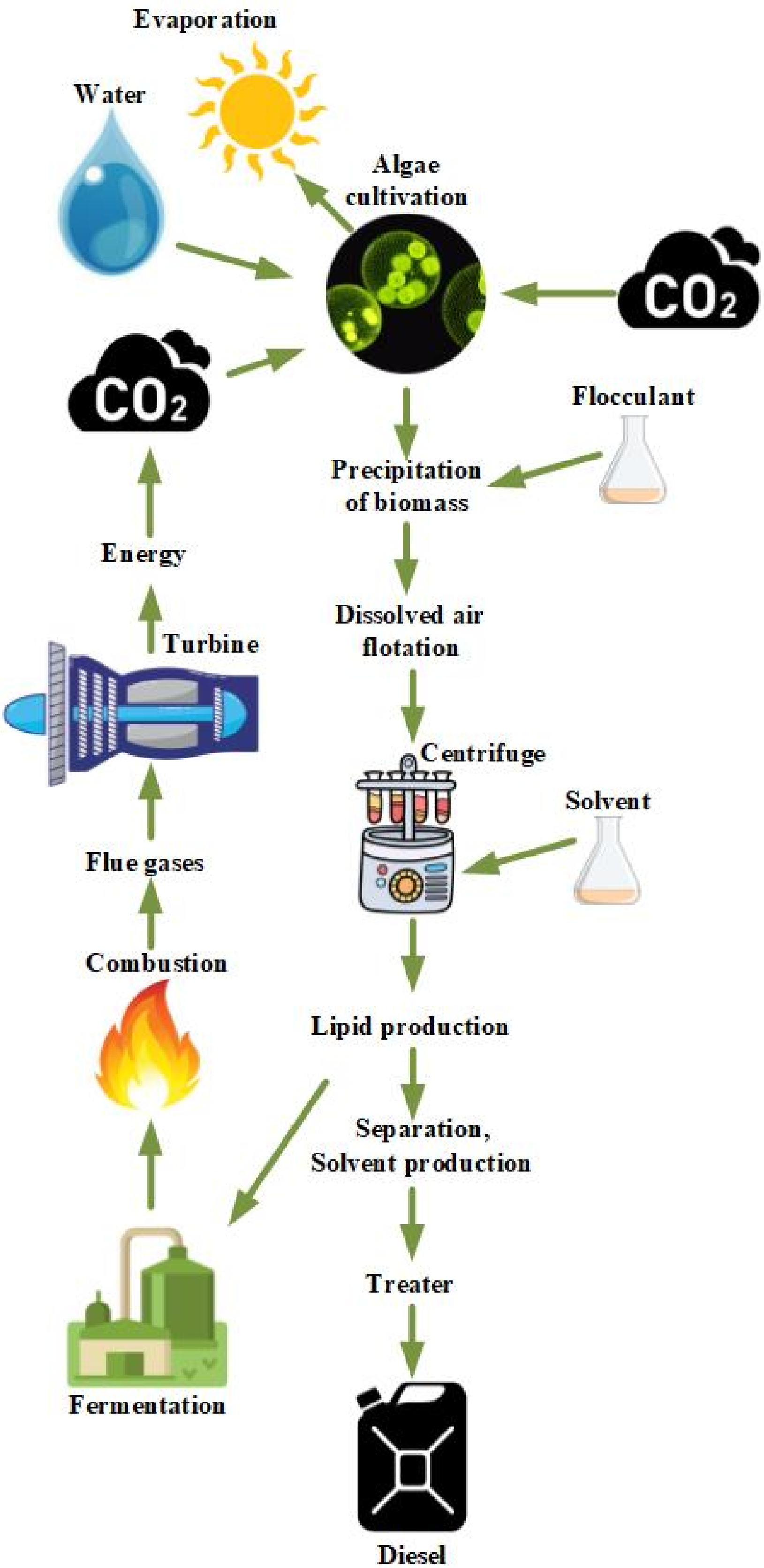

Figure 5. Scheme for the preparation and further utilization of algae biomass.

9. Drying and Flocculation of Biofuels

For effective reproduction of biomass from algae, proper cultivation is not enough because of lighting, temperature, photobioreactor, and other conditions. It is important to pay special attention to biofuel dewatering and drying technologies. The quality of the resulting product, its calorific value directly depends on this [129–133]. For example, with excess water remaining in biomass there may be negative consequences the production of bio-oil and biodiesel. Moreover, although constant harvesting gives an increase in the amount of algae mass by 50–200 times, the water content in the algae mass will remain high [134–137]. That is why flocculation is a necessary procedure for converting biomass into stable, storable form.

The most popular way to dehydrate algae is flocculation [138]. The good thing about flocculation is that it helps to separate the cells of the microalgae from large parts of the total mass. In general, flocculation is used in the world for the purification of drinking water. Flocculation can be carried out in a variety of ways. The principle of operation of one of the types of flocculation is to neutralize the charging on the surface of microalgae. The addition of cations with a charge of +3, such as aluminum sulfate and poly aluminum chloride, can effectively neutralize the negative charge of algae cells. However, this method has a significant drawback, which is inhibition of chemical reactions due to lipid-saturated biomass. Furthermore, polymer flocculants can effectively dehydrate algae.

Natural starch-based flocculants are widely used in the collection and dehydration of algae because of its wide availability and low cost. Flocculation is the most common procedure to increase the sedimentation rate of microalgae. In addition to chemical flocculation, there is electrical and biological flocculation, which also has a high potential for widespread use. Now the most commonly used processes for dewatering and drying algae are flotation, filtration, and centrifugation. However, Chen et al. [138] propose to pay attention to an alternative and more inexpensive method of dehydration—flocculation and sedimentation. This method is not suitable for all microalgae; therefore, the appropriate method of dehydration is determined purely individually for each case. The same approach applies to methods for drying biomass.

10. Illumination for Algae Growth

For optimal algae growth, there is a so-called light saturation threshold. The level of illumination at which the algae will be limited in their growth only by the speed of the physical and chemical reactions. It is important to take into account the factor that, beyond the optimal luminosity threshold, the growth rate of algae will begin to decline because of the deactivation of key proteins in photosynthetic units. The optimal threshold of luminosity can be calculated; for this, there is a ratio of the rate of photosynthesis and the intensity of light. There are several methods for calculating this optimal threshold. Some researchers believe that the hyperbolic tangential model is suitable for this, while others claim a simplified model of light deceleration, and still others associate this value with the Poisson distribution [139]. In addition to the instantaneous influence of the ratio of the rate of photosynthesis and the intensity of light, there is also a preliminary one. Excessive exposure of cultures to light beforehand will have a bad influence on the future growth of crops. At the time of this study, there were more than 40 models in the literature that could somehow predict the productivity of algae. However, most of these models have a common drawback—insufficient consideration of the impact of external factors [140,141].

The need for lighting control during algae cultivation is still relevant, despite numerous studies [142–146]. Appropriate lighting control can simultaneously make photosynthesis production as efficient as possible and fix the temperature of microalgae photobioreactors, resulting in lower overall production costs. Here Nwoba, Emeka G. et al. [147] are researching new technologies to increase the efficiency of light conversion and fixation temperature. These innovations include spectral filtering, plasma waveguides, spectral shift, wireless light emitters, and insulated glazing that increases production of photosynthesis fearing an uncontrolled increase in temperature in bioreactors. The use of infrared radiation lowers the sharp rise in temperature of biomass in bioreactors. Spectral shift, plasma waveguide, switchable glass and the innovations of insulated glazing are able to improve the quality of light that microalgae absorb. According to the authors [145,148–151], of all the options considered, they believe that the potential approach to growing microalgae cultures in artificial and natural bioreactors is a synergistic combination of existing and new lighting control technologies to increase biological efficiency, lower costs and lower impact on the environment.

A study on the effect of light intensity and photoperiod on the growth and content of lipids in *Nannochloropsis* sp. was carried out by the authors [152]. Earlier it was found that the green species of microalgae contains a proportionally high level of lipids, which indicates a higher calorific value compared to other types of algae. Among the marine microalgae *Nannochloropsis* sp. showed the best potential to create biofuels, because this type of microalgae has high biomass productivity and high lipid content. Photoperiod cycles have a significant influence on the speed of growth crops. For photoautotrophic crops, light regime and photoperiod are critical components in determining crop biomass production. For example, if microalgae are cultured insufficiently deep ponds, then the light intensity must be increased so that it can penetrate the microalgae. Research has shown that, with a light intensity of 100 Lmolm^2/s and a photoperiodic regime of 18/6 h, microalgae perform better. In short, the results indicated that the improvement in specific growth speed was accompanied by an increase in lipids.

11. Description of Flue Gas Disposal Experiments

The utilization of flue gases from various enterprises and thermal power plants is an extremely relevant topic. As mentioned earlier, algae are able to capture CO_2 and thereby increase their self-production [153–162]. Next, we will consider several different experiments devoted to the disposal of flue gases using the cultivation of algal biomass.

Chiu et al. [163] cultured *Chlorella vulgaris* use of exhaust gases from a coke oven of a steel mill. The study was carried out for 6 days based on an open photobioreactor with a volume of 50 L. When operating with intermittent air saturation of exhaust gases, the mean efficiency of carbon dioxide fixation was 60%, which is currently quite low. Moreover, the capture of NO and SO_2 could be maintained at 70% and 50%, respectively. In exhaust gases from the coke oven, the carbon dioxide content is 20–25%; therefore, the saturation of the flue gases with microalgae capable of capturing CO_2 is very high potential. The flue gas from the furnace was gathered in a spent gas storehouse and continuously blown into the bioreactor. The authors cultivated different strains of *Chlorella* sp. The growth ability of *Chlorella vulgaris* MTF-7 turned out to be much better than that of *Chlorella vulgaris* WT when saturated with exhaust gases. The highest biomass content in *Chlorella vulgaris* MTF-7 saturated with air 2%, 10% or 25% CO_2 were 1.67, 1.50 and 1.32 g/L. The growth potential of *Chlorella vulgaris* MTF-7 saturated with exhaust gases with steel mill coke oven flue gas, which contained approximately 25% CO_2, 4% O_2, 80 ppm NO, and 90 ppm SO_2, was higher than crops aerated with 2%, 10%, or 25% CO_2 enriched gas without pH control. This study concludes that the flue gas saturation of the *Chlorella vulgaris* MTF-7 is effective in capturing CO_2, NO, and SO_2.

The next work considered is an experiment with the saturation of flue gases, spent in a boiler unit, used as part of the medium for growing *Chlorella* sp. [164]. The total area of the culture was 55 m^2 and the thickness of the microalgae growth layer was 6 mm. This layer is continuously moving along the walls of the bioreactor at a speed of 50 cm/s; the partial pressure of dissolved CO_2 (pCO_2) above 0.1 kPa was kept in suspension at the end of the cultivation zone 50 m long to prevent limiting the growth of algae with CO_2. NO_X and CO gases (up to 45 mgm—3NO_X and 3 mgm—3CO in flue gases) did not have a negative effect on the growth of algae. Because of the study, it was determined that 4.4 kg CO_2 is required to obtain 1 kg (dry weight) of algal biomass. In addition, earlier (2005) it was estimated that, to capture CO_2 from exhaust gases from a thermal power plant with a capacity of 300 MW, an area of continuous microalgae harvest of up to 100 km^2 would be required.

However, researchers have already significantly reduced the amount of space required by properly adhering to environmental conditions.

The topic of the next experiment is to study the effect of flue gases on the cultivation of microalgae, the degree of accumulation of heavy metals in the biomass saturated with exhaust gases from thermal power plants. In this study, Guruvaiah, Mahendraperumal, and Keesoo Lee [165] cultivated green algae *Scenedesmus* sp. from wastewater from the Serna power plant, Missouri, USA. The biomass contained two- and four-celled cyanobacteria. Cell productivity doubled every 72–96 h. The exhaust gases were directed into a deep pond with a diameter of 4 m and a volume of about 4000 L. Flue gases were diluted with 2% carbon dioxide by compressing air. The gas mixture was fed daily for 3 h. The authors used two media for algae nutrition. The first medium F/2 contained sodium nitrate, sodium monophosphate, thiamine hydrochloride (vitamin B1), vitamin B12, and biotin. The second F/2A medium contained $FeCl_3$, $CoCl_2$, $ZnSO_4$, $CuSO_4$, $MnCl_2$, and Na_2MoO_4. Biomass was harvested at different times of the year: June, July, August, October, November, and December. In the period from June to July inclusive, the authors observed not only the growth of *Scenedesmus* sp., but also other species: the more dominant *Navicula* sp. and the less dominant *Chlorococcum* sp. From July to August, the authors notice a deceleration in increase when compared with the control biomass.

Analysis of the distribution of algae showed the appearance of large cells in two-cell coenobia up to four cells of Scenedesmus sp. The maximum number of cells in *Scenedesmus* sp. microalgae ranged from 50 cells to 210 (×106 cells/ml) for 30 days. During the cold season, an increase in *Nitzschia* was recorded. This species is salt-tolerant. Furthermore, a small number of *Coelastrum* sp. That is, this study showed that the genus *Scenedesmus* has a greater richness and amount of biomass in ponds that are saturated with exhaust gases. Diatoms include the genus *Navicula* sp., *Nitizchia* sp., and *Synedra* sp. presented the following subdominant abundance of ponds, and the species *Coelastrum* sp. was the most passive to growth among all identified strains. Concerning heavy metals, the authors found that heavy metals contained in flue gases actively penetrate microalgae.

The purpose of the study [166] is the development of a complex system for the biotransformation of carbon dioxide at oil refineries by cultivating *Aphanothece microscopica Nägeli* in a photobioreactor with a bubble column. The authors combined wastewater and wastewater saturated with gas from an oil refinery into a single system for the algae to capture CO_2 for photosynthesis.

Next, we will consider a method for reducing CO_2 emissions from a thermal power plant by capturing carbon dioxide by microalgae. De Morais et al. [167] for this purpose isolated two species of algae *Scenedesmus obliquus* and *Chlorella kessleri* from the treatment ponds of the Presidente Médici coal-fired power plant in the southern Brazilian state. Microalgae were cultivated in test tubes at a temperature of 30 °C and a 12-h light period. Cultures were examined every two days for their performance. The maximum density of *Scenedesmus obliquus* was shown with a concentration of carbon dioxide in the medium of 12%—1.14 g/L. This resistance to CO_2 can be easily attributed to the fact that samples of this microalga were collected in the wastewater of a coal-fired thermal power plant. In this study, biomass doubled in 3.2 days without CO_2 addition, and with 6% CO_2 in 2.7 days. The performance of the microalgae decreased over time, but the authors of the study did not affect the pH level, so a decrease in pH may be the reason for the low performance.

12. Conclusions

Based on this review of the literature, we can confidently conclude that microalgae are a third generation biofuel. However, for the successful use of microalgae as a biofuel, several important factors must be taken into account, for example, such factors as pH level in the range of 6–9, nutrient medium temperature 20–30 °C, the composition of the algae nutrient medium, nitrogen and phosphorus content in the nutrient medium. Currently, the vertical bioreactor equipped with bubble columns or split cylinders is the optimal method for cultivating micro and macroalgae. In addition, in this review, it was found that the most preferred of the five types of thermochemical regeneration is supercritical gasification to produce synthesis gas. At the moment, the topic of the cultivation of algae in the environment of exhaust flue gases has been little studied. This topic is now extremely relevant since algae can capture carbon dioxide while increasing their self-productivity. Therefore, the goals of our further research are analysis of the growth of algal cultures in laboratory conditions, thermodynamic analysis of gasification, and pyrolysis of microalgae of various species, both freshwater and marine.

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