Review

Algae: Nature’s Renewable Resource for Fuels and Chemicals

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Abstract: Microalgae-based renewable energy, industrial chemicals, and food have received great attention during the last decade. This review article highlights the versatility of algal biomass as a feedstock for producing various commodities and high-value products, including aromatic hydrocarbons and lipids within biorefinery systems. Lipid content and the composition of algal biomass cultivated in various media, specifically in wastewater streams generated at agricultural and industrial production facilities, are reviewed. Technical and chemical aspects of algal biomass conversion via thermochemical techniques including pyrolysis, hydrothermal liquefaction, and hydrothermal carbonization are discussed. The properties of the final products are reviewed based on the conversion process employed. Studies published within the last 5 years are reviewed. The importance of further research on inexpensive and more effective catalysts and the development of downstream processes to upgrade crude products obtained from thermal conversion processes is emphasized. This review concludes with an in-depth discussion of the opportunities and challenges involved in algal biomass-based bioproduct manufacturing and commercialization.

Keywords: biofuels; catalyst; microalgae; thermochemical conversion; wastewater

1. Introduction

With the ongoing worldwide energy crisis, research and development work on alternative sources of energy has been continuing for decades. Many clean sources like wind, solar, geothermal, and biomass have attracted attention for energy generation. However, an intermittent supply of solar and wind energy directly from the source requires the development and deployment of efficient and inexpensive energy storage systems, to meet the continuous energy needs of domestic and industrial users [1]. Biomass, among the various renewable sources, has been used for energy generation in various forms. For instance, oil from oilseed crops like canola and rapeseed are commonly used for biodiesel and renewable diesel production [2]. Lignocellulosic biomass, which is mainly composed of lignin, cellulose, and hemicellulose, can also be converted into liquid fuels. Although the utilization of lignocellulosic materials from crop residues, i.e., straw, bagasse, and forest residues, provides opportunities for value-added processing, the lower hydrogen and carbon contents of these materials lead to lower conversion efficiencies, consequently hindering the economic viability of the final product. Furthermore, land use change and the dedication of agricultural land needed for food production to energy crops is a major problem in using biomass from land-based plants for energy generation. The latter problem can be mitigated by utilizing microalgal biomass which does not need agricultural land for growth (Figure 1) [3]. Merits like a faster growth rate and a higher photosynthetic efficiency of many microalgae strains than higher plants offer tremendous opportunities for bioproduct manufacturing [1,4,5].

There are several techniques that can be utilized to obtain high value products from microalgal biomass. Some of these methods include biological, chemical, and thermochemical conversion techniques [1,3]. This article reviews the latest developments in the utilization of algal biomass for bioproduct manufacturing via thermal processing, including...
pyrolysis and hydrothermal processing. Pyrolysis refers to the thermal degradation of feedstock at high temperatures (usually above 350 °C) in an inert environment. Three types of products are produced during pyrolysis. These include char (solid); aqueous phase and bio-oil (liquid); and gas (gaseous). The quantity and quality of these products depends on the strain of microalgae used and the process conditions [6,7]. Dry feedstock is usually processed via pyrolysis, while hydrothermal processing utilizes wet biomass. Subcritical or supercritical water facilitates biomass conversion during hydrothermal liquefaction and carbonization processes [8,9].

Figure 1. Microscopic image (40×) of different strains of microalgae.

Considering that many of the microalgae strains attracting commercial interests grow in water and the rapidly diminishing availability of global freshwater, this article focuses on algal biomass grown in wastewater.

2. Selection of Research Articles

A thorough investigation of research articles were conducted using different online databases including ScienceDirect, Elsevier, and more. The search criteria were research articles published in 2019 or later and included the utilization of microalgae and its mixtures with other feedstock for pyrolysis, hydrothermal liquefaction, and carbonization. Some older research papers and review articles published prior to 2019 were included in the review process due to their important contributions to the topic of interest.

3. Growing Microalgae on Wastewater

A number of microalgae growth media compositions have been formulated to maximize the growth of various strains [10]. Yet, the preparation of these formulations requires fresh water and chemicals derived from petroleum, which can be quite expensive. The production of algal biomass to be converted into industrial products on wastewater enhances the sustainability of the entire system. Wastewater streams generated at municipal, industrial, and agricultural operations may contain nutrients, i.e., nitrogen, phosphorous, potassium, that are necessary for algae growth [11,12]. Microalgae cultivated in wastewater absorb and/or consume excess nutrients and other contaminants, while producing biomass that can be further processed to obtain valuable bioproducts.

The metabolic flexibility of microalgae performing photoautotrophic, heterotrophic, or mixotrophic metabolism (Figure 2) presents opportunities for designing efficient biological wastewater treatment within integrated systems [13]. In a wastewater treatment system, algal cells uptake and/or transform contaminants and produce oxygen via photosynthesis that can be used by the synergistic bacteria present in the system. Oxygen production by algal cells reduces the cost associated with oxygen supply for bacteria growth [14]. Some of the commonly evaluated strains of microalgae for wastewater treatment are *Chlorella sorokiniana*, *Scenedesmus obliquus*, *Chlorella vulgaris* (CV), and *Scenedesmus abundans* [15]. The publications highlighting N and P removal potential of different microalgal strains and their biomass productivity in various wastewater streams are summarized in Table 1.
Table 1. Various microalgal strains evaluated for their efficiency in the removal of N and P, along with their biomass productivity from different wastewater streams.

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Microalgal Strain</th>
<th>Reactor Type</th>
<th>Light Intensity</th>
<th>Wastewater Type</th>
<th>NH₄⁺ Removal Efficiency (%)</th>
<th>NO₃⁻ Removal Efficiency (%)</th>
<th>P Removal Efficiency (%)</th>
<th>Biomass Productivity (mg. L⁻¹. day⁻¹)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>1</td>
<td><em>Chlorella vulgaris</em></td>
<td>Mini—Photobioreactor</td>
<td>11,000 Lux</td>
<td>Dairy Processing Wastewater</td>
<td>91.4</td>
<td>79.4</td>
<td>96.4</td>
<td>530</td>
<td>[16]</td>
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<td></td>
<td><em>Chlorella pyrenoidosa</em></td>
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<td><em>Chlorella minutissima</em></td>
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<td>2</td>
<td><em>Synechocystis</em> sp.</td>
<td>Glass Bubbling Bottles</td>
<td>60 µmol m⁻² s⁻¹</td>
<td>Diluted Swine Wastewater</td>
<td>73.7</td>
<td>-</td>
<td>71.6</td>
<td>260</td>
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<td></td>
<td><em>Spirulina platensis</em></td>
<td>Conical Glass Flask</td>
<td>2000–4000 Lux</td>
<td>Domestic Wastewater</td>
<td>&gt;99</td>
<td>-</td>
<td>88.6</td>
<td>33.4</td>
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<td>3</td>
<td><em>Scenedesmus obliquus</em></td>
<td>Conical Glass Flask</td>
<td>4000–8000 Lux</td>
<td>Fertilizer Plant Wastewater</td>
<td>93.8</td>
<td>-</td>
<td>&gt;99</td>
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<tr>
<td>4</td>
<td><em>Chlorella pyrenoidosa</em></td>
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<td>95 µmol m⁻² s⁻¹</td>
<td>Domestic Wastewater Treatment Plant</td>
<td>&gt;98</td>
<td>78.3</td>
<td>&gt;78</td>
<td>47.3</td>
<td>[20]</td>
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<td></td>
<td><em>Scenedesmus Obliquus</em></td>
<td>Erlmeeyer Flask</td>
<td>120 µmol m⁻² s⁻¹</td>
<td>Activated Sludge</td>
<td>&gt;98</td>
<td>81.3</td>
<td>&gt;78</td>
<td>60</td>
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<tr>
<td>6</td>
<td><em>Chlorella vulgaris</em></td>
<td>Column Photobioreactor</td>
<td>6300 Lux</td>
<td>Wastewater Treatment Plant</td>
<td>&gt;90</td>
<td>&gt;90</td>
<td>&gt;90</td>
<td>9.28</td>
<td>[21]</td>
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<td>7</td>
<td><em>Tetraselmis</em> sp.</td>
<td>L—Shaped Glass Tubes</td>
<td>50 µmol m⁻² s⁻¹</td>
<td>Municipal Wastewater</td>
<td>98</td>
<td>-</td>
<td>82</td>
<td>157</td>
<td>[22]</td>
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<td></td>
<td><em>Parachlorella kessleri</em></td>
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<tr>
<td>8</td>
<td><em>Navicula venata</em></td>
<td>Glass based Batch Reactor</td>
<td>100 µmol m⁻² s⁻¹</td>
<td>Municipal Wastewater</td>
<td>96.9</td>
<td>-</td>
<td>99.8</td>
<td>7.1</td>
<td>[23]</td>
</tr>
<tr>
<td>9</td>
<td><em>Neochloris</em> sp.</td>
<td>Conical Glass Flask</td>
<td>Natural Sunlight (11:13 h/h Day: Night Cycle)</td>
<td>Poultry Slaughterhouse Wastewater</td>
<td>-</td>
<td>95</td>
<td>79.3</td>
<td>119.2</td>
<td>[24]</td>
</tr>
</tbody>
</table>

Figure 2. Schematic flow diagram of two different modes of metabolism in microalgae.

The efficiency of N and P removal from a wastewater stream depends on the microalgae strain cultivated and wastewater composition (Table 1). In some cases, utilizing a single source of wastewater may not be sufficient for efficient biomass production. For example, it has been shown that, although microalgae can be grown on wastewater generated during hydraulic fracturing of tight petroleum reservoirs, i.e., hydraulic fracturing wastewater...
(HFWW), biomass yields were quite low due to the extremely poor nutrient content in the growth media [25–29]. The cultivation of the Oklahoma native microalgae strain *Pic-ochlorium oklahomensis* (PO) in HFWW for 30 days resulted in biomass productivity of only 25 mg. L$^{-1}$. day$^{-1}$. Yet, supplementation of HFWW with animal wastewater (AW) rich in nutrients at ratios of HFWW:AW = 1:1, 2:1 and 5:1 v/v resulted in significant enhancement in biomass productivity [30,31]. The highest biomass productivity (60 mg. L$^{-1}$. day$^{-1}$) was obtained with the wastewater mixture of HFWW:AW at a ratio of 1:1 v/v, indicating the importance of optimization of the growth media composition for efficient production. These results can be attributed to the organic nutrients present in AW, leading to the proliferation of algal cells in the mixed wastewater stream [32]. The biomass productivity of PO cultivated in 100% AW was 75 mg. L$^{-1}$. day$^{-1}$.

The chemical composition of algal biomass is the key factor determining the type of conversion process to be used and quality of the final product. For example, lipid rich algal biomass is desirable for biodiesel and renewable fuel production. The effects of the growth medium composition and cultivation conditions on algal biomass composition is well-established [28,31]. PO cultivated in the HFWW:AW mixture of 1:1 v/v had a lipid productivity of 14 mg. L$^{-1}$. day$^{-1}$, which was higher than those of the biomass grown on pure HFWW (approximately 11 mg. L$^{-1}$. day$^{-1}$) and AW (5 mg. L$^{-1}$. day$^{-1}$). Although increasing the HFWW:AW ratio from 1:1 to 2:1 v/v led to a decline in lipid productivity (about 1 mg. L$^{-1}$. day$^{-1}$), a further increase in the HFWW:AW ratio to 5:1 v/v improved the lipid productivity to about 7 mg. L$^{-1}$. Day$^{-1}$. The latter results can be explained by the extreme nutrient stress due to low N (ammonium) content in the growth medium at HFWW:AW ratio of 5:1 v/v (NH$_4$ at various HFWW:AW ratios: 1:1 v/v HFWW:AW = 54 mg. L$^{-1}$, 2:1 v/v HFWW:AW = 38 mg. L$^{-1}$, 5:1 v/v HFWW:AW = 14 mg. L$^{-1}$ and AW = 86 mg. L$^{-1}$ NH$_4$) [30,33]. It is important to note that nutrient stress causes a decline in algal biomass productivity [34,35]. Hence, the optimization of the growth media composition and cultivation conditions is necessary to produce algal biomass with the desired properties and efficiency.

In some cases, co-culturing microalgae with other types of microorganisms rather than using a pure strain of microalgae is more effective not only in the removal of N and P, but also in increasing biomass productivity and its lipid content [36]. For example, the treatment of wastewater from molasses production with a consortium of microalgae (CV) and fungi (*Aspergillus* sp.) (microalgae: fungi ratio of 100 cells:1 spore) produced biomass containing 35.2 wt% lipids, which was much higher than those produced by pure algae and fungi, 22.2 and 37.7 wt%, respectively [37]. Lipids obtained from fungi had a higher saturated fatty acid (SFA) (33%) and mono-unsaturated fatty acid (MUFA) (26.8%) contents than those obtained from pure microalgae (21% SFA and 17.5% MUFA). Polyunsaturated fatty acid (PUFA) content of fungi (40.2%) was lower than that of the pure algal biomass (61.5%). A reason for the latter result might be that, unlike microalgae, fungi lack the enzyme desaturase (Δ-9, Δ-12 and Δ-15) which converts oleic acid (C18:1) to linoleic and linolenic acids (C18:2 and C18:3), increasing the PUFA content in algal oil [38]. Biomass from microalgae-fungi co-culture contained 32% SFA, 23.2% MUFA, and 44.8% PUFA. A very high PUFA content in oil reduces the oxidative stability of algae-based oil [38]. Biomass from microalgae-fungi co-culture contained 32% SFA, 23.2% MUFA, and 44.8% PUFA. A very high PUFA content in oil reduces the oxidative stability of algae-based biodiesel that is a major barrier for the commercialization of the biodiesel obtained from microalgae [39]. Similarly, treatment of wastewater from a biogas production reactor with a mixture of *Chlorella sorokiniana* P21 and the photosynthetic *Streptomyces thermocarboxydus* BMI 10 (1:3 wt/wt) produced biomass with higher lipid (0.45 g. L$^{-1}$) content than that of the biomass produced by pure microalgae (0.28 g. L$^{-1}$) [40]. The MUFA content of the lipids in the biomass obtained with the mixed culture (6.9%) was higher than that obtained with the microalgae monoculture (4%). The latter finding is consistent with the results reported in another study, where lipids produced by the binary mixtures of CV/*Rhodopseudomonas palustris* (21.1%), CV/*Rhodobacter sphaeroides* (24.5%) and *Chlorella pyrenoidosa*/*Rhodobacter sphaeroides* (29.3%) had a higher oleic acid content than those of the microalgae monocultures [41].
It has been also reported that the treatment of vinegar production wastewater with *Chlorella* or its binary mixtures with bacteria strains (*Bacillus firmus* or *Beijerinckia fluminensis*) did not have a significant effect on lipid yield [42]. Yet, the biomass from *Chlorella* and 10 wt% *Beijerinckia fluminensis* co-culture contained 35.6% palmitic acid, compared to 29.3% in the pure microalgae. Linoleic acid content in *Chlorella* and 10 wt% *Beijerinckia fluminensis* and 1% *Bacillus firmus* co-cultures were also higher, 24.7% and 27.9%, respectively, than that in pure microalgae, which was 16%. The latter results demonstrate the significant effects of microorganism types and wastewater composition used on the algal biomass properties produced. Palmitic acid is commonly used in the cosmetic industry and also as a food and soap additive [43]. Similarly, linoleic acid is a valuable feedstock for cosmetics and personal care products, especially for skin, hair, and nail care products [44]. Hence, lipid rich biomass can be a viable feedstock for high value product manufacturing.

4. Algal Biomass Conversion Processes

Algal biomass can be converted into various bioproducts through biological, chemical, and/or thermochemical processes. The chemical composition of the algal biomass used in any conversion process is the key factor determining final product properties. For instance, oil extracted from lipid rich algal biomass can be a viable feedstock to produce ethyl or methyl esters of fatty acids [34, 45–47]. Also, carbohydrates in algal biomass can be converted into bioethanol through hydrolytic cleavage (hydrolysis) and the saccharification of the carbohydrates, followed by the fermentation of the released simple sugars to alcohols and other products by yeast like *Saccharomyces cerevisiae* [48, 49]. Therefore, high carbohydrate content of microalgae positively correlates with a higher availability of desirable substrate for final product formation. Moreover, proteins in microalgae are known to be useful precursors for the synthesis of bioplastics [50, 51]. Hence, the selection of an algae strain and growth conditions are important factors that need to be carefully evaluated while designing efficient algal biomass-based production systems.

4.1. Thermal Conversion Processes

The treatment of algal biomass at a high temperature produces three different product streams, biochar (solid), bio-oil and aqueous streams (liquid) and biogas (gas) [52]. Chemical compositions of these streams depend on a variety of factors including, but not limited to, temperature, algal biomass composition, and duration of the treatment [53]. Pyrolysis, gasification, and hydrothermal treatment are some of the thermal processes that have been examined extensively for the conversion of biomass to various products [54]. This article reviews the recent research on pyrolysis and hydrothermal conversion processes.

**Pyrolysis**

This process can be categorized into slow, fast, and flash pyrolysis based on the process parameters used such as temperature, heating rate, and gas phase residence time [55, 56]. Multiple reactions occurring during pyrolysis can be classified into three stages based on temperature [10, 57]: (a) Dehydration (below 200 °C); (b) Devolatilization (between 200 and 400 °C); and (c) Decomposition of solid components (above 400 °C).

Proteins and carbohydrates decompose at temperatures below 400 °C. Around the pyrolysis temperature of 550 °C, lipids are broken down into fatty acids, which in turn may be converted to ketones, aldehydes, acids, alkenes, and other compounds [58]. The higher thermal stability of lipids than that of proteins and carbohydrates require higher pyrolysis temperatures for lipid decomposition and conversion reactions [59].

When biomass from three microalgae strains *Nannochloropsis* sp. (NC), *Tetraselmis* (TS) sp., and *Isochrysis galbana* (IG) were separately pyrolyzed at 500 °C, IG produced the highest bio-oil yield (about 66%) [60]. Alcohol was the major chemical compound found in pyrolysis oil. The latter results can be attributed to the thermal decomposition of carbohydrates and lipids present in the algal biomass [61]. The biochar yield was about 30 wt% from pyrolysis of pure NC and TS, while IG pyrolysis produced only 21 wt%
biochar. The O and H contents of the biochar from the three algal biomasses were lower (O content: 11.7 to 13 wt%; H content: 3.4 to 4.5 wt%) than that of the pure algal biomass (O content: 36.8 to 42.4 wt%; H content: 6.5 to 7.2 wt%). The latter result was due to aromatization, decarbonylation, decarboxylation, and dehydration reactions taking place during pyrolysis, leading to the reduction in O and H contents in the biochar [62]. However, C and N contents of the biochar were higher (C content: 71.8 to 72.5 wt%; N content: 10.5 to 11.5 wt%) than those from pure microalgae (C content: 43.5 to 48.4 wt%; N content: 7.3 to 7.6 wt%). The high C content of biochar makes it suitable for its utilization as solid fuel [1]. In addition to biochar, non-condensable gases generated during the pyrolysis of the three microalgal strains were composed of mainly CO\textsubscript{2} (50–65 vol%), along with significant quantities of CO and H\textsubscript{2} (10–19 vol%). A variety of hydrocarbons like methane, ethane, ethylene, propane, and propylene were also present in the non-condensable gas stream. Decarbonylation and decarboxylation of carbohydrates and proteins present in the algal biomass led to formation of CO and CO\textsubscript{2}, respectively. The degradation of ether bonds and carbonyl groups on organic molecules present in algal biomass produces CO during pyrolysis [63]. Dehydrogenation reactions taking place during thermal degradation of various organic compounds present in the biomass are responsible for the presence of H\textsubscript{2} in the gas stream [64]. Many other compounds present in the non-condensable gas stream can be attributed to the thermal degradation of lipids and cyclization of the degradation products [65].

With regard to the chemical composition of bio-oil, it has been shown that aromatic hydrocarbon content of the bio-oil from pyrolysis of \textit{Desmodesmus} biomass increased from 6% to 36.9% as the temperature increased from 450 to 750 °C [66]. An increase in temperature from 450 to 550 °C led to the formation of aromatic compounds like phenol and its derivatives from the carbohydrates present in the algal biomass. A further increase in temperature from 550 to 750 °C, (especially above 600 °C) promoted secondary reactions like dehydroxylation, demethoxylation, and demethylation along with simultaneous hydrogen abstraction and methylene addition to the phenolic compounds formed at lower temperatures, consequently increasing polyaromatic hydrocarbon content, like naphthalene in the bio-oil [67]. Another study on the pyrolysis of \textit{Desmodesmus} biomass reported similar findings of increasing aromatic hydrocarbon content in the bio-oil with an increasing pyrolysis temperature [68].

Co-pyrolysis of microalgal biomass with other types of biomasses may improve product yields and enhance the formation of desirable chemical compounds [4]. For example, microwave co-pyrolysis of 70 wt% CV and 30 wt% rice straw (RS) produced higher bio-oil yield (19.2 wt%) than the individual pyrolysis of microalgal biomass (15.17 wt%) and RS (13.5 wt%) [69]. Yet, pyrolysis of a mixture containing equal amounts of CV and RS resulted in only 17.1 wt% bio-oil yield. There was a further decline in bio-oil yield to 14.6 wt% when more RS was added to CV, i.e., 30 wt% CV and 70 wt% RS. Non-condensable gas yield from the CV-RS binary mixtures varied with CV/RS ratio. The addition of RS to CV up to 50 wt% increased bio-oil yield while decreasing non-condensable gas production. At RS/CV ratios higher than 50 wt%, more non-condensable gases were produced, resulting in a lower bio-oil yield. The amount of hemicellulose and lignin present in the pyrolysis feedstock significantly affects degradation reactions, consequently affecting product yields and compositions. The presence of a lower amount of hemicellulose in the mixture leads to less secondary cracking reactions and free radical formations, lowering non-condensable gas formation [70,71]. A higher amount of lignocellulosic material presence in the feedstock promotes secondary cleavage reactions, such as cleavage of methoxy groups present in lignin, enhancing gas yield [4].

The bio-oil obtained from the pyrolysis of pure RS and CV had about 92.7% and 17% of O—containing compounds (alcohol, phenol, ether, aldehyde, ketones, carboxylic acids and more). About 30, 38, and 10% of O-containing compounds were found in the bio-oil obtained from the blend of 30 wt% CV/70 wt% RS, 70 wt% CV/30 wt% RS, and 50 wt% CV/50 wt% RS, respectively. The presence of carbohydrates and lipids in CV and the
cellulose and hemicellulose component of RS led to the formation of aldehydes and ketones during their pyrolysis reaction with proteins present in CV. However, phenols, cellulose, and hemicellulose in RS reduces the amount of aldehydes as compared to that of ketones in the bio-oil [72,73]. Thermal breakdown of proteins and/or lignin led to the formation of phenolic compounds [74]. Finally, the formation of carboxylic acid can be attributed to the thermal degradation of lipids present in CV and/or hemicellulose in RS [73]. The effect of adding RS to CV on bio-char yield which varied between 30.1 wt% (Pure CV) and 33.8 wt% (Pure RS) was less significant than that on bio-oil and non-condensable gases.

The optimum conditions for bio-oil production from CV and lentil husk (LH) mixtures in a fixed bed reactor [75] were found to be 479 °C at the heating rate of 16 °C min−1 and blend ratio of 54 wt% CV and 46 wt% LH. The corresponding bio-oil, biochar, and non-condensable gas yields at the optimum conditions were 18, 33.6 and 32.6%, respectively. The bio-oil contained about 35.3% phenolic compounds. It was also shown that the elemental composition of the bio-oil and biochar varied with varying feedstock chemical composition and pyrolysis conditions. Higher concentrations of C, H, N, and lower O content in the biochar are beneficial for its utilization as a potential energy source, soil amendment, and fertilizer [76]. The non-condensable gas chemical composition also varied with pyrolysis process inputs. A higher concentration of CO2 and a lower CH4 content were found in the non-condensable gases produced from CV-LH blends compared to those obtained from pure CV and LH. The inhibition of demethoxylation of lignin components and fission of the lipids potentially led to a decline in the CH4 yield [65].

Pyrolysis of ternary mixtures of biomass from different sources (including microalgal biomass) has also been investigated [4]. It has been shown that the yield of aromatic compounds like phenols in the pyrolysis oil obtained from co-pyrolysis of algal biomass (AB), cedar wood (CW), and digested sludge (DS) was 44.3% higher than those obtained with pure AB (2.5%) and DS (13%). Catalytic pyrolysis of the latter biomass mixture using the zeolite catalyst ZSM-5 (ZSM-5:feedstock = 2:1 wt/wt) produced a bio-oil with very high aromatic hydrocarbon content, which was 83.4%. Catalytic pyrolysis of pure AB and DS under the same conditions used for the ternary biomass mixture produced bio-oil with 62 and 76.4% aromatic hydrocarbons, respectively. The latter results clearly show that biomass from different sources can be used to formulate mixtures for catalytic and/or non-catalytic pyrolysis to produce bio-oils with desirable chemical compositions for various applications. Table 2 summarizes the research findings on the chemical composition of the bio-oils obtained from pyrolysis and co-pyrolysis of microalgae with various feedstocks.

<table>
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<tr>
<th>Sl. No.</th>
<th>Feedstock (F)</th>
<th>Pyrolysis Temperature (°C)</th>
<th>Aromatic Hydrocarbon Yield (%)</th>
<th>Main Aromatic Hydrocarbon</th>
<th>Catalyst (C) Used</th>
<th>C:F Ratio (wt:wt)</th>
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<td>Nanochloropsis sp. (NS) Waste Tires (WT)</td>
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<td>Xylene</td>
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<td>NS:WT (2:3 wt/wt)</td>
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<td>63</td>
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<td>NS:WT (3:2 wt/wt)</td>
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<td>NS:WT (4:1 wt/wt)</td>
<td></td>
<td>52.8</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Spirulina Oil Shale</td>
<td>600</td>
<td>7.2</td>
<td>Toluene</td>
<td>CaOH2ZSM-5 (1:3 wt/wt)</td>
<td>1:1</td>
<td>[78]</td>
</tr>
<tr>
<td></td>
<td>Spirulina: Oil Shale (1:1 wt/wt)</td>
<td></td>
<td>3</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Chlorella sorokiniana (CS) Polystyrene (PS) Waste Tire (WT)</td>
<td>500</td>
<td>19</td>
<td>Toluene</td>
<td>-</td>
<td>-</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>CS:PS:WT (1:1:1 wt/wt)</td>
<td></td>
<td>77.5</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Biochar produced from pyrolysis of *Spirogyra* sp., *Cladophora* sp., *Microspora* sp., *Rhizoclonium* sp. and spent coffee ground (CG) mixtures at 400 °C and a heating rate of 10 °C. min⁻¹ (holding time = 1 h; slow pyrolysis) contained higher amount of N, 4–4.3 wt% than that in biochar obtained with pure CG (3.4 wt%) and dairy and swine manure (approximately 1.5 wt%) which are used as fertilizer [81]. The higher N content in the biochar from the algae/CG mixtures is due to the high amino acid/protein content in algae that is in CG [82]. Increasing the amount of algae in the algae/CG mixture from 33 to 67 wt% also resulted in an increase in the surface area of the biochar from 22.3 to 28.7 m²/g. The average pore size of the biochar was in the range of 4–8 nm, indicating that it can be classified as a mesoporous (2–50 nm) material suitable as soil amendment and removing some toxic materials from polluted water [83]. Electrical conductivity of the biochar from pure CG was below the measurement limit, while biochar from algal biomass displayed a very high conductivity (25.4 mS. cm⁻¹). As the weight proportion of algae in the CG blend was raised from 33 to 67 wt%, the electrical conductivity of the resulting biochar increased from 10 to 15 mS. cm⁻¹. The latter results could be attributed to the presence of Na, K, Mg, C salts and carbonates in the algal biomass [84]. If the biochar from algae/CG mixtures is to be used as soil amendment, the algae/CG blend ratio should be carefully adjusted to avoid any soil deterioration resulting from the high salt content of the biochar from algae/CG co-pyrolysis. However, high salt content in biochar is desirable when it is utilized as an electrode in fuel cells, owing to its high electric conductivity [85,86].

Microbial fuel cells (MFCs) which convert biochemical energy to electrical energy are used in various applications such as producing electrical energy while treating wastewater [87]. Although bacteria have been widely used in MFCs, the utilization of green algae in MFCs is gaining attention. For example, it has been shown that when *Chlorella* sp. of microalgae was used as a bioanode, biocathode, and a substrate, MFCs could generate 0.1–3.7 W. m⁻³ power [88–91]. Biochar produced from microalgae also has applications as a low-cost, high C content, and high specific surface area electrode material for MFCs applications. It has been reported that biochar from algae provides better electrical conductivity than the biochar obtained from higher plants [86,92], probably because of the higher salt content in algal biomass.

Among all the products that can be obtained from pyrolysis of algal biomass and/or co-pyrolysis of microalgae with suitable feedstock, bio-oil is the most studied in the literature. The utility of bio-oil depends on its chemical composition. For instance, bio-oil rich in aromatic hydrocarbons (like benzene) can be utilized directly for fuels and/or as a gasoline additive. Furthermore, interest has been aroused over the years in the application of bio-oil in conductive wire manufacturing industries, where it can be coated with electrode wire to improve its conductivity [1,4]. Potential applications of algal biomass-based biochar have not been explored to their full capacity. There are a few studies on the utilization of biochar as soil amendment and electrode for MFCs. But further research is needed for a better understanding of the effect of biomass composition and processing conditions on biochar properties and finding broad applications for its utilization.
4.2. Hydrothermal Processing

Hydrothermal processing of algal biomass in the presence of water at high temperatures and pressures promotes thermal degradation of the material [93]. This section reviews recent developments in hydrothermal processing techniques used for the conversion of algal biomass to various bioproducts.

4.2.1. Hydrothermal Liquefaction

Hydrothermal treatment of wet algal biomass at sub-critical temperatures—approximately between 250 and 350 °C—and pressures—5–30 MPa—produces three product streams, bio-crude oil, hydrochar, and gas. The process duration is usually about 15 to 60 min. Biomass degradation takes place in water which is a non-toxic and low-cost reaction medium [94]. There are three steps involved in the hydrothermal liquefaction of wet microalgae biomass [95,96]: (i) Depolymerization via disintegration of biomass, i.e., depolymerization of cellulose and hemicellulose into their building blocks, hexose, and pentose sugars, respectively; (ii) Decomposition, wherein water and CO₂ are removed via dehydration and decarboxylation, respectively; and (iii) Recombination, wherein high molecular weight compounds like char, also referred to as coke, repolymerize. One of the claimed advantages of this process is the reduced energy consumption due to the elimination of wet algal biomass drying after harvesting from the growth medium and before the hydrothermal processing. However, low biomass concentration in the growth medium, extremely short shelf-life of wet biomass and difficulty in storing large volumes of wet feedstock for extended periods negates most of the wet biomass processing advantage in large commercial operations.

Hydrothermal liquefaction (HTL) of microalgae *Tetraselmis* sp. MUR 233, sewage sludge, and pine wood separately showed that biocrude yield from microalgae (10–30 wt%) was higher than those obtained with sewage sludge (10–25 wt%) and pine wood (below 10 wt%) [97]. Although the process temperature had a significant effect on the biocrude yield from pinewood, the temperature effect on the biocrude yield from microalgae and sewage sludge was not substantial. The temperature-reaction time interaction was not significant either. Hence, there is a need for the development of kinetic models to understand the biocrude yield from HTL, as a function of both the process time and temperature as affected by biomass type and composition. Increasing the HTL temperature led to an increase in the number of compounds that could be identified in the biocrude obtained from microalgae, indicating that at high temperatures, the reaction mechanism involved in biomass conversion became more complex [98,99]. For instance, the major compounds detected in the biocrude obtained at 250 °C were phytol based compounds, esters, aromatic compounds, dicarboxylic and fatty acids, while at a higher temperature, 300 °C, sterols, ketones, amides, cyclic dipeptides and ethers were also identified in addition to the compounds found in the biocrude at 250 °C. The biocrude produced at 350 °C had even more compounds such as pyridine, pyrazine, phenolic compounds, and alkanes, indicating the significant effect of processing temperature on the composition of the product streams from HTL. Hydrochar yield from HTL of pine wood (26–58%) was higher than those from sewage sludge (20–30 wt%) and microalgae (20–40 wt%). The latter result can be attributed to the higher thermal stability of lignin in pine wood than the other organic compounds like proteins, lipids, and carbohydrates present in microalgae and sewage sludge. This leads to relatively lower biocrude and gas yield from pine wood than sewage sludge and microalgae, thereby maximizing the solid yield from pine wood [4]. Gas yield from HTL of microalgae (20–54 wt%) was higher than that obtained from sewage sludge (11–27 wt%) and pine wood (9–27 wt%). The high gas yield from HTL of algal biomass could be due to the decarbonylation and decarboxylation of lipid molecules present in algae cells [100].

Biocrude yield from HTL of *Scenedesmus obliquus* increased from 9 to 18 wt% while hydrochar yield decreased from 67 to 32 wt%, as the process temperature was raised from 250 to 350 °C [101]. During the same process, the gas yield increased from 22 to 50 wt%. The reason for the improved biocrude yield is that greater activation energy needed for
the dissociation of biomass via extensive decomposition/depolymerization reactions and the breakage of the chemical bonds was made available at high temperatures. During HTL, lipids present in algal biomass decompose into fatty acids and glycerol. Fatty acids are recovered in the bio-oil phase and glycerol ends up in the aqueous phase. At high temperatures, glycerol is hydrolyzed to form smaller molecular weight alcohols and/or aldehydes which are soluble in bio-oil, improving the biocrude yield from the HTL [102]. Increased secondary degradation reaction rates at high HTL temperature reduces biochar yield, while increasing gas and biocrude yields [103]. In the latter study, it was found that the yield of biocrude from HTL of algal biomass produced under low nutrient conditions (nitrogen deficient) was higher (12.5 wt% (250 °C); 39.1 wt% (350 °C)) than that from algal biomass produced at nutrient rich conditions (8.6 wt% (250 °C); 17.2 wt% (350 °C)). It is well-established that nutrient deficient growth conditions results in algal biomass having high lipid and carbohydrate contents. HTL processing of lipid rich biomass produces higher amounts of biocrude and gas than hydrochar. The major compounds in the bio-oil obtained from the biomass grown under nutrient limited conditions were fatty acids, which are generated via lipid hydrolysis occurring during HTL process.

HTL of a microalgal biomass and peat mixture produced a higher amount of biocrude (34–37 wt%) than that from pure microalgae (31 wt%) and peat (26 wt%) [104]. The high ash content in the microalgae—peat mixture may act as a catalyst improving the biomass conversion to biocrude [105]. HTL of pure peat and microalgae separately resulted in the highest hydrochar (67 wt%) and biogas (36 wt%) yields, respectively. An explanation for the higher biogas yield from algal biomass could be the higher volatile matter (5.7 wt%) content in algal biomass than that in peat (4.6 wt%) [4,106].

HTL of a red algae Cyanidioschyzon merolae (CM) and oilseed Salicornia bigelovii Torr. (SL) mixture (4:1 wt/wt CM:SL ratio) at 300 °C and 2.9 MPa yielded a higher amount of biocrude (about 33 wt%) than theoretical yield (about 29.2 wt%). This biocrude yield from the co-liquefaction of CM and SL was higher than that of pure SL (7.7 wt%) and almost identical to the biocrude yield from pure CM (34.6 wt%) [105]. Hexadecanoic acid was one of the major compounds in the biocrude obtained from HTL of a CM/SL (4:1 wt/wt) mixture. Oleic acid and phenols were the other major chemical compounds in the biocrude from CM and SL, respectively. Cyclo-(l-Leucyl l-Prolyl) and arachidamide, N-methyl-, were also present in the biocrude from CM, which can be attributed to the thermal degradation of proteins and carbohydrates present in the original feedstock. Cyclo-(l-Leucyl l-Prolyl) is known to have antioxidant properties [107,108]. Oleic acid content of the biocrude from CM:SL mixture (4:1 wt/wt) was higher (8.5%) than that in the biocrude from pure CM (4.7%) and pure SL (5.3%). Oleic acid has been used in the pharmaceutical industry and as a lubricant in cosmetics [109]. These results clearly indicate the effects of feedstock composition, along with the HTL temperature on the HTL product yields and compositions (Table 3).

**Table 3.** Yield of biocrude (wt%) and its characteristics from HTL of microalgae with different feedstocks from various reports.

<table>
<thead>
<tr>
<th>SL No.</th>
<th>Feedstock</th>
<th>Temperature (°C)</th>
<th>Biocrude Yield (wt%)</th>
<th>Bio—Oil Characteristics</th>
<th>HHV *</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Chlorella pyrenoidosa (CP)</td>
<td>300</td>
<td>43.1</td>
<td>C 8.5, H 7.6, N 0.6, S 9.8, O 35.4</td>
<td></td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>CP-SPR (3:1 wt:wt)</td>
<td></td>
<td>40</td>
<td>C 7.3, H 8.1, N 0.5, S 9.2, O 35.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sweet Potato Residue (SPR)</td>
<td></td>
<td>37</td>
<td>C 7.0, H 6.7, N 0.4, S BDL, O 22.1, H 29.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Nannochloropsis sp. (NS)</td>
<td>350</td>
<td>45.1</td>
<td>C 75.8, H 7.5, N 5, S BDL, O 11.6, H 35.9</td>
<td></td>
<td>[110]</td>
</tr>
<tr>
<td></td>
<td>NS:RS (1:1 wt:wt)</td>
<td></td>
<td>42.2</td>
<td>C 77.2, H 7.1, N 4.6, S BDL, O 11.1, H 32.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rice Straw (RS)</td>
<td></td>
<td>32.5</td>
<td>C 77.8, H 6.6, N 2.4, S BDL, O 13.3, H 33.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Chlorella vulgaris (CV)</td>
<td>350</td>
<td>18.3</td>
<td>C 66.2, H 8.1, N 5, S 0.7, O 20.1, H 31.9</td>
<td></td>
<td>[111]</td>
</tr>
<tr>
<td></td>
<td>Green Waste (GW)</td>
<td></td>
<td>4.4</td>
<td>C 76.6, H 3.1, N 7.4, S 0.1, O 12.8, H 32.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CV-GW (1:1 wt:wt)</td>
<td></td>
<td>10.9</td>
<td>C 75, H 4.5, N 8.5, S 0.2, O 11.7, H 32.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sewage Sludge (SS)</td>
<td></td>
<td>12</td>
<td>C 71.3, H 3.8, N 8.4, S 1.7, O 14.7, H 32.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CV-SS (1:1 wt:wt)</td>
<td></td>
<td>16.4</td>
<td>C 72.1, H 4.4, N 8.4, S 1, O 14.1, H 32.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Cont.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Feedstock</th>
<th>Temperature (°C)</th>
<th>Biocrude Yield (wt%)</th>
<th>Bio—Oil Characteristics</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>4.</td>
<td>Chlorella vulgaris (CV)</td>
<td>21</td>
<td>65.4</td>
<td>8.8</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>CV:SB (1:1 wt:wt)</td>
<td>250</td>
<td>20.9</td>
<td>62.3</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>Sugarcane Bagasse (SB)</td>
<td>12</td>
<td>58</td>
<td>6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

a HHV = High Heating Value (MJ kg⁻¹); b BDL = Below Detection Level.

The bio-oil produced via HTL and pyrolysis of microalgal biomass have high acidity and viscosity, and low heating value [95]. These properties can be attributed to the presence of O-containing functional groups like carboxylic acids, aldehydes, and furans in the bio-oil that impede its utility as a high-grade source of energy [113]. High acidity bio-oil is highly corrosive [114], high viscosity increases pumping costs and the low heating value of bio-oil confers poor thermal stability [115]. Hence, combining microalgal biomass with some other suitable feedstock, along with fine tuning of process parameters, is essential to obtaining bio-oil with improved and desirable properties.

4.2.2. Hydrothermal Carbonization

In Hydrothermal carbonization (HTC), the wet biomass undergoes thermal degradation at a lower temperature (ranging from about 180 to 250 °C), pressure (usually within 2 to 6 MPa), and longer process time (several hours) than those used for HTL [116]. HTC is an exothermic and spontaneous process that takes place in hot compressed water, which plays multiple roles as a reactant, solvent, and acid/ base. During HTC, increasing the temperature reduces the dielectric constant of water, thus, making it a non-polar solvent (hydrophobic). Consequently, water solubility of non-polar organic compounds present in biomass is increased during the HTC. For example, dielectric constant of water at 200 °C is similar to that of methanol which is a relatively non-polar solvent [117]. The main products obtained from HTC are hydrochar (solid), aqueous phase (liquid), and gases (mostly CO₂) [118]. Hydrochar has many applications including use as solid fuel, soil amendment, and low-cost adsorbent. The utility of hydrochar depends on its physical and chemical characteristics [119,120]. The HTC process is designed to maximize hydrochar yields, while liquid biocrude is the main target product from HTL.

The effect of removing ash from Scenedesmus sp. from the hydrochar yield from HTC process has been examined [121]. The latter HTC study evaluated three temperatures (180, 220 and 260 °C) at 2 MPa pressure for 4 h in an argon gas atmosphere. Feedstock: water ratio was 1: 15 wt/wt. Increasing the temperature from 180 to 260 °C led to a decline in hydrochar yield from 41 to 28 wt% when algal biomass was used as is, without deashing. At high temperatures, solid residue undergoes further degradation reducing the hydrochar yield [122]. Deashing microalgal biomass (reduction in ash content from 44.7 to 14.5 wt% using 4 M HCl solution) increased hydrochar yield by 26 wt%. The high ash content (44.7 wt%) in the original algal biomass acted as a catalyst, increasing biomass degradation to biocrude and gas. Increasing the HTC temperature from 180 to 260 °C resulted in a higher C content in the hydrochar from 53.5 to 59.1 wt%, while O content decreased from 32.6 to 22.3 wt%. High HTC temperature promotes condensation and aromatization reactions, increasing the C content of the hydrochar. Simultaneously, there is enhancement of dehydration and decarboxylation reactions, which lead to lower O content of hydrochar [123]. Similar trends in C and O contents in hydrochar were also observed with the HTC of deashed microalgal biomass.

Hydrochar yield from HTC of Chlorella vulgaris at 210 °C using a biomass: water ratio of 1:100 wt/v for 30 min was slightly lower (53 wt%) when the feedstock was defatted prior to the process compared to that from the original (full fat) algal biomass (57.8 wt%) [124]. C and H contents of the hydrochar from defatted algal biomass (C content—59.5 wt%; H content—7.8 wt%) were higher than those from full fat algal biomass (C content—44.4 wt%; H content—6.8 wt%). Interestingly, the energy content of the hydrochar from defat-
ted microalgal biomass (26 MJ/kg) was higher than that from the full fat algal biomass (16.6 MJ/kg), but the removal of lipids from the microalgal biomass did not significantly affect hydrochar yield from the HTC process. It has been reported that the removal of lipids from *Chlorella vulgaris* significantly increases the H content in the defatted biomass (65 wt%) compared to that of the full fat microalgae (4.9 wt%) leading to the production of hydrochar with a higher energy content [125,126]. Full fat biomass produced a higher amount of aqueous phase (AP) than the defatted biomass (34.2 wt% full fat biomass and 28.5 wt% from defatted algal biomass) while N and P contents in the AP from both processes were similar (149.5 mg. L$^{-1}$ total N and 3.3 mg. L$^{-1}$ total P and 150.9 mg. L$^{-1}$ total N and 2.1 mg. L$^{-1}$ total P in AP from full fat and defatted algal biomass, respectively). Considering that total N content of the AP produced by both types of algal biomass were significantly higher than that of organic fertilizer (26.5 mg. L$^{-1}$ total N), AP from HTC of algal biomass might be a viable source to provide N for plant growth [127,128].

The results from catalytic and non-catalytic HTC of algal biomass have also been compared [129]. For example, non-catalytic HTC of *Chlorella vulgaris* demonstrated that hydrochar yield decreased from 40.8 to 24.3 wt% with an increase in temperature from 180 to 220 °C, while fixed C and ash content of the hydrochar increased from 12.2 to 19.8 wt% and 2.1 to 6.7 wt%, respectively. During the same process, volatile matter content of the hydrochar decreased from about 85.7 to 75 wt% while its total organic C (TOC) content increased from 10 to 50 g. L$^{-1}$.

Catalytic HTC of *Chlorella vulgaris* with acetic acid addition to the feedstock (biomass + water) at weight proportions of 5 and 10 wt% reduced the biochar yield from 40.7 to 13.8 wt% and 40.7 to 20.6 wt%, respectively. This was accompanied by a respective decline in volatile matter content from 78.8 to 74.4 wt% and 82.1 to 71.6 wt% and an increase in fixed C content of hydrochar from 16.9 to 24.3 wt% and 16.4 to 23.8 wt%, respectively. A possible explanation for the latter results could be the addition of acetic acid to *Chlorella vulgaris*, which improved the degradation of carbohydrates and proteins present in the algal biomass via dehydration, decarboxylation, and deoxygenation reactions, increasing the fixed C content while lowering the volatile matter content of the hydrochar [130]. Hence, the utilization of a mild homogenous catalyst like acetic acid can help in improving the properties of hydrochar for its utility as a solid fuel. Combining algal biomass with agricultural wastes that are rich in organic acids prior to HTC treatment could be a lower cost alternative to the addition of pure acetic acid to improve hydrochar properties.

A comparison of the data from HTC of microalgal biomass from various strains and other feedstocks (Table 4) clearly indicates the significant effect of biomass composition and HTC temperature on the product properties.

### Table 4.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Feedstock</th>
<th>Temperature (°C)</th>
<th>Hydrochar Yield a</th>
<th>C b</th>
<th>H</th>
<th>Hydrochar Characteristics</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><em>Chlorella</em> sp.</td>
<td>220</td>
<td>28</td>
<td>49.3</td>
<td>7.4</td>
<td>9.6 0.9 31.7 1.2 21.2</td>
<td>[131]</td>
</tr>
<tr>
<td>2</td>
<td><em>Nannochloropsis</em> gladina</td>
<td>222</td>
<td>40</td>
<td>49.4</td>
<td>7</td>
<td>5.9 0.5 32.1 5.1 22.1</td>
<td>[132]</td>
</tr>
<tr>
<td>3</td>
<td><em>Picochlorum</em> oculatum</td>
<td>200</td>
<td>30.8</td>
<td>65.1</td>
<td>7.5</td>
<td>6 0.4 21.1 8.1 28.9</td>
<td>[133]</td>
</tr>
<tr>
<td>4</td>
<td><em>Spirulina</em> platensis</td>
<td>180</td>
<td>47.3</td>
<td>46.1</td>
<td>6.7</td>
<td>8.7 0.6 31.8 6.1 19.4</td>
<td>[134]</td>
</tr>
<tr>
<td>5</td>
<td>Farm Digestate</td>
<td>250</td>
<td>51</td>
<td>62.9</td>
<td>5.6</td>
<td>1.7 0.4 17.2 12.3 26.5</td>
<td>[135]</td>
</tr>
<tr>
<td>6</td>
<td>Almond Shells</td>
<td>220</td>
<td>62</td>
<td>50.7</td>
<td>6</td>
<td>0.4 BDL 43 1.4 20.3</td>
<td>[136]</td>
</tr>
<tr>
<td>7</td>
<td>Food Waste</td>
<td>230</td>
<td>10</td>
<td>54.8</td>
<td>6.1</td>
<td>2.3 0.2 22.3 14.3 23.7</td>
<td>[137]</td>
</tr>
<tr>
<td>8</td>
<td>Agricultural Waste</td>
<td>240</td>
<td>42</td>
<td>63.7</td>
<td>5.8</td>
<td>0.8 0.2 27.9 1.6 25.3</td>
<td>[138]</td>
</tr>
<tr>
<td>9</td>
<td>Rice Husk</td>
<td>220</td>
<td>75.9</td>
<td>58.8</td>
<td>5.9</td>
<td>0.4 BDL 34.8 21.2 22</td>
<td>[139]</td>
</tr>
</tbody>
</table>

a The units of hydrochar yield along with C, H, N, S, O and ash are all in wt%; b The unit of HHV is in MJ. kg$^{-1}$. c BDL = Below Detection Level.

In Table 5, the vast potential of algal biomass towards obtaining vast array of bioproduct (based on research publications within the last 5 years) are highlighted.
Table 5. Application of algal biomass in different fields of research within the last 5 years.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Microalgal Strain</th>
<th>Process Utilized</th>
<th>Target Bioproduct</th>
<th>Major Outcome</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><em>Chlorella pyrenoidosa</em></td>
<td>Dark fermentation of acid treated microalgal biomass (cultivated in wastewater)</td>
<td>Biohydrogen (Biofuel Application)</td>
<td>Biohydrogen Produced: 45.5 mL H$_2$ / g Volatile Solids</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td><em>Scenedesmus obliquus</em></td>
<td></td>
<td></td>
<td>Biohydrogen Produced: 38.4 mL H$_2$ / g Volatile Solids</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Chlorella sorokiniana</em></td>
<td></td>
<td></td>
<td>Biohydrogen Produced: 34.8 mL H$_2$ / g Volatile Solids</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td><em>Poterioochromonas malhamensis</em></td>
<td>Microalgae cultivated in Bold Basal media (with optimized NH$_4$Cl content)</td>
<td>Carbohydrate (Food Preservative and Pharmaceutical Applications)</td>
<td>Chrysolaminarin Productivity: 8.2 g. L$^{-1}$. day$^{-1}$</td>
<td>[140]</td>
</tr>
<tr>
<td>3.</td>
<td><em>Dunaliella salina</em></td>
<td>Microalgae grown in Artificial Sea Water medium (Carbon Source = NaHCO$_3$)</td>
<td>Pigment Production (Food and Nutraceutical Applications)</td>
<td>β—Carotene Produced: 4.6 mg. L$^{-1}$. day$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td><em>Aurantiochytrium</em> sp.</td>
<td>Genetically engineered microalgae grown in PYG medium</td>
<td>Ω-3 Polyunsaturated Fatty Acids (Health Supplement Application)</td>
<td>Eicosapentaenoic Acid Produced: 0.5 g. L$^{-1}$. day$^{-1}$</td>
<td>[141]</td>
</tr>
<tr>
<td>5.</td>
<td><em>Nannochloropsis</em> sp.</td>
<td>Catalytic Pyrolysis (Catalyst Used = Zeolite HY)</td>
<td>Bio-Oil (Valuable precursor for high value compounds)</td>
<td>Bio-oil Yield = 38.3 wt%; Aromatic Hydrocarbon Content of Bio-oil = 96.3 area%</td>
<td>[143]</td>
</tr>
<tr>
<td>6.</td>
<td><em>Chlorella vulgaris</em></td>
<td>HTL</td>
<td>Biocrude Oil (improved properties for utilization as fuel and/or fuel additive)</td>
<td>Biocrude Oil Yield = 36.2 wt% (C = 68.2 wt%; H = 8.7 wt%; N = 7 wt%; O = 16.1 wt%; S = BDL*)</td>
<td>[144]</td>
</tr>
<tr>
<td></td>
<td><em>Arthrospira platensis</em></td>
<td></td>
<td></td>
<td>Biocrude Oil Yield = 39.6 wt% (C = 70.8 wt%; H = 9 wt%; N = 6.6 wt%; O = 13.6 wt%; S = BDL)</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td><em>Chlorella vulgaris</em></td>
<td>HTC</td>
<td>Hydrochar (Utility as Soil Amendment; electrode material and more)</td>
<td>Hydrochar Yield = 38 wt%; (C = 49.1 wt%; H = 6.2 wt%; N = 4.1 wt%; O = 11.5 wt%; S = BDL; Ash = 29.1 wt%)</td>
<td>[145]</td>
</tr>
</tbody>
</table>

* BDL = Below Detection Level.

5. Conclusions and Outlook

The thermal treatment of algal biomass grown on wastewater produces liquid, solid, and gas streams that can be further processed into various types of industrial chemicals and fuels. Biomass chemical composition, the type of processing technique and process parameters used including temperature and treatment time, has significant effects on the composition and yield of the product streams. Considering that the chemical composition of the feedstock plays a vital role in the final product properties, customization of the feedstock chemical composition by preparing mixtures of biomass from various sources, such as mixtures of algal biomass with forest and crop residues, and processing byproducts, could enhance the desired product yield and properties while improving the sustainability of the entire process. Additionally, the combination of microalgae with such abundantly available feedstock can help to counteract the problems of obtaining products with less desirable qualities, especially low C and H contents, providing a good balance between economic and technical feasibility for the conversion of biomass into various products via different conversion techniques. Catalytic thermal conversion processes can improve product yields and composition. However, catalyst to biomass ratios used in most of the published thermal conversion processing research studies are extremely high, potentially adversely affecting commercial viability of the proposed techniques. There is an urgent need for the development of more effective and low-cost catalysts that can promote the conversion of algal biomass components to high value products, improve yields, and reduce the impact of processing on the environment.
Although hydrothermal processing of wet algal biomass may lower the energy requirement for the conversion process, the storage and handling of wet feedstock to be used in commercial operations creates huge logistical problems, making it unattainable. Transportation of wet biomass will increase the cost of the final product. Short storage stability of wet biomass is a very significant drawback of hydrothermal processes, creating significant challenges for maintaining not only the feedstock quality, but also final product properties manufactured at large scale operations.

The most studied product from thermal algal biomass processing is bio-oil or biocrude. Unfortunately, most of the work performed in this area has been performed at laboratory scale and information on the scale-up potential of these processes is limited. Although several studies examined the chemical composition of crude bio-oil, commercial applications of this stream will require downstream processing to refine the product for specific applications. The solid product obtained from thermal degradation of algal biomass, biochar, or hydrochar has many potential applications, but only a few of them i.e., adsorbent, electrode, soil amendment, have been researched. Downstream processing of non-condensable gases produced during thermal algal biomass treatment via Fischer-Tropsch synthesis produces lighter or short chain hydrocarbons.

There is certainly an urgent need for further research on the mathematical modeling of thermal algal biomass conversion processes, their scale up potential, economic feasibility, life-cycle assessment, and a better understanding of the correlations between feedstock and bio-oil compositions. Conversion of algal biomass grown on wastewater to various bioproducts within a biorefinery system that integrates wastewater treatment and bioproduct manufacturing at a close proximity provides tremendous opportunities for product diversification and operational flexibility by onsite biomass availability, reducing transportation costs and the potential utilization of waste and byproduct streams generated during the biomass conversion process. Multiple product manufacturing from locally produced renewable feedstocks within a biorefinery system eases the reliance on petroleum-based feedstock and products, reduces greenhouse gas emissions, and most importantly, promotes the sustainable use of limited resources.

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