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Review

The Application of Catalytic Processes on the Production of Algae-Based Biofuels: A Review

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Abstract: Over the last decades, microalgal biomass has gained a significant role in the development of different high-end (nutraceuticals, colorants, food supplements, and pharmaceuticals) and low-end products (biodiesel, bioethanol, and biogas) due to its rapid growth and high carbon-fixing efficiency. Therefore, microalgae are considered a useful and sustainable resource to attain energy security while reducing our current reliance on fossil fuels. From the technologies available for obtaining biofuels using microalgae biomass, thermochemical processes (pyrolysis, Hydrothermal Liquefaction (HTL), gasification) have proven to be processed with higher viability, because they use all biomass. However, due to the complex structure of the biomass (lipids, carbohydrates, and proteins), the obtained biofuels from direct thermochemical conversion have large amounts of heteroatoms (oxygen, nitrogen, and sulfur). As a solution, catalyst-based processes have emerged as a sustainable solution for the increase in biocrude production. This paper's objective is to present a comprehensive review of recent developments on the catalyst-mediated conversion of algal biomass. Special attention will be given to operating conditions, strains evaluated, and challenges for the optimal yield of algal-based biofuels through pyrolysis and HTL.

Keywords: microalgal biomass; thermochemical conversion; catalytic upgrading; liquid fuels; hydrothermal liquefaction; pyrolysis; gasification

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1. Introduction

Fossil fuels have been a critical commodity for the economic and social development of the modern world. However, their consumption has inevitably increased the levels of anthropogenic carbon dioxide (CO_2) emissions to concentrations that exceed the earth's absorption capacity through the natural carbon cycle [1]. Biomass-based fuels (or biofuels) are considered as a substitute for traditional fossil fuels [2] for both developed and non-developed countries due to their abundance and distribution [3].

Over the last years, several biomass resources such as grass, wood, crops and residues, animal waste, municipal solid waste, and even aquatic plants have been studied to produce biofuels [4]. However, up to date, microalgae are considered one of the most attractive sources of renewable energy and raw materials; it diversifies the scope of different industries in the elaboration of food and feed, pharmaceuticals, pigments, colorants, bioplastics, and protein hydrolysates [5].

Microalgae and cyanobacteria are a diverse group of photosynthetic microorganisms that naturally grow in lakes, rivers, and oceans. Microalgae offer several advantages over plant-based biofuels such as (i) high growth rate, (ii) use of non-arable lands, (iii) can be grown in wastewater, (iv) high consumption of CO_2, and (v) their production can be directed toward the synthesis of several compounds of commercial interest [6].

To obtain biomass with a high concentration of specific metabolites is one the cornerstones of microalgae biotechnology. Several authors have proved that specific culturing conditions such as nutrient concentration [7], photobioreactor configuration [8], environmental conditions (temperature and illuminance), agitation, and pH [9] directly influence the cellular composition, resulting in the final concentration and productivity of the strain, as well as the variation in the content of specific metabolites (lipids, carbohydrates, proteins, and other components) [10].

The transformation of algal biomass into biofuels is not new. Several studies have covered different areas on the strain selection, culture method, and transformation into biofuel, which is the critical link in the production chain toward obtaining sustainable biofuels from microalgae.

The algal biomass produced under specific conditions can be transformed into energy by applying thermochemical and biochemical methods. Biofuel such as Bio-oil, biochar, synthesis gas (syngas), and heat are obtained through thermochemical conversion. On the other side, biodiesel, biohydrogen, biomethane (or biogas), and bioethanol can be produced via the biochemical conversion of algal biomass [1]. Although different forms of cultivation and production have been developed in recent years, it is still necessary to find an effective and sustainable production mechanism to reach the full potential of microalgae-based biofuels, especially in large-scale industrial applications.

One possible solution to achieve the potential of algae as a feedstock for biofuels is the use of reactions that employ whole biomass such as anaerobic digestion (AD) and thermochemical conversion. Biogas is the main product of AD and is considered one of the most promising biofuels that can address rising concerns about fossil fuels [11]. Another alternative is the application of catalytic-based processes such as Hydrothermal Liquefaction (HTL) and pyrolysis. Through thermochemical conversion, the biomass is decomposed under oxygen/air deficient conditions to produce Bio-oil, Biochar (specially on HTL and pyrolysis process), and syngas (especially on gasification process), which primarily consists of carbon monoxide (CO) and carbon dioxide (CO_2) [12], the quantity and quality of the final product depends upon the process, reaction temperature, heating rate, and oxygen supply [13]. In comparison to the biochemical conversion of algal biomass, the thermochemical approach is a more straightforward route to produce biofuels due to several factors: (i) the entire biomass is employed as feedstock, (ii) the process times is shorter, and (iii) the final yield can be improved by the addition of chemical catalyst [14]. The present study is intended to give a comprehensive overview of the state-of-the-art usage of catalysts on the thermochemical conversion of algal biomass into solids, liquids, and gas biofuels. Special attention will be given to operating conditions, strains evaluated, and challenges for the optimal yield of algal-based biofuels through pyrolysis and HTL.

2. Algae-Based Biofuels

Biofuels are broadly classified by generations. First-generation (1st gen) biofuels are produced from food feedstock (corn, sugarcane, soybean, potato, beet, soybeans, coconut, sunflower, rapeseed, palm oil, switchgrass, Jatropha, Camelina, Cassava). Although 1st gen is considered a sustainable source of energy due to the reduction on greenhouse gas (GHG) emissions, specific details such as their competition with food supply, high requirement of government subsidies, large amounts of non-sustainable fertilizers, and environmental concerns due to the loss of biodiversity linked to the promotion of deforestation for large monoculture areas [15] hinder their true impact as a cleaner and more sustainable option over fossil fuels.

Second-generation (2nd gen) was conceived as a partial solution of several drawbacks of 1st gen biofuels. This generation relies on nonfood items such as cellulosic biomass, straw, manure, used cooking oil, and other non-conventional sources, which usually finish in landfills once their useful portion has been removed [12]. However, 2nd gen is still not industrially profitable due to biomass complexity and problems associated with its production, storage, and transportation [2].

Third-generation (3rd gen) focuses on the upgrade of aquatic feedstock, such as microalgal and cyanobacterial biomass, into different fuels. Microalgae have been praised as a better solution for the energy problem due to specific qualities of algal production: (i) do not compete with human and animal food stock, (ii) harvesting can be done through the year, (iii) can employ saline and wastewater, (iv) have better growth rate than higher plants, (v) can convert up to 183 G tons of CO_2 to produce 100 G tons of biomass in comparison to higher plants such as wood crops (165 G tons of CO_2 to produce 100 G tons of biomass) [16], and (vi) the concentration of transformable metabolites (lipids and carbohydrates) is stable in the biomass. First, the selected strain had to be cultured until it reaches the largest possible biomass concentration in the photobioreactor; once reached, the biomass is removed from the culture media (centrifugation, flocculation, filtration, and other techniques) and dried. Then, the dried biomass is ready to be used as feedstock for several biofuels (biodiesel, bioethanol, biogas, and so on). These different sections have been the main topic of research over the last 20 years, attracting the attention of different universities, research centers, and energy companies worldwide such as Ecopetrol (Colombia), Exxon Mobile, Shell (US), Petrobras (Brazil), and Total (France).

2.1. How the Production of Algae-Based Biofuels Changed over Time

Several companies worldwide such as Solix biofuels, Corbion (previously known as Terravia or Solazyme), Cellana, Sapphire Energy, Seambiotic, Oil Fox, Synthetic genomics, Euglena, and others started the race for algae-based biofuels. However, after years of research, none of the companies proved the economic balance of algal-based biofuels [2]. The latter can be due to several problems identified through the last decade. First, the microalgal biodiversity is so vast that after ten years of research, we are still far from identifying the total diversity of algae and cyanobacteria [15]. Another problem related to the strains is the stability of their growth on industrial photobioreactors and the synthesis of the target metabolite [5,6].

Limited studies reported that few species of microalgae and cyanobacteria possess an inherent capacity for lipid synthesis and storage (Table 1).

Table 1. Different strains studied for biodiesel production.

Strain	Lipids (wt%)	Carbohydrates (wt%)	Proteins (wt%)	Reference
Arthrospira platensis	30.23	31.89	16.81	[17]
Auxenochlorella protothecoides	42	26	30	[18]
Botryococcus braunii	45	10	44	[19]
	60	20	18	[20]
Chlamydomonas reinhardtii	22.11	52.2	23.69	[21]
Ch. reinhardtii CC-400	28.5	n/a	n/a	[22]
Ch. Reinhardtii CC-4349	64.25	n/a	n/a	[23]
Chlorella sp G-9	36.5	n/a	n/a	[24]
C. kessleri	20	18.7	53.8	[25]
C. pyrenoidosa	19.8	14.8	57.3	[26]
C. vulgaris UTEX 259	28	35	20	[27]
C. vulgaris UTEX 1803	12	36	41	[28]
C. vulgaris Mutant (UV715)	41	n/a	n/a	[29]
Chlorococcum oleofaciens	20	42	35	[30]
Dunaliella tertiolecta	15	10	56	[31]
Nannochloropsis gaditana	17.6	n/a	24.1	[32]
Pseudokirchneriella Subcapitata	40	20	30	[30]
Phaeodactylum tricornutum	55.7	9	22	[33]
Scenedesmus almeriensis	13.1	n/a	30	[34]
S. obliquus	32.5	n/a	n/a	[35]
	24.9	n/a	n/a	[36]
	35	22	32	[37,38]
Tetraselmis suecica	9.03	20	37.27	[39]
	25.07	17.52	42.05	[40]

Initially, the studies focused on applying industrially relevant strains such as *Spirulina* (*Arthorspira*) [17], *Auxenochlorella* [18], *Botryococcus* [19,20], *Chlamydomonas* [21–23], *Chlorella* [24–29], *Dunaliella* [34], *Scenedesmus* [38–43], and *Tetraselmis* [44,45]. Over time, other strain with a unique capacity for the synthesis of lipids and hydrocarbons such as *Botryococcus braunii* [19,20] were isolated and identified, and more recently, the scientific community has opted for the production of mutant strains with large lipid storage [22,23,31].

Microalgae can be produced under autotrophic, mixotrophic, or heterotrophic conditions. Different systems for the production of algae are available for their culture under the three conditions, as mentioned earlier [41]. Autotrophic systems are the most common, since the algae only require light as an energy source and dissolved CO_2 as a source of carbon. Usually, algae growth under autotrophic systems can be produced in open or closed photobioreactors. Open ponds are the simplest of all systems for algal production, and it requires low energy inputs. It has easy maintenance; however, it is severely affected by seasonal variations and is prone to contamination by other microbes [42]. Mixotrophic and heterotrophic production of algae requires the addition of organic carbon sources (glucose, acetate, and others), which can lead to contamination by the presence of bacteria and fungi; therefore, these systems require closed photobioreactors (PBR). Closed PBR offers several advantages over open systems: (i) aseptic growth conditions, (ii) increased cell concentration due to better light distribution, (iii) improved pH control, and (iv) reduced water loss due to evaporation. However, their operation cost, maintenance, and energy inputs are considerably higher than in open ponds [42].

After biomass production, the cells are harvested from the media. Due to their nature, microalgal cells have a small size and low specific gravity; therefore, their concentration and harvesting are energy and time-intensive [43]. Several techniques are available at industrial scale such as centrifugation, filtration, flocculation, flotation, electroflotation, and so on [10]. However, the method's selection and application lie on the technical and economic analysis since some of them can be extremely expensive and energy-intensive for the production of algal-based biofuels [44]. Once the biomass is removed from the media, most of the cell water content must be removed via spray drying, drum drying, freeze-drying, or solar drying to avoid any interference with the extraction [41]. Following drying comes the extraction of lipids and carbohydrates, which is considered as the crucial step that inhibits the industrial-scale production of algae-based biofuels [44]. The microalgal cell wall is made of polysaccharides and cellulose synthesized from silicic acid [45], and it must be broken in order to release both lipids and carbohydrates; as a consequence, only a fraction of the biomass is used in biofuel process production. Therefore, biodiesel and bioethanol production are still not economically feasible due to the high cost and energy inputs in almost all stages [46]. Other biofuels such as biogas and biohydrogen have gained attention as sustainable alternatives for energy production using microalgal biomass.

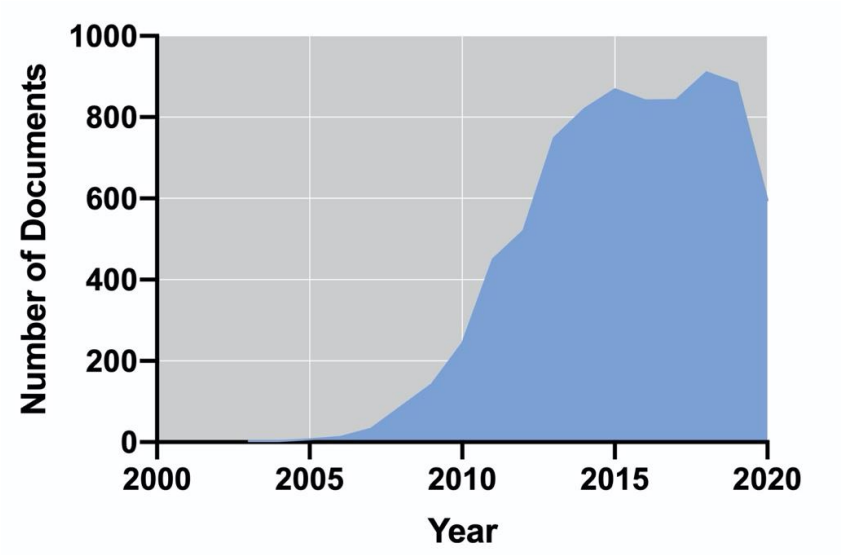
2.2. Biochemical Conversion for Third-Generation Biofuel

The biochemical conversion of algal biomass into third-generation biofuels are divided into biodiesel, bioethanol, biogas, and biohydrogen. Biodiesel from algae requires the extraction and conversion of lipidic fraction into low atomic weight compounds, biodegradable fatty acid methyl esters (FAME), for hands ready usage in engines through transesterification [47]. In the transesterification reaction in the presence of a chemical (acid, alkali) or biological (lipase) catalyst [48], methanol or ethanol is used to increase the reaction rate and maintain a balance change toward the production of fatty acid esters with glycerol as a by-product [49]. The biodiesel derived from algal biomass has a petrodiesel-like calorific value (39–41 MJ/kg) [50]; it also has a higher percentage of unsaturated fatty acid compared to saturated fatty acid, which is a prerequisite for fuel engineering [51]. A higher degree of unsaturation leads to better cold flow; however, insoluble particle production is simultaneously increased [52].

Microalgae are an alternative resource for bioethanol production as they showed higher productivity than certain feedstocks for bioethanol production, such as sugarcane and corn [53]. Several strains accumulate carbohydrates in excess (mainly as insoluble starch and cellulose, with the absence of lignin) of up to 50% of their dry weight (DW) [54]. These carbohydrates are not readily fermentable to bioethanol [55]; thus, pretreatment processes, including chemical (acid and alkaline) or enzymatic hydrolysis, are crucial [56–58].

There are many pretreatment methods (acid, basic, and enzymatic hydrolysis); however, their cost can significantly contribute up to 30% of the total cost of bioethanol production [59]. Acid hydrolysis is quicker and cheaper under high temperatures and pressures but can decompose sugar into inhibitors [60–62]. Conversely, under mild temperatures and pressure, enzymatic hydrolysis can be achieved, but it is slower, more costly, and still involves physical or chemical pretreatment [63].

Biogas is produced via a sequence of biochemical processes converting the organic material: hydrolysis, fermentation, acetogenesis, and methanogenesis, also known as anaerobic digestion (AD) [64]. In this process, the whole biomass is used for the production of methane (55–75%) and carbon dioxide (25–45%) [65]; therefore, the energy performance is higher in comparison to biodiesel and bioethanol [66]. Additionally, nutrients such as organic nitrogen or phosphorus may be mineralized and subsequently recycled for algae cultivation [67]. Unlike biogas, biohydrogen is produced via their metabolic pathways along with the cell growth; therefore, it does not require further processing of the biomass (i.e., harvesting, dewatering, drying, and extraction), and it is considered clean and renewable, with higher energy production (142 MJ/Kg) [68]. Biohydrogen can be obtained by photofermentation, dark fermentation, direct and indirect biophotolysis [69]; however, hydrogen production cannot be achieved amidst effective photosynthesis, as oxygen inactivates hydrogenase [70]. The Research and Development on algal-based biofuels is a field that, in recent years, has been maintained with a considerable number of publications. Figure 1 shows the number of publications per year in the last 18 years, according to the Scopus database (Elsevier). It is possible to observe an exponential increase in the number of publications between 2006 and 2015. Since 2016, the number of documents has remained almost constant up to a final number of 8022 (including accepted manuscripts for 2021). The United States, China, India, South Korea, and the United Kingdom dominate the scientific publication on algal-based biofuels.



(**a**)

Figure 1. *Cont.*

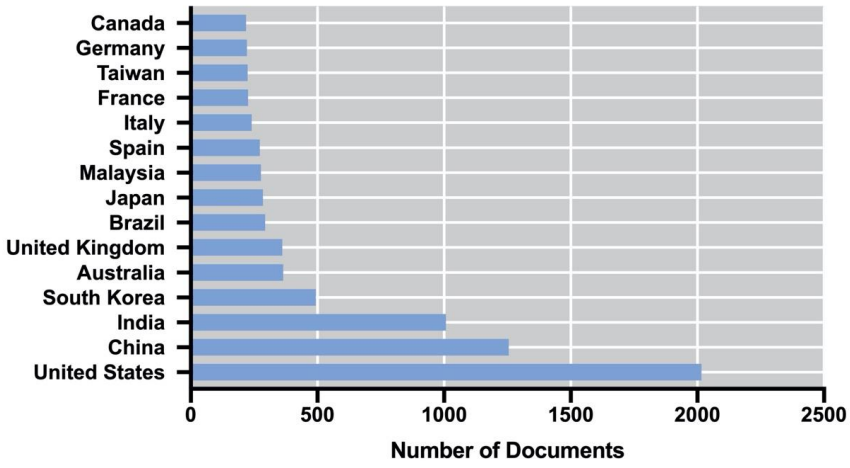


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Figure 1. Evolution of the number of publications from 2003 to 2020 on algal biofuels (**a**) and their country of origin (**b**).

3. Thermochemical Conversion of Algal Biomass

Thermochemical methods can be grouped into four classes (Figure 2): hydrothermal liquefaction, pyrolysis, gasification, and torrefaction [71]. In the thermochemical process, the algal biomass is thermally decomposed into usable biofuels such as syngas, bio-oil, and biochar (Figure 2). Unlike the biochemical production of biofuels, thermochemical processes do not require the extraction of lipids nor carbohydrates; therefore, the entire biomass can be used. Finally, the reaction time is short, providing a simpler route for the biofuel production [10].

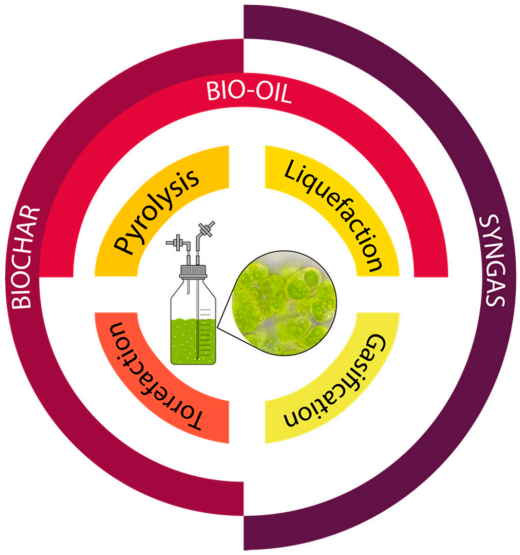
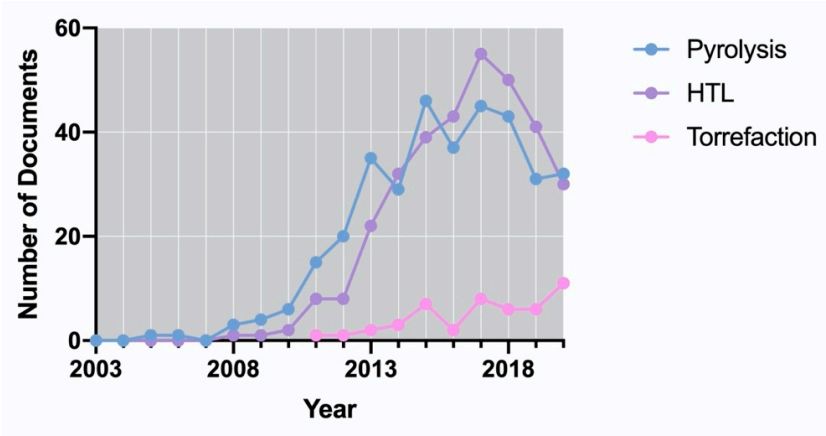


Figure 2. Different thermochemical conversion methods of microalgal biomass and their main products.

3.1. Microalgal Torrefaction

Torrefaction (usually called mild pyrolysis) is a pretreatment process focused on altering the physicochemical properties of biomass to improve their fuel characteristics and applicability in thermal conversion processes [72]. Their application of microalgae is relatively new (Figure 3a), with the first reported use in 2011. Usually, the reaction temperature of the torrefaction process occurs between 200 and 300 °C, under slow heating rates (<50 °C/min), mainly in an inert environment [73,74]. The torrefied biomass poses several

advantages: higher heating value, lower atomic O/C and H/C ratios, lower moisture content, higher water-resistivity, and improved reactivity [72]. There are several reports of torrefaction (both wet and dry) on algal biomass upgrade. The torrefied biomass of *S. platensis* (300 °C and 30 min) showed an increase in the higher heating value (from 20 to 25.92 MJ/kg) and a lower moisture content (from 7.61 to 1 wt%) in comparison to untreated biomass [73]. In a different study, *C. vulgaris* ESP-31 was torrefied in the presence of water (20 g dried microalga and 100 g of distilled water) using different temperatures (160, 170, and 180 °C) for 10 min. The torrefied biomass showed an increased fixed carbon (25.29 and 16.39 wt% respectively) and Higher Heating Value (HHV) in comparison with raw biomass (24.49 and 22.02 MJ/kg, respectively) [75]. In a complementary study, the treated biomass of *C. vulgaris* ESP-31 was further transformed through gasification [76]. As a result, the biomass reached the devolatilization peak at lower temperatures (between 266 and 270 °C) compared to raw samples (287.7 °C). The efficiency of torrefaction is linked to temperature and time reaction [77]. According to Chen et al. [78], 300 °C and 30 min increased the final HHV content in Chlamydomonas sp. JSC4 (from 19.27 to 25 MJ/kg). Another possibility is the application of wet torrefaction for the co-production of biochar and bioethanol; Yu et al. [79,80] torrefied *C. vulgaris* ESP-31 biomass addition of 0.2 M H_2SO_4 (170 °C, 10 min). Their results show a significant increase in the HHV, from 19.23 to 32.35 MJ/kg, while the hydrolysate contained a considerably high content of total reducing sugar (7.31–98.11 g/L).



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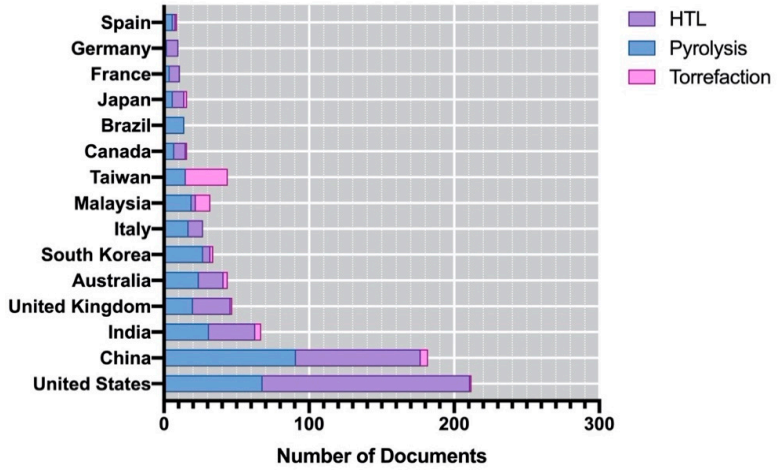

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Figure 3. Evolution of the number of publications from 2003 to 2020 on torrefaction, pyrolysis and Hydrothermal Liquefaction (HTL) using algal biomass (**a**) and their country of origin (**b**).

3.2. Pyrolysis of Microalgae

Pyrolysis is the thermal decomposition of biomass at high temperature (400–600 °C), in an atmospheric-pressure inert environment. Compared to other conversion technologies, the pyrolysis of algal biomass has achieved reliable and promising outcomes that could lead to commercial exploitation [81]. Due to the lipid and protein content of algal biomass, the bio-oils obtained have a higher heating value (10–35 MJ/kg) [82], higher aromatics, and lower acidity (pH 3.7) compared to lignocellulosic biomass (15.14–30.47 MJ/kg, pH < 3) [83–85].

Pyrolysis can be categorized in five modes: (i) slow, (ii) intermediate (iii) fast, (iv) flash, and (v) microwave pyrolysis; each one possesses a differential heating rate, the presence, and/or heating route [9]. Slow pyrolysis is characterized by the heating of biomass under a "slow" heating rate (0.1–0.8 °C/s), with moderate temperature (300–500 °C) and long retention times (5–60 min) [86–88]. Their main product is biochar with by-products such as bio-oil and syngas [89]. Under slow pyrolysis, different particle sizes can be processed; therefore, both macro and microalgae can be used without mechanical pretreatment. Intermediate pyrolysis is carried out using the intermediate conditions between slow and fast pyrolysis [90]. Normally, intermediate pyrolysis occurs at moderate temperatures of reaction (up to 500 °C), 0.5–25 min residence times for feedstocks, and 2–4 s moderate residence times for vapor [91]. The main product from intermediate pyrolysis is bio-oil (40–60%) followed by non-condensable syngas (20–30%) and biochar (15–25%) [92], the bio-oil obtained has a reduced viscosity with a small concentration of tar [93], and the syngas is mainly composed of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4) [94]. Both bio-oil and syngas can be further refined into fuels for energy, heat, and transport [95]. One interesting product from intermediate pyrolysis is hydrogen. Generally, H_2 is not expected in conventional pyrolysis gas, as no reduction process for H_2 formation occurs; however, the contact between hot char and water vapor lead to CO and H_2 [96].

Biochar is a carbon-rich charcoal material that can be obtained from any biomass feedstock by thermal decomposition under minimal oxygen (O_2) supply [97] and contains most of the feedstock mineral components [98]. As mentioned above, slow pyrolysis is the preferred method for biochar production. Biochar has a high heat value, carbon content, porosity, and strong capacity reduction [99]. Due to its sustainable nature and its carbon-neutral properties [100], biochar is mainly focused on carbon reduction, soil amendment, energy resources, and water treatment [101], More recently, several researchers used biochar to synthesize metal-supported catalysts due to their unique physical properties and low price [102]. In a study on the slow pyrolysis of six genera of macroalgae, the authors obtained high yields of biochar (45.3–62.4 wt%) with moderate HHV values (10.7–17.8 MJ/kg) [84]. On another study, *Chlorella* sp. produced higher biochar yield (41 wt%) with relatively high heating value (21.5 MJ/kg) in comparison of the macroalga *Sargassum* sp. (39 wt% and 18.5 MJ/kg) [99]. Temperature is an important parameter on biochar production; when biomass from *Laminaria japonica* was subjected to higher temperatures under slow pyrolysis (600 °C) the yield of biochar was reduced from 78.34 to 27.05%, while ash content increased from 22.92 to 64.19% [103]. Finally, unlike most studies, Wang et al. [98] obtained a higher biochar yield (31 wt%) under fast pyrolysis of *C. vulgaris*; however, this result can be due an unusually high ash content on the biomass.

The preferred method for optimizing bio-oil production is fast pyrolysis; this method is carried out at elevated temperatures (850–1100 °C), fast heating rate (>1 °C/s), and short pyrolysis time (0.5–10 s) [104,105]. These conditions reduce secondary reactions (secondary cracking, condensation, and polymerization of intermediates), which contribute to the production of high bio-oil yields, making it efficient for biomass conversion [83,106]. Flash pyrolysis uses high temperatures (950–1250 °C), high heating rates (>1000 °C/s), and a reduced time (0.5–10 s), with bio-oil as their main product (90 wt%) [89,107]. Finally, Microwave-Assisted Pyrolysis (MAP) employs a heating rate between conventional pyrolysis and fast pyrolysis [107]. It is considered a more energy-efficient method than other pyrolysis-related systems [108], since it can use different particle size biomass. Over the last

years, several studies have been conducted to increase the efficiency of pyrolysis process using microalgal genera such as *Arthrospira* sp. [109], *Chaetocerous* sp. [93], *Chlamydomonas* sp. [4,110], *Chlorella* sp. [83,111–115], *Desmodesmus* sp. [116], *Dunaliella* sp. [93], *Haematococcus* sp. [93,117], *Isochrysis* sp. [118–120], *Microcystis* sp. [105], *Nannochloropsis* sp. [121–124], *Oscillatoria* sp. [125], *Pavlova* sp. [126,127], *Schizochytrium* sp. [128], *Tetraselmis* sp. [118,119], *Spirulina* sp. [112,129,130], and *Synechococcus* [119]. A detailed list of species studied can be found in Table 2.

The application of catalyst on microalgal pyrolysis is an alternative to increase selectivity for certain pyrolytic products (liquid, solid or gas) and improve process parameters (reduced temperature and processing time) [98]; it can also lead to in situ upgrading of generated bio-oil with less oxygenic compounds, which prevent polymerization and condensation [83,131]. Another advantage is that catalysts used for pyrolysis can be recycled to the reactor [83]. Various catalysts such as acid type, base type, metal type, zeolite type, carbon type or a combination of different materials may be used to improve pyrolysis [98]. The most common catalysts used include Na_2CO_3, metallic-based catalysts such as Ni, Mo, and ceria-based catalysts (NieCe/Al_2O_3 and NieCe/ZrO_2) have shown great catalytic efficiency [126]. On the other hand, other metal catalysts including Ce, Ti, Co, Mg, and Al did not show obvious catalytic effect [107]. ZSM-5-based zeolites such as H-ZSM-5, Fe-ZSM-5 Cu-ZSM-5, Ni-ZSM-5, and Ga-HZSM-5 are considered as the most effective catalyst for the pyrolysis of algal biomass. Ga-ZSM-5 is called a bifunctional catalyst, where Ga promotes decarbonylation and olefin aromatization reactions, while the remaining reactions (e.g., oligomerization and cracking) are catalyzed by the ZSM-5 [132]. In the study on the catalytic pyrolysis of *C. vulgaris* with egg whites, Ga-HZSM-5 and Cu-ZSM-5 increased the Aromatic production from 16.72% for normal HZSM-5 (30) to 21.16% and 18.03%, respectively [133]. Another study [132] found that Ga/ZSM-5 catalysts increased the yield of aromatics using Catalytic fast pyrolysis (CFP) by 40% compared to ZSM-5 catalyst. In the catalytic pyrolysis of Jatropha residues, [134] found that Ga/HZSM-5 yield the highest aromatics (95%) high monocyclic aromatic hydrocarbons (MAHs) and low polycyclic aromatic hydrocarbons (PAHs) selectivity of 87% and 13%, respectively. Other zeolites such as ITQ-2 and MCM-22 had a similar but less effective function [135]. In a study on the catalytic pyrolysis of *Nannochloropsis* sp. [121] were able to significantly reduce the oxygen content (from 30 to 19 wt%) and a higher calorific value (from 24.6 to 32.5 MJkg). Other studies such as [136–138] proved the ability of catalytic-mediated pyrolysis to increase the yield of bio-oil.

Du et al. [137] found that an increase in catalyst-to-biomass ratio from 1:1 to 5:1 using HZSM-5 significantly improved the aromatic yields. On the other hand, Gao et al. [138] obtained bio-oil with less nitrogenated compounds through the usage of Mg–Al layered double oxide/ZSM-5 composites on the pyrolysis of cyanobacterial biomass. On another study, Aysu et al. [118] improved the yield and quality of bio-oil from *Tetraselmis* sp. and *Isochrysis* sp. in a fixed bed reactor with the addition of NieCe/Al_2O_3 and NieCe/ZrO_2. Campanella et al. [111] investigated the efficiency of five different zeolite-based catalysts (H-, Fe-, Cu-, and Ni-ZSM-5) in the bio-oil production from *Chlorella* biomass, and they found that HZSM-5 increased the yield of the hydrocarbon fraction in the organic phase from 21 to 43 wt%. Finally, Mo et al. [129] evaluated the efficiency of MgO and ZSM-5 under environment enriched with N_2 and CO_2, where maximum bio-oil (46.2 wt%) was obtained with basic metal MgO. Figure 3 shows the evolution of the number of publications per year along the last 16-year period. According to the data obtained from the Scopus database (Elsevier), it is possible to observe an exponential increase in the number of publications between 2008 and 2017. Finally, the United States, China, India, South Korea, and the United Kingdom dominate the scientific publication on the application of torrefaction, pyrolysis, and HTL.

Table 2. Strains studied on catalytic pyrolysis and their catalyst.

Strain	HHV (MJ/kg)	Heating Rate (°C/min)	Pyrolysis Time (min)	Pyrolysis Temperature (°C)	Catalyst	Bio-oil (wt%)	Bio-char (wt%)	Syngas (wt%)	Reference
Arthrospira plantensis	21.45	100	30	400–700	Ni/HMS-ZSM5	32.52	34.04	33.44	[109]
					Fe/HMS-ZSM5	30.01	31.84	38.15	
					Ce/HMS-ZSM5	31.80	31.79	36.41	
Chlamydomonas reinhardtii	20.47	150	10–34	500	hydrotalcite	54.84	37.59	7.57	[110]
Ch. debaryana	21.9	>200	30	500–800	β-zeolite	23.5	n/a	n/a	[4]
					Activated charcoal	43.8	n/a	n/a	
	21.2	n/a	30	300–450	Na_2CO_3	41.0	54.4	34.1	[83]
Chlorella sp.	19.5	n/a	10	500	Fe-ZSM-5	43.1	29.7	27.1	[111]
					Cu-ZSM-5	46.9	27.9	24.6	
					Ni-ZSM-5	45.1	30.1	25.4	
	n/a	n/a	50	350–650	Magnetite	53.8	27.4	22.8	[112]
					Activated carbon	49. 4	37.3	13.3	
C. vulgaris	16.8	10	30	700	H^+ZSM-5	25	24	n/a	[113]
	n/a	10	30	300–600	Ni-ZSM-5	18.97	n/a	n/a	[114]
	18.6	48	30	500	H^+ZSM-5	52.7	25.7	21.6	[115]
Desmodesmus communis	n/a	n/a	20	460	HZSM-5	8	42	n/a	[116]
Haematococcus pluvialis	8.98	10	n/a	600	KCl	12	60	28	[117]
					KOH	11	65	76	
					K_2CO_3	13	64.8	22.2	
					MgO	12.5	62	25.5	
					Al_2O_3	15	61	24	
					CaO	13	63	24	
					Microalgae Residue	15	60	25	
Isochrysis sp.	12.38	100	60	500	CeO_3	23	30	47	[118]
					Ce/Al_2O_3	25	32	42	
					$NiCe/Al_2O_3$	24	32	43	
					$MgCe/Al_2O_3$	23	31	46	
					Ce/ZnO_2	25	29	54	
					$NiCe/ZnO_2$	23	27	50	
					$MgCe/ZnO_2$	23	28	49	
	15	100	20	500	Li-LSX-zeolite	29	35	36	[119]
	15	100	20	500		42.5	33	24.5	[120]

Table 2. *Cont.*

Strain	HHV (MJ/kg)	Heating Rate (°C/min)	Pyrolysis Time (min)	Pyrolysis Temperature (°C)	Catalyst	Bio-oil (wt%)	Bio-char (wt%)	Syngas (wt%)	Reference
	n/a	10	120	300–500	HZSM-5	25	38	n/a	[121]
Nannochloropsis sp.	15.17	50	60	400–600	Ni–Ce/Al_2O_3	23.3	30.9	n/a	[122]
	n/a	n/a	15	500–900	HZSM-5	49	40	10	[123]
N. oculata	18	n/a	n/a	400–600	Co-Mo/γ-Al_2O_3	26	42	n/a	[124]
Oscillatoria sp.	14.26	20	120	550	TiO_2, ZnO	33.33	43.05	26.25	[125]
					CeO_3	21.07	47.96	45.92	
					TiO_3	20.04	48.18	45.10	
	12.96	100	60	450–550	Ce/TiO_3	21.67	47.44	46.26	[126]
					Ni/TiO_3	22.55	47.66	45.39	
					Co/TiO_3	20.4	48.28	44.61	
Pavlova sp.					CeO_2	21.07	37.86	41.07	
					TiO_2	20.04	39.49	40.47	
	12.96	100	60	450–550	Ce/TiO_2	21.67	37.46	40.87	[127]
					Ni/TiO_2	22.55	37.16	40.29	
					Co/TiO_2	20.41	38.85	40.74	
Schizochytrium limacinum	25.8	n/a	n/a	350–800	ZYNa	26	9	n/a	[128]
					CeO_3	23	19	58	
					Ce/Al_2O_3	25	17	58	
					NiCe/Al_2O_3	25	17	58	
					MgCe/Al_2O_3	23	16	51	
Tetraselmis sp.	12.07	100	60	500	Mg/ZnO_2	23	18	59	[118]
					Ce/ZnO_2	23	17	58	
					NiCe/ZnO_2	23	16	51	
					MgCe/ZnO_2	23	17	58	
Spirulina sp.	n/a	n/a	50	350–650	Magnetite	49.4	25.4	25.2	[112]
					Activated carbon	46.4	33.2	20.4	
S. platensis	17.6	15	60	350–500	ZSM-5	44.8	21.1	34.1	[129]
					MgO	46.2	29.5	24.3	
	18.6	10	n/a	400	Ce(II)/HZSM-5	49.7	20	30.3	[130]

3.3. Hydrothermal Liquefaction of Algal Biomass

One of the problems with algal biomass is the necessity to remove the high-water content prior to the production of biofuels. In this case, Hydrothermal Liquefaction (HTL) stands out as a promising technology for the thermochemical conversion of biomass into more useful liquid fuels [139]. Unlike pyrolysis, HTL can convert high-moisture biomass to biocrude in water medium and thus does not require preliminary drying processes [140]. HTL is performed in the presence of water under high pressure (5–25 MPa) and subcritical water temperature (280–370 °C). Under these conditions, macromolecules found within algal biomass (including lipid, protein, and carbohydrate) undergoes depolymerization reactions (fragmentation, hydrolysis, dehydration, deoxygenation, aromatization, and repolymerization) [141] for the production of several products such as bio-oil, gas, solid residue, and aqueous phase by-products [142]. HTL is considered a more robust thermochemical technology, not only for the usage of wet biomass, but also due to their high biocrude yield (24–64 wt%) [143]; some essential nutrients (N, P, Mg, and K) can be recycled for microalgal culture [144]. Additionally, up to 50% of oxygen can be removed, resulting in a biocrude with a Higher Heating Value (HHV) ranging from 30 to 40 MJ/kg [145,146]. However, the algae-derived biocrude possesses some disadvantages such as a high-water content, high viscosity, and high heteroatom content, which impede its upgrade into usable fuels [143]. Several studies underline that the biomass load/ratio, reaction temperature, residence time, pressure, catalyst (including homogenous and heterogeneous catalyst), and reaction medium influence the yield, composition, and physicochemical properties of biocrude obtained under HTL [147]. The application of catalysts on HTL reaction is an interesting opportunity to improve the process in several aspects such as the yield and quality of biocrude [148,149], inhibition of side reactions, decrease of reaction temperature, and pressure reduce its viscosity and the processing time [150]. The catalysts employed can be separated into homogeneous (water soluble) and heterogeneous (non-water soluble) [139]; Table 3 presents a list of homogeneous and heterogeneous catalysts employed on the conversion of algal biomass into biofuels.

3.3.1. Homogeneous Catalysis

Homogeneous catalysts are water-soluble at room temperature. During the reaction, the formation of char/tar is inhibited while enhancing product yield by expediting the water–gas shift reaction [150]. The most common forms include alkali salts (Na_2CO_3 and KOH), mineral and organic acids (CH_3COOH and HCOOH), and metallic cations (Zn^{2+} and Co^{3+}) [149,150]. Over the last years, several studies have been conducted to test the efficiency of different homogeneous catalyst using micro and macroalgal genera such as *Chlorella* sp. [151–154], *Cyanidioschyzon* sp. [155], *Dunaliella* sp. [156], *Enteromorpha* sp. [157], *Isochrysis* sp. [158], *Laminaria* sp. [159], *Microcystis* sp. [160], *Nannochloropsis* sp. [151,158,161], *Pavlova* sp. [158], *Porphyridium* sp. [151], *Spirulina* sp. [152,162,163], *Tetraselmis* sp. [163], *Ulva* sp. [164]; and a unknown mixture of algal species [165]. A detailed list of species and the catalyst studied can be found in Table 3.

Na_2CO_3 is the most common catalyst employed, and they can enhance the production of BTEX (benzene, toluene, ethylbenzenes, and xylenes) and C5 to C18 aliphatic hydrocarbons, which are critical elements of gasoline and diesel fuels [139]. In their work, Ref. [158] observed that Na_2CO_3 enhanced the yield of bio-crude from *Nannochloropsis* sp. at 250 °C. However, at higher temperatures (300–350 °C), other species studied such as *Pavlova* and *Isochrysis* sp. have higher bio-oil yields (50–60%). The difference between results can be explained by the difference on biomass composition, since *Pavlova* and *Isochrysis* sp. have high lipid and carbohydrate contents. These results are consistent with those reported by [151], who observed that algae with high carbohydrate content were efficiently liquefied. In other study, [163] found that Na_2CO_3 increased the bio-oil yield up to 52% (29% higher than for the uncatalyzed process) on *Spirulina platensis*, and $Ca_3(PO_4)_2$ and NiO produced a negative effect on bio-oil yield. On the other hand, [153] found that Na_2CO_3 does not improved the formation of bio-oil on a strain of *C. vulgaris*. KOH has been reported as an interesting catalyst; according to [155], in the catalytic HTL of *Cyanidioschyzon merolae*, KOH can increase the bio-oil yield in the range of 5–10% of bio-oil (from 16.9 to 22.7%) than for the non-catalytic process under similar reaction conditions. The performance of alkali catalyst is significantly affected by the temperature of the process, irrespective of the species evaluated [153,160]. For example, the formation of aliphatic and cyclics are directly affected with an increment of temperature (300 °C); however, at higher temperatures, their concentrations declined due to subsequent cracking [139]. Apart from alkaline catalysts, both organic (HCOOH and CH_3COOH) and inorganic acid (H_2SO_4) catalysts have been used [153,166]. According to Zhuang et al. [167], a concentration of 6% of H_2SO_4 increased up to 70% the bio-oil production from macroalga *Ulva prolifera* sp.; however, the bio-oil contained large quantities of O, S, and N (52.89, 3.23, and 1.43 wt% respectively) which must be eliminated before it can be used as a fuel. In another research, [166] found that 2.4% H_2SO_4 had a positive effect on the bio-crude oil production from *Dunaliella tertiolecta*; it can be highlighted that the bio-oil obtained is composed mainly of esters, carboxylic acids, and ketones. In the application of HCOOH and CH_3COOH in a reaction with *C. vulgaris* (300–350 °C for 1 h), Ross et al. [152] demonstrated that acid catalyst produced a higher bio-crude oil yield with a better flowability of oil product. Yang et al. [157] obtained a maximum yield of 28% of bio-oil using H_2SO_4 and CH_3COOH in the catalytic HTL of *Enteromorpha prolifera.* There are certain challenges that hinder the prospect of industrial application of homogeneous catalysts on HTL. Catalysts based on carbonates (hydroxides or simple carboxylic acids) have a low efficiency on the decarboxylation, isomeration, and aromatization of fatty acids [140]. Formic acid and acetic acid can induce the formation of gas fractions (30 wt% and 16–22 wt%, respectively) [152], and are consumed through the reaction stage; therefore, this type of catalyst must be removed and disposed [150].

3.3.2. Heterogeneous Catalysis

Heterogeneous catalysts, or water-insoluble catalysts, exist in the different phases with liquefaction medium; therefore, they can be recovered and recycled [147]. Another major advantage over homogeneous catalysts is their low corrosion rate and high catalytic activity under severe reaction conditions, which often damage the homogeneous catalysts [139]. Several genera such as *Chlorella* sp. [154,168–171], *Dunaliella* sp. [172,173], *Nannochloropsis* sp. [168,174–176], *Spirulina* sp. [177–179], *Ulva* sp. [180], and a mixture of microalgal species [181] have been studied using different heterogeneous catalysts of including supported metal catalysts (such as Pd, Pt, Ni, and Ru), metal oxide catalyst, and metals supported on Al_2O_3, SiO_2, and zeolites. However, the influence of metal catalysts in the biocrude yield is complex, and not all of the evaluated metals can positively improve the yield, even some of them can significantly reduce the overall performance of HTL.

According to the results obtained by Nava Bravo et al. [181], the composition of algal biomass (carbohydrates, lipids, protein, and ash content) and the catalyst play a crucial role in bio-oil yield. In this scenario, bio-oil from *C. vulgaris* was positively affected by Pt/Al_2O_3 and $CoMo/Al_2O_3$ (from 34 to 39 wt%); on the other hand, the bio-oil yield from *N. occulata* was reduced by each of the three heterogeneous catalysts. Similar results were reported by [174], who evaluated different metal catalysts on *Nannochloropsis* sp. biomass (Pd/C, Pt/C, Ru/C, $Ni/SiO_2-Al_2O_3$, $CoMo/\gamma$-Al_2O_3, and zeolite). Their results show that metal-based catalysts (especially $Ni/SiO_2–Al_2O_3$) reduce the bio-oil yield. The promotion of gas formation can explain this process by gasification reactions [182]. However, only Pd/C effectively increased the bio-oil yield (from 35 to 57 wt%). In another study, Yang et al. [173] evaluated the efficiency of REHY and Ni/REHY in *D. salina* conversion. The results showed an increase of bio-oil yield from 35% up to 52 and 72% for REHY and Ni/REHY, respectively. The Ni-based catalyst can improve the overall biomass conversion by catalyzing bond cleavages and the depolymerization process. In another study, Raney-Ni and HZSM-5 type zeolite (using ethanol as solvent) were evaluated on the catalytic efficiency over *C. pyrenoidosa* biomass [182]. The results show that the catalyst does not improve the yield of bio-oil for the different conditions considered. However, the catalyst employed enhanced the concentration of other reaction products such as light fuel-range (gasoline range) hydrocarbons. Other zeolite-based catalysts such as H-ZSM-5 and Ce/H-ZSM-5 have been reported for the conversion of *C. pyrenoidosa* biomass [171], and their results highlight the efficiency of zeolite-based catalysts, due to a raise in the yield of bio-oil from 32% to 38% and 52% for H-ZSM-5 and Ce/H-ZSM-5, respectively. Even after all the different research highlighted in the present review, there is no clarity on the underlying mechanism of heterogeneous catalysts in the liquefaction process of algal biomass. According to the literature, heterogeneous catalysts are considered superior to their counterpart; however, there are some conditions that hamper their efficiency. Xu et al. [171] found that biomass impurities such ash and excess of media nutrients can produce catalyst deactivation after a certain period in a continuous operation. It is found that found that a high concentration of S, N, and O derivatives can accelerate the deactivation of heterogeneous catalyst [183–185].

Table 3. Strains evaluated and their catalyst.

Strain	HHV Biomass (MJ/kg)	Catalyst	Temperature (°C)	Residence Time (min)	Catalyst Type	Bio-oil Yield (wt%)	HHV Bio-oil (MJ/kg)	Reference
Chlorella vulgaris	23.2	HCOOH	320	30	homogeneous catalysts	28	33.2	[151]
		Na_2CO_3				28	37.1	
	23.2	KOH	300–350	60		27.3	37.2	[152]
		CH_3COOH				22.4	35.7	
		HCOOH				20.4	34.1	
	n/a	HCOOH	275	50		19.1	34.7	[153]
		Na_2CO_3				29.39	36.03	
C. pyrenoidosa	n/a	NaOH	240–280	20–50		12.5	31.8	[154]
		Na_2CO_3				41–47.5	n/a	
		CH_3COOH				31–45		
Cyanidioschyzon merolae	18.11	NaOH	300	30		21.23	33.36	[155]
		KOH				21.78	32.89	
		H_2SO_4				22.67	33.6	
						16.98	33.76	
Dunaliella tertiolecta	n/a	Na_2CO_3	340	60		42.0	n/a	[156]
Enteromorpha prolifera	13.4		290	20		23.0	29.5	[157]
Isochrysis sp.	22.97		300	60		42.5	35.61	[158]
Laminaria saccharina	14.46	KOH	350	15		63	34.18	[159]
Microcystis viridis	n/a	Na_2CO_3	300–340	30–60		33	28–30	[160]
	24.02		350	60		48.67	33.71	[158]
Nannochloropsis sp.	17.9	HCOOH	320	30		28	39	[151]
						28	35.5	
Pavlova sp.	23.88	Na_2CO_3	250	60		24.2	38.31	[161]
	22.69		350	60		47.7	36.93	[158]
Porphyridium cruentum	14.7		320	30		27.1	22.8	[151]
Spirulina sp.	21.2	KOH	300–350	60		15.2	35.7	[152]
		Na_2CO_3				20	37.8	
		CH_3COOH				16.6	34.1	
		HCOOH				14.2	34.7	
S. platensis	20.52	$Ca_3(PO_4)_2$	350	60		34.5	35.07	[162]
		NiO				30.2	38.41	
		Na_2CO_3				51.6	36.29	
Tetraselmis sp.	n/a	Na_2CO_3	250–350	30		35	38.65	[163]
						40	35.58	

Table 3. *Cont.*

Strain	HHV Biomass (MJ/kg)	Catalyst	Temperature (°C)	Residence Time (min)	Catalyst Type	Bio-oil Yield (wt%)	HHV Bio-oil (MJ/kg)	Reference
Ulva prolifera		KOH	290	30	heterogeneous catalysts	26.7	33.6	[164]
		NaOH				25.2	29.8	
		Na_2CO_3				19	29.2	
Green macroalgal blooms	9.45	CaO	270	45		20.1	25.59	[165]
		TiO_2				14.6	23.8	
						17.3	25.37	
Chlorella sp.	n/a	CuO/Al-SBA-15	170–350	30		45.1	n/a	[168]
	17.31	Pt/C	350	30		37.9	33.2	[169]
C. pyrenoidosa	n/a	HZSM-5	250–300	60		73	n/a	[170]
		NaY				68		
		USY				66		
		HY				64		
		Ce/H-ZSM−5	300	20		49.87	26.09	[171]
		HZSM-5				34.02	21.77	
		Pd/Al_2O_3	240–280	30		27.5–48	n/a	[154]
		Pd/C				30–42.5		
		Pt/Al_2O_3				34–46		
		Pt/C				33–45		
C. vulgaris		Raney Ni	350	60		33–50	n/a	[168]
		Pt/Al_2O_3				38.9		
		Ni/Al_2O_3				30		
		$Co/Mo/Al_2O_3$				38.7		
D. tertiolecta	17.81	KtB	360	30		49.09	32.36	[172]
		ZrO_2/SO_4^{2-}				29	33.24	
		HZSM-5				31.1	33.67	
D. salina	18.47	MgO/MCM-41	200	60		36	33.17	[173]
		Ni/REHY				72	30.11	
		REHY				51.6	26.88	
N. oculata	n/a	Pt/Al_2O_3	350	60		30.2	n/a	[168]
		Ni/Al_2O_3				18.1		
		$Co/Mo/Al_2O_3$				25.5		

Table 3. *Cont.*

Strain	HHV Biomass (MJ/kg)	Catalyst	Temperature (°C)	Residence Time (min)	Catalyst Type	Bio-oil Yield (wt%)	HHV Bio-oil (MJ/kg)	Reference
Nannochloropsis sp.	18.5	Pd/C	350	60		57	38.9	[174]
		Pt/C				49	40.1	
		Ru/C				50	38.4	
		Ni/SiO_2-Al_2O_3				50	39.4	
		$CoMo/Al_2O_3$				55	38.6	
		Zeolite				48	38.5	
		Pd/C	350	60		48	n/a	[175]
		Fe/HZSM-5	365	60		38.1	n/a	[176]
Spirulina sp.	n/a	HZSM-5	380	120		30.63	28.32	[177]
		HZSM-5@MS				32.45	29.51	
		Pd/HZSM-5				34.9	29.43	
		Pd/HZSM-5@MS				35.62	29.21	
S. platensis		CeO_2	250	30		34	39.21	[178]
		Fe_3O_4	272	37		27.6	30.98	[179]
Ulva prolifera		ZSM-5	280	15		29.3	34.8	[180]
Microalgae consortium		H-ZSM−5	350	120		16.0	37.7–41.6	[181]

4. Conclusions

This paper reviews the experimental aspects of conventional and catalytic thermochemical conversion of microalgal biomass and their product distribution, yields, and quality. The thermochemical conversion of algal biomass is a promising route to obtain alternative fuels for energy generation; however, several challenges must be overcome to increase the sustainability of algal-based biofuels. Torrefaction proved to be an effective pretreatment for algal biomass prior to pyrolysis process; so far, the scientific literature on this pretreatment is still rare, and further research must be done in order to improve its efficiency. Pyrolysis is a well-established technology that shows the right concentration of bio-oil, char, and syngas. Macroalgal biomass can be more interesting for this technology due to the necessity of dried biomass. On the other hand, hydrothermal liquefaction can convert high-moisture biomass to biocrude in water medium and thus does not require preliminary drying processes, which makes HTL the most promising process an energetic point of view for the conversion of algal-based biofuels. The application of catalyst (both homogeneous and heterogeneous) has increased the overall efficiency of conversion of algal biomass in bio-oil, bio-char, and syngas. ZSM-5-based zeolites such as H-ZSM-5, Fe-ZSM-5 Cu-ZSM-5, Ni-ZSM-5, and Ga-HZSM-5 have shown exciting results in the conversion of biomass into bio-oil and bio-char. Therefore, it can be considered the most effective catalyst for the pyrolytic transformation of algal biomass. In HTL reactions, heterogeneous catalysts, specially Pd/C, Ni-based catalyst, and zeolite-based catalyst have shown more consistent data in converting the selected biomass into bio-oil; their recycling ability and low corrosion rate make them a more suitable option. However, particular challenges hinder the prospect of industrial application of catalysts, such as possible corrosion on the reaction equipment, low recycling capacity, and catalyst deactivation after a certain period in a continuous operation. Therefore, designing novel catalysts for the selective conversion of microalgae into biofuels is a mandatory step to increase the efficiency of the process.

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