Type of the Paper (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 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, HTL, gasification) have proven to be processed with higher viability, because they use all biomass. However, because of the complexity 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 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]. The production of biomass-based fuels (or biofuels) are considered as one of the prospective replacements to the conventional fossil fuels [2] for both developed and non-developed countries due to its 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 is 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, and 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 of 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 towards 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 or steam under deficient conditions to produce synthetic gas or syngas which primarily consist of hydrogen (H_2), 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) employ the entire biomass as feedstock, (ii) the process times is shorter, and (iii) their 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) is 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-non-sustainable fertilizers, and environmental concerns due to the loss 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) its harvesting can be done through the year, (iii) can employ saline and wastewater, (iv) have better growth rate than higher plants, (v) can convert 183 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 on 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. The dried biomass is then 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 like Ecopetrol (Colombia), Exxon Mobile, Shell (US), Petrobras (Brazil), Total (France).

2.1. How algae-based biofuels changed over time

Companies like Solix biofuels, Corbion (previously known as Terravia or Solazyme), Cellana, Sapphire Energy, Seambiotic, Oil Fox, Synthetic genomics, Euglena, and others attracted over 200 million dollars from private and public sectors. However, after years of research, none of the companies reach the economic balance for algal-based biofuels. 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 (Table 1). Another problem related to the strains is the stability of their growth on industrial photobioreactors and the synthesis of the target metabolites.

Table 1. Different strains studied for biodiesel production.

Strain	Lipids	Carbohydrates	Proteins	Reference
Arthrospira platensis	30.23 wt%	31.89 wt%	16.81 wt%	[17]
Auxenochlorella protothecoides	20.58 wt%	--	--	[18]
Botryococcus braunii	17.85 wt%	--	12.54 wt%	[19]
	60 wt%	20wt%	--	[20]
Chlamydomonas reinhardtii	25.25 wt%	--	--	[21]
Ch. reinhardtii CC-400	28.5 wt%	--	--	[22]
Ch. Reinhardtii CC-4349	64.25 wt%	--	--	[23]
Chlorella sp G-9	32.6 – 34.2 (mg/L/day)	--	--	[24]
C. kessleri	14.42 – 24.19% TVSS	--	--	[25]
C. protothecoides	12.94 – 19.48% TVSS			
C. pyrenoidosa	20.9 – 25.48 wt%	--	--	[26]
C. vulgaris	18.75 wt%	--	--	[27]
	32 – 38 wt%	--	--	[28]
C. vulgaris LBL3-M	10 wt%			[29]
C. vulgaris UTEX 1803	9 wt%	--	--	[30]
C. vulgaris Mutant (UV715)	41 wt%	--	--	[31]
Chlorococcum oleofaciens	34 wt%	--	--	[32]
Coccomyxa sp strain Obi (AG125)	43 wt%	1 wt%	--	[33]
Dunaliella tertiolecta	15 wt%	--	--	[34]
	23.4 wt%	--	--	[35]
Nannochloropsis gaditana	17.6 wt%	--	24.1 wt%	[36]
Phaeodactylum tricornutum	55.7 wt%	9 wt%	22 wt%	[37]
Scenedesmus almeriensis	24.6 wt%	--	--	[38]
S. dimorphus	15.15 – 24.4 wt%	--	--	[26]
S. obliquus	32.5 wt%	--	--	[39]
	24.9 wt%	--	--	[40]

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	25.2 wt%	--	--	[41]
	60 wt%	--	--	[42]
S. quadricauda	22.5 wt%	--	--	[43]
Tetraselmis suecica	26 wt%	18 wt%	15 wt%	[44]
	53.8 wt%	--	--	[45]

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 [46]. 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 [47]. 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 [47].

Once the biomass within the reactor reached the expected concentration comes the harvesting; due to their nature, microalgal cells have a small size, low specific gravity, and are highly diluted on the culture media; therefore, their concentration is labor, energy, and time-intensive step [48]. 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 [49]. Once the biomass is removed from the media, most of cell water content must be removed via spray drying, drum drying, freeze-drying, or solar drying to avoid any interference with the extraction [46]. 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 [49]. The Microalgal cell wall is made of polysaccharides and cellulose synthesized from silicic acid [50], and must be broken in order to release, both lipids and carbohydrates; in 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 [51]. Other biofuels such as biogas and biohydrogen have gained attention as sustainable alternatives for energy production using microalgal biomass.

Biogas is produced via a sequence of biochemical processes converting the organic material: hydrolysis, fermentation, acetogenesis, and methanogenesis, also known as Anaerobic Digestion (AD) [52]. In this process, the whole biomass is used for the production of methane (55–75%) and carbon dioxide (25–45%) [53]; therefore, the energy performance is higher in comparison to biodiesel and bioethanol [54]. Additionally, nutrients like organic nitrogen or phosphorus may be mineralized and subsequently recycled for algae cultivation [55]. 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 is considered clean and renewable, with higher energy production (142 MJ/Kg^{-1}) [56]. Biohydrogen can be obtained by photofermentation, dark fermentation, direct and indirect biophotolysis [57], however Hydrogen production cannot be achieved amidst effective photosynthesis as oxygen inactivates hydrogenase [58]. 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 evolution of the number of publications per year along the last 18 years period. According to the data obtained from the Scopus database (Elsevier). It is possible to observe an exponential increase in the number of

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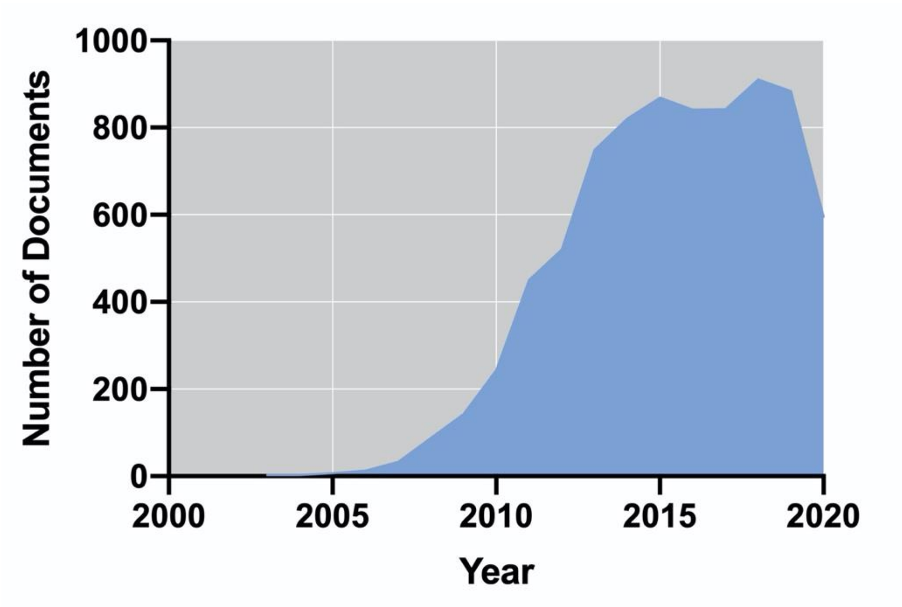
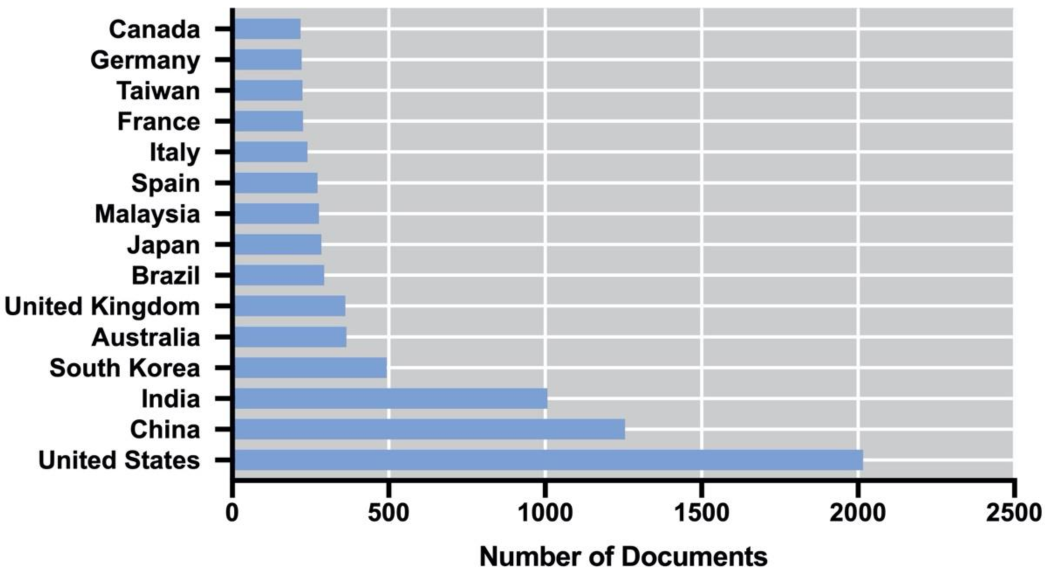
publications between 2006 to 2015. Since 2016, the number of documents has remained almost constant up to a final number of 8022 (including accepted documents for 2021), where United States, China, India, South Korea, and United Kingdom dominate the scientific publication on algal-based biofuels.



(a)



(b)

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 (figure 2) can be grouped into four classes, hydrothermal liquefaction, pyrolysis, gasification, and torrefaction [59]. In thermochemical process, the algal biomass is thermally decomposed into usable biofuels such as syngas, bio-oil and biochar (figure 2). Unlike biochemical production of biofuels, thermochemical processes does 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].

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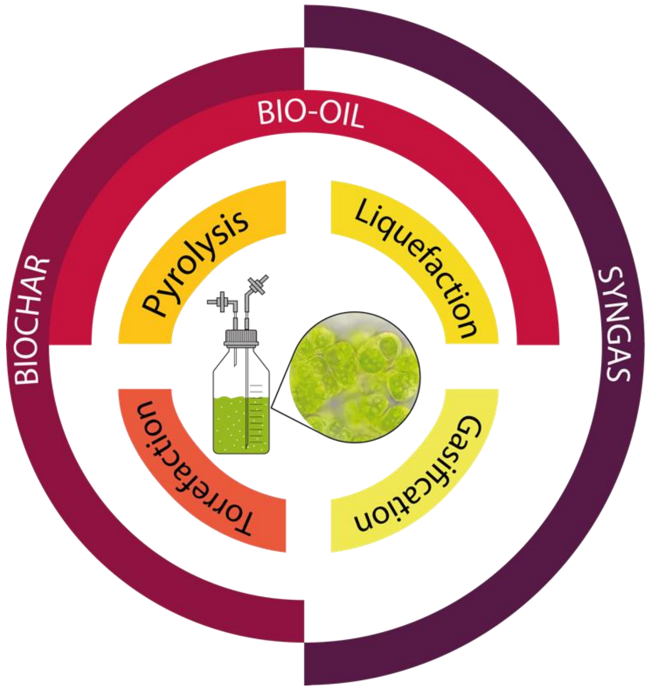

Figure 2. Different thermochemical conversion methods of microalgal biomass and their main products.

3.1. 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, pyrolysis of algal biomass has achieved reliable and promising outcomes that could lead to commercial exploitation [60]. The bio-oils obtained from the pyrolytic reaction of algal biomass, due to the lipid and protein content, had a higher heating value, higher aromatics, and lower acidity compared to lignocellulosic biomass. [61]; while bio-oils derived from wood holds solids with chemically dissolved oxygen concentrations [8]; implying that better quality algae-based bio-oil could be produced from catalytic pyrolysis.

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 a moderate temperature (550–900°C) and long retention times (> 5 min) [62]. Their main product is biochar with by-products such as bio-oil and syngas [63]. Under slow pyrolysis different particle sizes can be processed, therefore both macro and microalgae can be used without mechanical pre-treatment. Intermediate pyrolysis is carried out using the intermediate conditions between slow and fast pyrolysis [64]. 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 vapour. [65]. The main product from intermediate pyrolysis is bio-oil (40– 60%) followed by non-condensable syngas (20-30%) and biochar (15-25%) [66]. The bio-oil obtained is characterized by reduced viscosity and low tar content with small concentration of tar [67]. 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 (0.5-10s) [68], this conditions reduce secondary reactions (secondary cracking, condensation, and polymerization of intermediates) which contribute to the production of a bio-oil with enhanced qualities.

Flash pyrolysis use high temperatures (950–1250 °C), high heating rates (1.000-10.000 °C/s) and short pyrolysis time (0.5–10s). due to the fast reaction, bio-oil is the main product of the reaction (90 wt%) [69]. Finally, Microwave-Assisted Pyrolysis (MAP) is a gentle and medium speed process, with a heating rate between conventional pyrolysis and fast pyrolysis [70]. This process has gained large

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attention in the recent years because is considered as a more energy-efficient method in comparison with other pyrolysis-related systems [71] and there is no requirement of mechanical pretreatment of biomass, resulting in substantial energy savings.

From pyrolysis it can be obtained bio-oils, chars, and non-condensable gases; however, the final content and amounts will depend directly form the operation conditions and microalgae properties and reaction type [70]. Under lower temperatures chars are the major product; at moderate temperatures (400 – 550°C) with short residence times (2–3s) liquid production if favored. Finally, the gas product increases when the temperature is increased [9]. Over the last years, several studies have been conducted to increase the efficiency of pyrolysis process using microalgal genera such as *Arthrospira* sp [72], *Chaetocerous* sp [67], *Chlamydomonas* sp [4,73], *Chlorella* sp [74-79], *Desmodesmus* sp [80], *Dunaliella* sp [67], *Haematococcus* sp [67,81], *Isochrysis* sp [82,84], *Microcystis* sp [69], *Nannochloropsis* sp [85-88], *Oscillatoria* sp [89], *Pavlova* sp [90,91], *Schizochytrium sp* [92], *Tetraselmis* sp [67, 82], *Spirulina* sp [76,93,94], and *Synechococcus* [67]. A detailed list of species studied can be found on table 2.

In order to exploit the potential of pyrolysis in microalgal conversion, the process has to be improved towards a higher bio-oil yield [63] with less oxygenic compounds to prevent polymerization and condensation. Suitable catalyst could lead to in situ upgrading of generated bio-oil [74,95], Another advantage of catalytic pyrolysis is that catalysts used for pyrolysis can be recycled to the reactor [74]. The most common catalysts used for microalgae pyrolysis include Na_2CO_3, metallic based catalyst such as Ni, Mo and ceria-based catalysts (NieCe/Al_2O_3 and NieCe/ZrO_2) [90] have shown great catalytic efficiency. On the other hand, other metal catalysts including Ce, Ti, Co, Mg, and Al did not show obvious catalytic effect [70]. ZSM-5-based zeolites such as H-ZSM-5, Fe-ZSM-5 Cu-ZSM-5 and Ni-ZSM-5 are considered as the most effective catalyst for the pyrolysis of algal biomass. Other zeolites such as ITQ-2 and MCM-22 had a similar but less effective function [96].

In a study on the catalytic pyrolysis of *Nannochloropsis* sp, [85] were able to significantly reduce the oxygen content (from 30 to 19wt%) and a higher calorific value (from 24.6 to 32.5MJkg). Other studies such as [97-99] proved the hability of catalytic-mediated pyrolysis to increase the yield of bio-oil. In another study, [99] used HZSM-5 and found that an increase in catalyst-to-biomass ratio from 1:1 to 5:1 significantly improved the aromatic yields. On the other hand, [100] studied pyrolysis of cyanobacteria over Mg-Al layered double oxide/ZSM-5 composites, and the pyrolytic bio-oil contained less nitrogenated compounds. On another study, [82] 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. In another study, [75] investigated the efficiency of five different zeolite-based catalyst (H-, Fe-, Cu-, and Ni-ZSM-5) in the bio-oil production from *Chlorella* biomass, they found that HZSM-5 increased the yield of the hydrocarbon fraction in the organic phase from 21 to 43 wt%. Finally, [93] 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.

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

Strain	Catalyst	Bio-oil wt%	Bio-char wt%	Syngas wt%	Reference
Arthrospira plantensis	Ni/HMS-ZSM5	33.44	32.52	27.67	[72]
	Fe/HMS-ZSM5	38.15	30.01	58.94	
	Ce/HMS-ZSM5	36.41	31.80	28.58	
Chlamydomonas reinhardtii	hydrotalcite	54.84	37.59	7.57	[73]
Ch. debaryana	β-zeolite	23.5	--	--	[4]
	Activivated charcoal	43.8	--	--	
Chlorella sp	Na_2CO_3	41.0	54.4	34.1	[74]
	Fe-ZSM-5	43.1	29.7	27.1	[75]
	Cu-ZSM-5	46.9	27.9	24.6	
	Ni-ZSM-5	45.1	30.1	25.4	

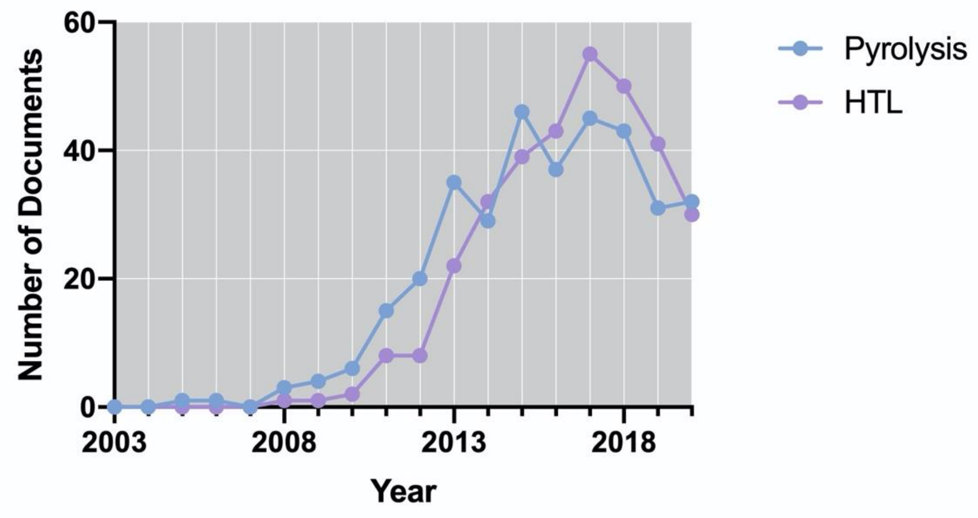
	Magnetite	53.8	27.4	22.8	[76]
	Activated carbon	49. 4	37.3	13.3	
	H^+ZSM-5	25	24	--	[77]
Chlorella vulgaris	Ni-ZSM-5	18.97	--	--	[78]
	H^+ZSM-5	52.7	25.7	21.6	[79]
Desmodesmus communis	HZSM-5	8	42	--	[80]
Haematococcus pluvialis	KCl	12	60	28	[81]
	KOH	11	65	76	
	K_2CO_3	13	64.8	22.2	
	MgO	12.5	62	25.5	
	Al_2O_3	15	61	24	
	CaO	13	63	24	
	Microalgae Residue	15	60	25	
Isochrysis sp	CeO_3	23	30	47	[82]
	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	
Nannochloropsis sp	Li-LSX-zeolite	29	35	36	[83]
		42.5	33	24.5	[84]
	HZSM-5	25	38	--	[85]
	$Ni–Ce/Al_2O_3$	23.3	30.9	--	[86]
	HZSM-5	49	40	10	[87]
N. oculata	$Co-Mo/\gamma-Al_2O_3$	26	42	--	[88]
Oscillatoria sp	TiO_2, ZnO	33.33	43.05	26.25	[89]
Pavlova sp	CeO_3	21.07	47.96	45.92	[90]
	TiO_3	20.04	48.18	45.10	
	Ce/TiO_3	21.67	47.44	46.26	
	Ni/TiO_3	22.55	47.66	45.39	
	Co/TiO_3	20.4	48.28	44.61	
	CeO_2	21.07	37.86	41.07	[91]
	TiO_2	20.04	39.49	40.47	
	Ce/TiO_2	21.67	37.46	40.87	
	Ni/TiO_2	22.55	37.16	40.29	
	Co/TiO_2	20.41	38.85	40.74	
Schizochytrium limacinum	ZYNa	26	9	--	[92]
Tetraselmis sp	CeO_3	23	19	58	[82]
	Ce/Al_2O_3	25	17	58	
	$NiCe/Al_2O_3$	25	17	58	
	$MgCe/Al_2O_3$	23	16	51	
	Mg/ZnO_2	23	18	59	
	Ce/ZnO_2	23	17	58	
	$NiCe/ZnO_2$	23	16	51	
	$MgCe/ZnO_2$	23	17	58	
Spirulina sp	Magnetite	49.4	25.4	25.2	[76]
	Activated carbon	46.4	33.2	20.4	
Spirulina platensis	ZSM-5	44.8	21.1	34.1	[93]
	MgO	46.2	29.5	24.3	
	Ce(II)/HZSM-5	49.7	20	30.3	[94]

3.2. 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 [101]. Unlike pyrolysis, HTL can convert high-moisture biomass to biocrude in water medium and thus does not require preliminary drying processes [102].

Hydrothermal liquefaction is performed in the presence of water under high pressure (5-25 MPa), subcritical water temperature (280-370°C). Under this conditions, all the macromolecules found within algal biomass (including lipid, protein, and carbohydrate) undergoes depolymerization reactions (fragmentation, hydrolysis, dehydration, deoxygenation, aromatization and repolymerization) [103] for the production of several products such as bio-oil, gas, solid residue and aqueous phase-by-products [104]. 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%) [105], some essential nutrients (N, P, Mg, and K) can be recycled for microalgal culture [106]. 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 [107,108]. However, the algae-derived biocrude possess some disadvantages such as a high-water content, high viscosity, and high heteroatom content, which impede its upgrade into usable fuels [105]. Several studies underline that biomass load/ratio, reaction temperature, residence time, pressure, catalyst (including homogenous and heterogenous catalyst), reaction medium, influence the yield, composition and physico-chemical properties of biocrude obtained under HTL [109].

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 [110,111], inhibition of side reactions, decrease of reaction temperature, pressure, reduce its viscosity, and reduction in the processing time [112]. The catalysts employed can be separated into homogeneous (water soluble) and heterogeneous (non-water soluble) [101], Table 3 presents a list of homogeneous and heterogeneous catalyst employed on the conversion of algal biomass into biofuels. Figure 3 Shows the evolution of the number of publications per year along the last 16 years 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 to 2017. Finally, where United States, China, India, South Korea, and United Kingdom dominate the scientific publication on the application of the pyrolysis and HTL.



(a)

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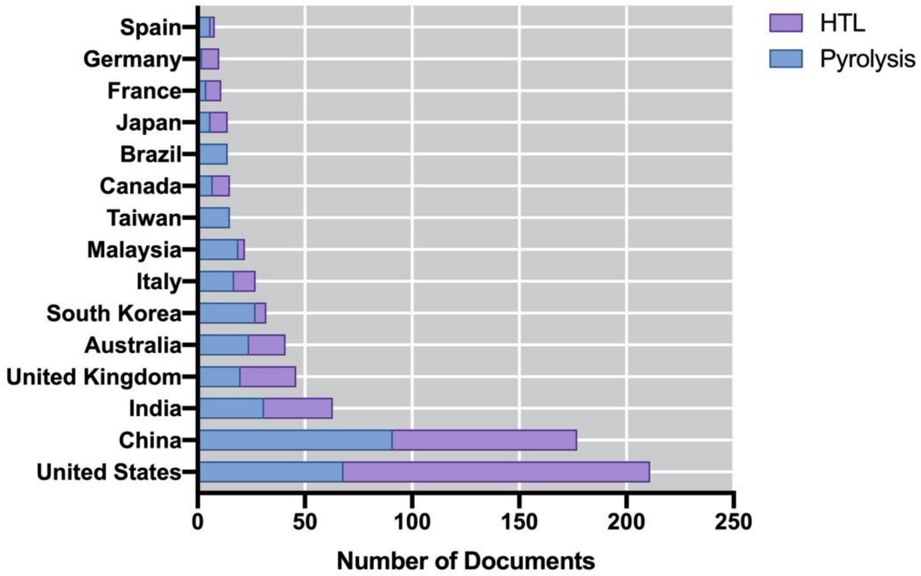

(b)

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

3.2.1. Homogeneous catalysis.

Homogeneous catalysts are water-soluble at room temperature. During its reaction the formation of char/tar is inhibited while enhancing product yield by expediting water-gas shift reaction [112].

The most common forms include alkali salts (Na_2CO_3 and KOH), mineral and organic acids (CH_3COOH and HCOOH), metallic cations (Zn^{2+} and Co^{3+}) [111,112]. Na_2CO_3 is the most common catalyst employed, and 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 [101]. In their work, [113] observed that Na_2CO_3 enhanced the yield of bio-crude from *Nannochloropsis* sp at 250 ℃. 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 explained by the difference on biomass composition, since *Pavlova* and *Isochrysis* sp has high lipid and carbohydrate contents. These results are consistent with those reported by [114], who observed that algae with high carbohydrate content was efficiently liquefied. In other study, [115] found that Na_2CO_3 increased the bio-oil yield up to 52% (29% higher than for the uncatalysed process) on *Spirulina platensis*, and $Ca_3(PO_4)_2$ and NiO produced a negative effect on bio-oil yield. On the other hand, [116] 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 [117], in the catalytic HTL of *Cyanidioschyzon merolae*, KOH can increase the bio-oil yield in 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 [116,118]. For example, the formation of aliphatics and cyclics are directly affected with an increment of temperature (300 °C); however, at higher temperatures their concentrations declined due to subsequent cracking [101].

Apart from alkaline catalysts, both organic (HCOOH and CH_3COOH) and inorganic acid (H_2SO_4) catalysts have been used [116,119]. According to [120], a concentration of 6% of H_2SO_4 increased up to 70% the bio-oil production from macroalga *Ulva prolifera* sp, with oxygenates as the dominant products in the bio-oil. In another research, [119] 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

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and CH_3COOH in a reaction with *C. vulgaris* (300-350 °C for 1 h) [120] demonstrate that acid catalyst produced a higher bio-crude oil yield with a better flowability of oil product. [121] obtained a maximum yield of 28% of bio-oil using H_2SO_4 and CH_3COOH in the catalytic HTL of *Enteromorpha* sp.

There are certain challenges that hinder the prospect of industrial application of homogeneous catalyst on HTL. Alkali and acidic catalyst negative affect the pH of the reaction, leading to corrosion on the reaction equipment [122]. Catalysts based on carbonates (hydroxides or simple carboxylic acids) have a low efficiency on the decarboxylation, isomeration and aromatization of fatty acids [102]. Formic acid and acetic acid can induce the formation of gas fractions (30wt% and 16–22wt%, respectively) [118] and are consumed through the reaction stage; therefore, this type of catalyst must be removed and disposed [112].

Table 3. Strains evaluated and their catalyst.

Strain	Catalyst	Catalyst type	Bio-oil Yield (wt%)	Reference
Chlorella sp	Na_2CO_3		28	[114]
	Formic acid		28	
	CH_3COOH		15.7	[119]
	KOH		13.6	
C. pyrenoidosa	Na_2CO_3		41.78	[123]
Cyanidioschyzon merolae	CH_3COOH		21.23	[117]
	NaOH		21.78	
	KOH		22.67	
Dunaliella tertiolecta	Na_2CO_3		42.0	[124]
	KOH		49.09	[125]
Enteromorpha prolifera	Na_2CO_3		23.0	[126]
Isochrysis sp	Na_2CO_3		50	[113]
Laminaria saccharina	KOH	homogeneous catalysts	67.0	[126]
Microcystis viridis	Na_2CO_3		33.0	[127]
Nannochloropsis sp	Na_2CO_3		40	[113]
	Formic acid		28	[114]
	Na_2CO_3		28	
	Na_2CO_3		24.2	[128]
Pavlova sp	Na_2CO_3		50	[113]
Porphyridium	Na_2CO_3		27.1	[114]
Spirulina sp	KOH		9.0	[118]
	CH_3COOH		19.5	
S. platensis	Na_2CO_3		51.6	[115]
	Na_2CO_3		35	[129]
Tetraselmis sp.	Na_2CO_3		40	
Ulva prolifera	KOH		26.7	[130]
Green macroalgal blooms	Na_2CO_3		20.1	[131]
Chlorella sp	CuO/Al-SBA-15		65.7	[132]
C. pyrenoidosa	Pt/C		37.9	[133]
	Raney nickel	heterogeneous catalysts	50	[134]
	H-ZSM–5		34.2	
	Ce/H-ZSM–5		49.87	
	Pd/C		4	[145]
	Pd/Al_2O_3		8	

	H-ZSM−5	73	[134]
	Pt/Al_2O_3	38.9	
C. vulgaris	Ni/ Al_2O_3	30.0	[135]
	Co/Mo/Al_2O_3	38.7	
D. tertiolecta	KtB	49.09	[125]
	Pt/Al_2O_3	30.2	
N. oculata	Ni/Al_2O_3	18.1	[142]
	Co/Mo/Al_2O_3	25.5	
	Pd/C	57	
	Pt/C	49	
	Ru/C	50	[143]
	Ni/SiO_2-Al_2O_3	50	
Nannochloropsis sp.	CoMo/Al_2O_3	55	
	Zeolite	48	
	Nano-Ni/SiO_2	30	[128]
	Pd/C	40	[135]
	Pd/C	38	
	Fe/HZSM-5	38.1	[136]
Spirulina sp	Pd/HZSM-5@MS catalyzed	37.3	[137]
S. platensis	CeO_2	34	[138]
	Fe_3O_4	27.6	[139]
Ulva prolifera	ZSM-5	29.3	[140]
Microalgae consortium	H-ZSM−5	16.0	[141]

3.2.1. Heterogeneous catalysis.

Heterogenous catalyst, or water-insoluble catalyst, exists in the different phases with liquefaction medium, therefore they can be recovered and recycled [109]. Another major advantage over homogeneous catalyst is their low corrosion rate and high catalytic activity under severe reaction conditions that often damage the homogeneous catalysts [101].

Several catalysts have been studied for HTL of algal biomass (table 3) including supported metal catalysts (such as Pd, Pt, Ni, 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 [142], the catalytic activity of Pt, Ni and CoMo supported in Al_2SO_3 had a positive influence on the yield in the HTL obtained from *C. vulgaris* and *Nannochloropsis occulata*. Results proved that the intrinsic characteristics of each strain (carbohydrates, lipids, protein and ash content) and the catalyst composition play a crucial role on the yield of bio-oil. 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 biocrude yield of *N. occulata* was reduced with each of the three heterogeneous catalysts. Results from strains of the same genera can be completely different. [143] evaluated the performance of several metal catalyst (Pd/C, Pt/C, Ru/C, Ni/SiO_2−Al_2O_3, CoMo/γ-Al_2O_3 (sulfided), and zeolite) for the conversion of *Nannochloropsis* sp biomass. Their results show a similar of those obtained by [142], since the yield of biocrude obtained with Ni/SiO_2-Al_2O_3, was lower than without catalyst, the reduced oil yield could be due to the promoted gas formation by gasification reactions [109]. However, Pd/C effectively increased the bio-oil yield (from 35 to 57 wt%). In another study, [122] evaluated the efficiency of REHY and Ni/REHY in the conversion of *Dunalliela salina*. Results shown an interesting increase of bio-oil yield from 35%, up to 52 and 72% for REHY and Ni/REHY respectively. The authors found that Ni/REHY catalyst favored the deoxygenation and desulfurization, since the bio-oils were composed mainly of hydrocarbons whereas the content O- and S bearing compounds was negligible; therefore Ni-based catalyst may improve the overall biomass conversion by catalyzing bond cleavages and depolymerization process. Raney-Ni and HZSM-5 type zeolite (ethanol rather than water as solvent) were evaluated on the catalytic efficiency over *Chlorella pyrenoidosa* biomass [144]. Results show that either catalysts do not improve the yield of bio-oil for the different conditions evaluated. However, the catalyst employed did improved the concentration of different reaction products such as light fuel-range (gasoline range) hydrocarbons. Other zeolite-based catalyst such as H-ZSM-5 and Ce/H-ZSM-5 has been reported for the conversion of *C. pyrenoidosa* biomass [145], their results highlight the efficiency of zeolite-based catalyst, 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 heterogenous catalyst in the liquefaction process of algal biomass. According to literature, heterogeneous catalyst is considered superior to their counterpart; however, there are some conditions that hamper their efficiency. [146] found that biomass impurities such ash and excess of media nutrients can produce catalyst deactivation after a certain period in a continuous operation. [143,147] found that high concentration of S, N and O derivatives can accelerate the deactivation of heterogeneous catalyst.

5. Conclusions

This paper critically reviews the experimental aspects of conventional and catalytic thermochemical conversion of microalgal biomass and their product distribution, yields, and quality. 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. Pyrolysis is a well-established technology that shows the right concentration of bio-oil, char and syngas, decent quality, and macroalgal biomass. It 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 and syngas; however, particular challenges hinder the prospect of industrial application of catalyst, such as possible corrosion on the reaction equipment, low recycling capacity, 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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