

Review

Effect of catalyst and temperature on the quality and productivity of HTL bio-oil from microalgae: A review



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ABSTRACT

Algae biomass has been recognized as one of the most suitable, efficient, and reliable feedstocks for bio-oil production. Among the different processes, hydrothermal liquefaction (HTL) is emerging as an effective technology for the valorization of various types of wet or dry biomass. Several factors, including temperature, retention time, and catalyst, significantly influence the overall efficiency of HTL products. The temperature $\sim 280 \pm 40$ °C is reported to be the most suitable range to achieve maximum bio-oil. Both homogeneous and heterogeneous catalysts have been used to improve bio-oil yield. For several advantages, heterogeneous catalysts are the preferred choice due to improved bio-oil generation, easy recovery, and uses. The eco-friendly approach and the reduction of heteroatoms in bio-oils make heterogeneous catalysts an ideal choice to be fortified. Alkaline catalysts have been considered most suitable to improve HTL yield. Variations in temperature and catalysts not only influence the yield of the bio-oil but also influence the characteristics of the bio-oil (e.g. high heating value, oxidative stability, gaseous emission, etc.) simultaneously. This review reveals interesting features including HTL temperature vs. yield, catalysts vs. yield, and the effect of wet and dry biomass on bio-oil properties, and finally, observations, remarks/limitations are presented for future studies.

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1. Introduction

The growing energy demand has led to extensive use and overexploitation of fossil reserves, leading to the energy crisis and simultaneous environmental pollution [1,2]. In this context, the use of biomass for the generation of biofuels has been considered a suitable alternative [3,4]. Based on biomass resources, the respective generations of biofuels have been classified as first, second, or third-generation biofuels. The first-generation biofuel is that obtained when food crops are used as feedstock. Second-generation biofuel refers to fuel derived from non-food crops and biofuels derived from microalgae are third-generation biofuels [5–9]. Due to several advantages associated with algae cultivation (Fig. 1) and its inherent potential to produce biofuel, algae have been recognized as the promising source and the most suitable alternative to non-renewable fuel sources [10,11]. High lipid content, fast growth, high photosynthetic efficiency, high yield in specific areas, an eco-friendly approach, minimal nutrient requirement and a simple cultivation process are some of the characteristics of algae that support their cultivation for purposes, including biofuel production. The cultivation of algae for the production of bio-oils has been considered a suitable alternative and renewable source of energy [12]. In addition to the production of bio-oils, the cultivation of algae has been explored with the integrated applications including bioremediation of wastewater, synthesis of pigments, CO₂ sequestration, antibiotics and other useful metabolites. Substantial work has been done to identify the inherent potential of widespread microalgal species to produce bio-oil [13]. The interpretations derived from the findings of different studies carried out to reveal the biochemical composition of the algal species and the techniques adopted significantly influenced the overall biofuel production from algal feedstock [14,15]. In hydrothermal reactions, the characteristics of the water change from polar characteristics to non-polar characteristics over the critical values of temperature and pressure under supercritical conditions. Hot water under pressure has high reactivity and reactions generally called hydrolysis reactions, i.e., catalyzed by acids, or can simply arise from hydrothermal transformations because CO₂ dissolved in water increases the accessibility of protons. The hydrolysis of microalgae biomass provides a route to obtain fuel from non-food biomass materials [16,17].

The review emphasizes the effect of HTL operating temperature and catalyst on microalgae bio-oil. The approaches implemented in HTL of microalgae biomass in the last ten years, using different catalysts, have been deliberated [18]. Also, the biochemical parameters of different microalgae strains, the current advantages, and limitations of HTL to be resolved before scaling have been highlighted. The high oil production efficiency and bio-oil production potential of different microalgae have also been discussed. In addition, the impact of different homogeneous/heterogeneous catalysts, as well as different temperatures in the relationship of bio-crude oils and value-added compounds for hydrothermal liquefaction of microalgae biomass, has been explored. The main focus of the review is to project the importance of the operating temperature and the effect of a homogeneous and heterogeneous catalyst on the yield and properties of the bio-oil reported in the data published in the last ten years (2010–2020).

2. Algal biomass

Algae are predominantly aquatic photosynthetic organisms that inhabit both marine and freshwater bodies, including oceans,

ivers, lakes, ponds distributed throughout the world in various temperate, tropical, and Antarctic environmental zones. Together with the aquatic-terrestrial forms, they are well known. Algae exhibit an enormous diversity in their forms and types [10]. Algae have been recognized as an organism with the potential to contribute to sustainable development due to its widespread applications (Fig. 1). Being photosynthetic, they release O₂ into the environment and simultaneously sequester CO₂. The inherent potential of algae to accumulate lipids and the processing of algal biomass to produce biofuel has established that algae are a potential alternative energy source to conventional fuel [19]. Several species of algae have been reported to detoxify (bioremediation) contaminated water using an ecological approach without producing toxic products [20–22]. Algae species also synthesize pigments, medicinally important and pharmacological metabolites, value-added products, including biofertilizers, bioplastics, etc. [23–28]. The widespread application of algae becomes more pronounced considering the various advantages associated with its cultivation. The photosynthetic nutrition mode allows the cultivation of algae with a minimal requirement of nutrients. Compared to other organisms, algae cultivation is a simple and convenient process. Algae can be grown in open ponds as well as in a closed photobioreactor system with minimal nutrient requirements and exhibit a rapid growth rate. However, despite possessing numerous applications and simple cultivation techniques to implement commercial/extensive cultivation of microalgae to achieve documented applications, several challenges must be addressed, including scale-up of the laboratory process, availability of improved strains, presence of toxins in the environment and competitive organisms (usually microbes). Along with the above challenges, several factors influence the algal growth process, among which temperature, light, nutrients, and CO₂ are key players.

Among the many applications, the processing of algal biomass to generate biofuels is of utmost importance because the feedstock from algae has been considered the most promising substitute energy resource. The biochemical components of the algae are the main factor that governs the efficiency of the bio-oil produced from microalgae. The high lipid content will improve the overall production of bio-oils from algal species, while the implementation of techniques such as hydrothermal liquefaction (HTL) results in the conversion of non-lipid biomolecules (proteins and carbohydrates) also into biofuel. In an investigation, naturally grown freshwater algal biomass has been transformed into a liquid, solid, and gaseous biofuel products by supercritical liquefaction. The solvents viz. acetone, ethanol, and isopropanol were used to examine the effect of catalysts and temperature. The most effective temperature, catalyst, and solvent were found to be 295 °C, ferric chloride, and acetone, respectively. This study suggested the generation of high HHV biofuels from algal biomass by supercritical liquefaction [29].

Several reports have been shown to analyze the variation in the biochemical composition of numerous algae species (Table 1). Melina et al. (2016) studied marine algae *Nannochloropsis* sp. and reported the algae to possess high PUFAs (polyunsaturated fatty acids) content and to be extremely suitable nutrition for aquaculture [30]. Also, *Tetraselmis* spp. exhibits high biomass, carotenoids, and lipid extraction among the investigated algae species. Biller and Ross (2014) implemented the technique of Py-GC-MS to analyze the biochemical compositions of microalgae and reported *Scenedesmus obliquus* to possess protein 11.1%, carbohydrate 40.7% and highest lipid content of 25.7% in a raceway with traditional media stressed condition [31]. Outdoor raceway conditions were

reported to be favorable for *Pseudochoricystis ellipsoidea* with lipid production from algae to be 45.4%, while it showed a moderate impact on the protein (27.5%) and carbohydrate (19.3%) concentration. Under photobioreactor *Chlorogloeopsis fritschii* was reported to accumulate protein 41.8%, carbohydrate 37.8%, and lipid 8.2%.

Barreiro et al. (2013) analyzed the influence of the HTL process on several algal strains to determine the proportionate distribution of biomolecules in selected algae strains and their growth environment [6]. The highest protein and lipid content was reported to accumulate in *Scenedesmus almeriensis* followed by *Nannochloropsis gaditana*, *Dunaliella tertiolecta*, *Porphyridium purpureum*, *Chlorella vulgaris*, *Tetraselmis suecica*, and *Scenedesmus obliquus*. The utilization of microalgae as a natural resource at both commercial and industrial levels has been supported due to their active alkaloid content [32,33]. The study focused on various algae species, in which *Prymnesium parvum*, *Scenedesmus dimorphus* and *Botryococcus braunii* reported the prime source of lipid content (~30–40%), while in *Spirulina maxima*, *Spirulina platensis*, *Synechococcus* spp., *Chlorella pyrenoidosa*, *Scenedesmus obliquus*, *Anabaena cylindrica*, *Chlorella vulgaris*, *Dunaliella salina*, *Tetraselmis maculata*, *Dunaliella bioculata*, *Chlamydomonas reinhardtii* and *Scenedesmus quadricauda* found high protein contents (in the range 45–70%) of total dried biomass. *Spirogyra* spp., *Porphyridium cruentum*, and *Scenedesmus dimorphus* had been listed as excellent sources of carbohydrates.

In another study, three strains of *Botryococcus braunii* (AP103, AP104, and AP105) were cultivated to analyze their biofuel production potential [34]. All three strains were cultivated under the laboratory as well as in open raceway ponds. Among the species, AP103 was reported to accumulate maximum biomass concentration under both conditions. However, an open raceway pond was found to be a superior cultivation system with biochemical composition to be protein (18%), carbohydrate (33%), and lipid (19%). Eight algal species were isolated from the Sunderbans, and their respective biochemical composition was analyzed [35]. The study revealed *Enteromorpha intestinalis* to possess the highest (7.13%) lipid to be extremely rich in carbohydrate (30.58%) content, followed by *Polysiphonia mollis* and *Catenella repens* (Table 1). In comparison, in between all species *Lola capillaries* (40.87%), *Rhizoclonium riparium* (21.09%) and *Polysiphonia mollis* (16.59%) were reported as high protein-containing species. *Ulva lactuca* (35.27%), *Catenella repens* (28.96%) rich in carbohydrates whereas *Dictyota ceylanica* and *Gelidiella acerosa* are considered to be a moderate source of nutrition. An investigation was demonstrated to assess the effect of salt enrichment along with the Zarouk medium on the growth rate of *Spirulina fusiform* is along with biochemical composition and pigments. The study reported concentration of salt could potentially alter the concentration of biomolecules synthesized in algae species, in the study in the presence of salt resulted in variation protein content from 38 to 58.2%, carbohydrate 18.5–36.4%, and similarly lipid 7.5–19.6% [36].

3. Hydrothermal liquefaction

Various methods and techniques have been used to extract bio-oil from various species of algae. Pyrolysis and HTL remain the most widely used techniques to process algal biomass to generate bio-crude oil [41]. The conventional thermochemical method (pyrolysis) requires dry biomass to produce gas and bio-crude since algal biomass has a high moisture content, so a significant amount of energy is required for the drying process if the pyrolysis technique

is adopted for the extraction of bio-crude oil from algae species [42,43]. Similar to the case of the transesterification technique, which is also among the common approaches for the conversion of algal biomass into biofuels, but the process is limited due to the involvement of a large amount of energy required to dry the wet algal biomass. The HTL process, on the other hand, converts wet algal biomass directly into bio-crude oil without any intermediate drying steps. Based on energy consumption, HTL has been believed to be a superior method compared to pyrolysis to extract bio-oil from wet algal biomass [44,45]. Hydrothermal liquefaction is a promising method for converting organic biomass to biofuel. The technique involves the thermal and hydrolytic decomposition of biomolecules (carbohydrates, proteins and lipids) found in the feedstock to produce biofuel [46]. HTL-derived biofuel can be characterized by lower oxygen content, higher stability and high heating value. The HTL process has been reported to produce liquid biofuel from biomass with a moisture content of 80% [47–49].

Along with this, when compared to pyrolysis and gasification, the HTL process is operated at a lower temperature range hence requiring less energy input [50]. Also, bio-oil obtained through the pyrolysis of algae is rich in oxygen content as compared to oil obtained through the HTL process. The oil obtained through the HTL process possesses lower oxygen content as oxygen is eliminated in the form of water and CO₂ through dehydration and decarboxylation, respectively [51,52]. Bio-oil is the primary/desirable product of the HTL process; other by-products include gases (CO₂, CH₄, and H₂), solid residue (bio-char), and water. However, bio-crude oil needs up-gradation before the same can be utilized as biofuel. Vlaskin et al., 2017 have emphasized challenges to be met to optimize bio-oil production from algal HTL [46,53,54]. Availability of suitable algae strain/species with the potential of yielding high bio-oil and high biomass is the primary factor influencing overall efficiency and productivity of any HTL process, besides feedstock optimization of temperature, reaction time, utilization of catalyst, the solvent system also confers crucial impact on HTL process (Fig. 2).

A ratio of wet biomass and water generally kept in the range 1:5–1:10 and catalysts are also added for an increase in reaction rate. The mixer was heated at high temperatures 280–370 °C in high pressure involved with 10–25 MPa [55,56]. With this high pressure during the process, water was still in the liquid state and around the critical point, which was observed at 374 °C and 22.1 MPa. In these conditions, water assumes particular properties: the ionic products increase so that water can act as an active medium for acid-base catalyzed organic reaction. At the same time, the viscosity reductions provide an improved diffusion coefficient which leads to enhanced reaction rates [57]. Different products like biofuels, water, and solid residue are separated after the completion of the process.

Emiliania huxleyi cultivated under laboratory conditions with vacuum pyrolysis in a fixed batch reactor at various temperatures in the range 100–500 °C resulted in maximum yield for pyrolytic gas (183 ml g⁻¹ dry cells) at 400 °C. *E. huxleyi* has been recognized as an excellent source to produce renewable biofuels [58]. Fast pyrolysis of microalgae *Chlorella protothecoides* and *Microcystis aeruginosa* conducted at 500 °C with a flow rate of 0.4 m³ h⁻¹ and 2–3s vapour residence times have resulted in the 18% and 24% yields from microalgae *Chlorella protothecoides* and *Microcystis aeruginosa*, respectively [59,60]. Thermal conversion under slow pyrolysis conditions was studied for microalgae *Tetraselmis chuii*, *Chlorella* spp., *Chlorella vulgaris*, *Dunaliella tertiolecta*, and *Synechococcus* [61]. The oil produced at 500 °C was subjected to matrix-assisted

laser Desorption Ionization (MALDI) to assess molecular weight. The study reported the technique of pyrolysis to produce oil from 24% to 43% and gas from 13% to 37% in different species of microalgae. Shuping et al. (2010) reported the production and characterization of bio-oils obtained from HTL of microalgae [62]. They reported the maximum yield of bio-oil 25.8% and concluded that thermochemical conversion of biomass residue into biofuel by hydrothermal liquefaction process. In another study, direct pyrolysis and catalytic pyrolysis of *Nannochloropsis* spp. were followed for bio-oil production. The study utilized different concentrations of HZSM-5 as a catalyst with nitrogen flow in the reactor to determine the effect of temperatures and catalysts on the yield of products and concluded *Nannochloropsis* spp. to be a potential renewable energy source [63]. Biller and Ross (2011) revealed the yields and properties of bio-oil of different Microalgae such as *Chlorella vulgaris*, *Porphyridium cruentum*, *Nannochloropsis oculata*, and *Spirulina* through hydrothermal liquefaction [64]. Babich et al. (2011) reported high-quality liquid biofuels from catalytic pyrolysis of microalgae [65]. They studied the occurrence of a catalyst to the pyrolytic conversion of *Chlorella* algae and found high-quality production of bio-oil with energy recovery of 40%. An investigation study was conducted to analyze the effect of various solvents on HTL of *Nannochloropsis* spp. and described the polar and non-polar solvents system to significantly influence bio-oil yield along with product composition [66]. Hydrothermal liquefaction of *Chlorella* and *Spirulina* microalgae was conducted under batch and continuous flow hydrothermal, and the batch process has been reported to result in higher productivity [67]. Significant work has been conducted to analyze the efficiency of HTL of various algae

species over a range of cultural conditions. Table 2 enlists various studies along with the yield of bio-oil obtained in the respective study under specific reaction conditions.

4. Improvement of HTL by using different catalysts

Whenever a scientific technique/process is developed, designed, or formulated to achieve a particular goal, substantial efforts are continually made to further improve technological advancement. Since algae species have been documented as a potential biofuel resource, several techniques and processes have been reported for the extraction of bio-oils from algal feedstock, among which HTL is a well-known technique. Studies have been conducted to improve the conventional HTL process for producing algae bio-oil. Among these catalysts, the assisted HTL processes stand out, since the use of the catalyst not only improves the yield of the bio-oil but at the same time increases the properties of the biofuel. The effectiveness of catalysts in HTL can be traced to the natural development of fossil fuel creation. Fossil fuels are believed to have originated as a product of the thermochemical process (heat and pressure) of the reserve of organic matter in the lithosphere. Furthermore, during the process, it is believed that the clay acted as a catalyst [71,72]. Numerous petroleum-based catalysts, such as Pt/C, Ru/C, Ni/SiO₂-Al₂O₃, Pd/C, Raney-Ni, HZSM-5, NiO, and zeolite have been reported to increase the productivity of bio-crude oil [73,74]. In an investigation, the hydrothermal liquefaction of lignocellulosic biomass was determined using metal powders of Zn, Fe and Zn + Fe as catalysts. The Fe catalyst has been determined to be the most effective catalyst for producing light bio-oil and heavy bio-oil.

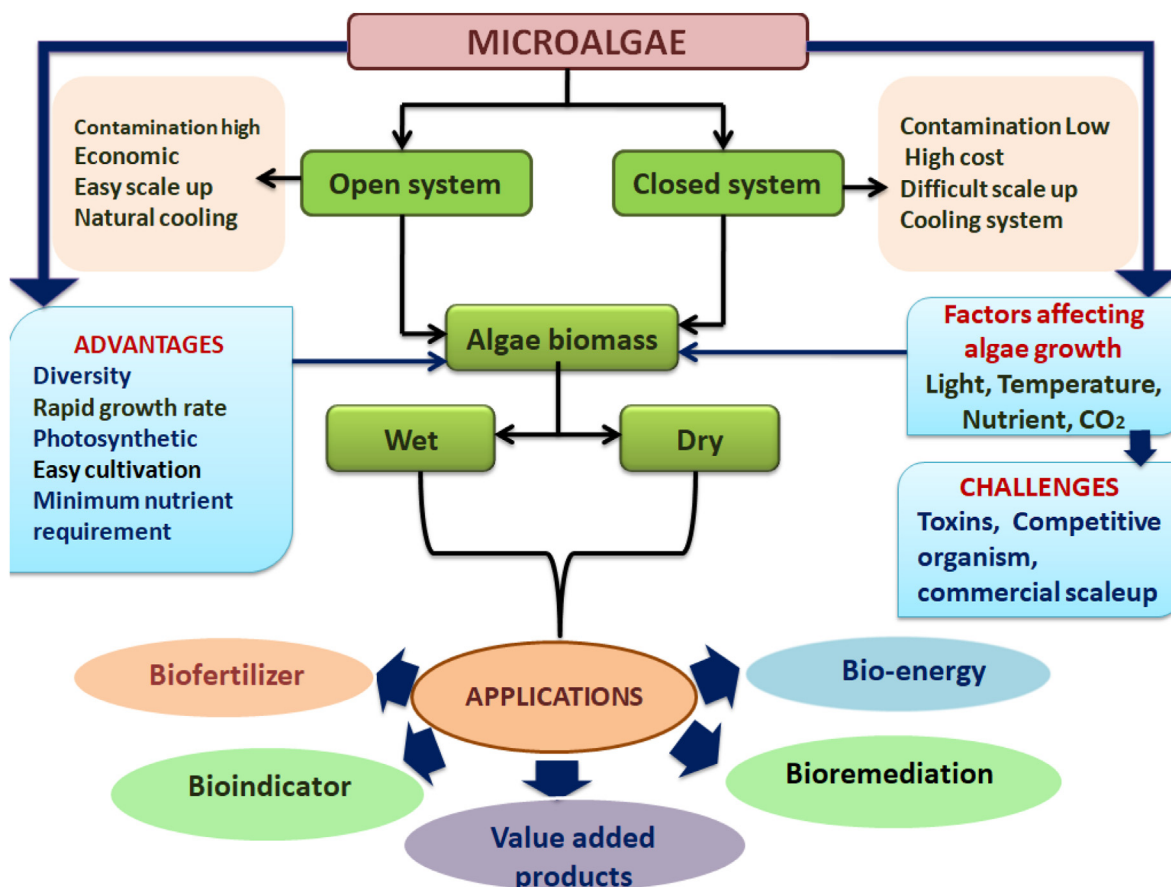


Fig. 1. Summary of the integrated system of cultivation and application of microalgae biomass.

Another Zn + Fe catalyst has been determined to be the most effective catalyst in the gas + aqueous phase. It has also been revealed that the content of the obtained liquid products effectively has the formation of monoaromatics with Fe catalyst, formation of polyaromatic and aliphatic compounds with Zn catalyst and formation of oxygen compounds with Zn + Fe catalyst system [75]. Catalytic processes are highly preferred over non-catalytic processes, as the presence of a catalyst reduces the activation energy, making the process more efficient. The catalytic process helps to remove oxygenates and crack high molecular weight compounds into lower chain molecules/compounds [76]. Generally, catalysis is complemented by a multitude of reactions including cracking, hydrocracking, C–C bond cleavage, aromatic side-chain cleavage, isomerization, polymerization, hydrogen transfer, decarboxylation, dehydration, decarbonylation, ketonization, condensation, alkylation, cyclization and/or aromatization [76].

5. Homogeneous and heterogeneous catalyst

Homogeneous as well as heterogeneous catalysts have successfully implicated the improvement of bio-oil yield obtained using HTL from algal biomass. Metal salts, alkali acids are commonly used as homogeneous catalysts, and transition metal oxides, rare metals are among the common heterogeneous catalysts used in the HTL process [77–80]. In the homogeneous catalysis, the reactant and the catalyst have been in a similar phase, in liquid or gaseous form, and are together with the reactant in the reaction medium. However, heterogeneous catalysis occurs between reactants and catalysts that are in different phases. The catalysts are generally reliable and the reagents are in liquid or gaseous form. On a comparative note, several advantages associated with heterogeneous catalysts make them a preferred choice over homogeneous catalysts. Fig. 3 summarizes the effect of homogeneous and heterogeneous catalysts. Heterogeneous catalysis (compared to homogeneous catalysis) shows easy reaction and separation products, minimizes reactor corrosion, and broader ranges of possible reaction environments, which is significant when equilibrium limits the reaction to extreme parameters. The heterogeneous catalyst not only improves the efficiency of bio-oil production but simultaneously results in the reduction of the heteroatom (oxygen, nitrogen and sulfur), which is otherwise higher in oil obtained through non-catalytic HTL [50]. Transition metal has been used explicitly as catalysts in the HTL process, as it has been reported to improve bio-oil yields and has the potential to reduce heteroatom content in crude bio-oil [81–84]. The reduction of heteroatoms in the bio-oil improves the quality of the bio-oil by increasing the HHV and also the oil becomes much more suitable for combustion. In any catalyst, process-dependent reuse of the catalyst for multiple batches or cycles is crucial as the process becomes economically favorable by reusing the catalyst. Another significant advantage of the heterogeneous catalyst includes its easy and convenient reuse, which is lacking in the case of homogeneous catalysts. Table 3 lists several studies performed to identify the impact of catalysts on the yield and quality of the bio-oil produced.

A study has been conducted to evaluate the catalytic efficiency of five transition metal catalysts, viz., Ni/TiO₂, Fe/TiO₂, Mo/TiO₂, Mn/TiO₂, and Co/TiO₂. Among the different catalysts, Ni/TiO₂ exhibited the maximum catalytic efficiency with a maximum yield of 48.23%. HTL of *Nannochloropsis* sp. has been carried out at 350 °C with a reaction time of 20 min; the obtained bio-crude (insoluble in water) was subsequently subjected to hydrothermal up-gradation at 450 °C for a reaction time of 60 min. The study analyzed several experimental conditions to optimize the up-gradation process, including the use of catalyst: Ni–Ru/CeO₂ or Ni/CeO₂

with or without H₂. The maximum yield has been achieved when the up-gradation was carried out in the presence of Ni–Ru/CeO₂ + H₂, which supposedly represented the synergistic effect of the catalyst and hydrogen, which improved the overall yield percentage by inhibiting gas formation [85].

Shakya et al. (2015) in their study analyzed the impact of temperature variation (250 °C, 300 °C and 350 °C) and the presence or absence of a catalyst (Na₂CO₃) in HTL of three species of algae; two carbohydrate-rich *Pavlova* sp. and *Isochrysis* sp., and one protein-rich *Nannochloropsis* sp [77]. The study reported on the use of catalysts to enhance bio-oil production at high temperatures (300 °C and 350 °C) in the carbohydrate-rich species *Pavlova* sp. and *Isochrysis* sp.; however, in the protein-rich *Nannochloropsis* sp., the presence of catalyst resulted in a high yield of bio-oil at a lower temperature (250 °C).

The catalytic HTL of the macroalgae *Enteromorpha prolifera* has been reported an increase to produce bio-oil from 20.4% to 23.4% with 5% sodium bicarbonate acting as a catalyst. The study reported that sodium bicarbonate (alkali carbonates) promotes liquefaction and increases bio-oil yield because alkaline carbonates effectively react with water to form the respective bases and bicarbonates that increase bio-oil yield [86].

In another comparative study, the analysis of six different heterogeneous catalysts on HTL of *Nannochloropsis* sp. has been examined and an increase in bio-oil from 35% to 57% was reported when palladium/carbon (5% palladium) acted as a catalyst [81]. Yan et al., 2019 studied the effect of KOH, NaOH, and Na₂CO₃ as a catalyst to produce bio-oil through HTL and reported an increase in bio-oil from 12.7% to 26.7% with KOH used as a catalyst [87]. Similarly, the catalytic HTL of *Nannochloropsis* sp. was carried out with Ni/C, ZSM-5, Ni/ZSM-5, Ru/C, and Pt/C catalyst, it was found that Ni/C resulted in the production of a maximum bio-oil yield (61% by weight) at 350 °C and the noble metal catalysts (Ru/C and Pt/C) offered the improved bio-oils in terms of nitrogen values, acidity and heating value of the bio-oil [88]. Most of the available literature on HTL of algae involves cultivating microalgal species and subjecting the harvested algal biomass to HTL. However, harmful algal biomass has also been used as feedstock, and HTL was carried out at 270 °C with a retention time of 45 min and the process was carried out with and without the use of catalyst [89]. The bio-oil yield of 14.6% was reported in the absence of catalysts, which increased to 20.1%, 18.74%, and 17.37% when Na₂CO₃, TiO₂, and CaO were used as catalysts, respectively. The study not only supports the use of catalysts in the HTL process but at the same time reported that harmful algal blooms serve as suitable feedstock for the production of bio-oils. Recently, the study reported that the catalyst-mediated HTL process results in the bio-oil having a high HHV compared to the HHV of the oil obtained by the non-catalytic process [90]. The study subjected *Sargassum tenerrimum* macroalgae as feedstock to the HTL process with a solid CaO catalyst (supported on CeO₂, ZrO₂ and Al₂O₃). Water, ethanol and the water-ethanol co-solvent system were used, and the highest yield of 33.0% by weight (with the highest conversion rate of 70.5%) was obtained when CaO/ZrO₂ acted as a catalyst and water-ethanol served as the solvent. The study emphasized that, along with the profound effect of the catalyst on the productivity of HTL studies, the solvent system also influences the HTL process. The comparative analysis of the impact of three different solvents: water, methanol and ethanol on HTL of *Sargassum tenerrimum* revealed the achievement of a maximum yield of bio-oil 16.33% by weight when water was used as a solvent. However, the yield increased to 22.8% by weight and 23.8% by weight when methanol and ethanol served as solvents, respectively [91]. The presence of a catalyst in the hydrothermal liquefaction process influences the decomposition behavior (disintegration of bio-molecular compositions in bio-oils, gaseous

Table 1
Percentage distribution/composition of biomolecules of algal species.

S. No.	Algae strains	Type	Culture condition	Protein	Carbohydrate	Lipids	References
1	<i>Anabaena cylindrica</i>	microalgae	Open pond and Raceway pond	43–56	25–30	4–7	[32]
2	<i>Scenedesmus quadricauda</i>	microalgae	Open Raceway	47	–	1.9	[32]
3	<i>Spirogyra</i> spp.	microalgae	–	6–20	33–64	11–21	[32]
4	<i>Scenedesmus dimorphus</i>	microalgae	Flask	56	25	13	[32]
5	<i>Spirulina maxima</i>	microalgae	Open pond	60–71	13–16	6–7	[32]
6	<i>Spirulina platensis</i>	microalgae	Open Ponds	42–63	8–14	4–11	[32]
7	<i>Porphyridium cruentum</i>	microalgae	Flask	28–39	40–57	9–14	[32]
8	<i>Tetraselmi smaculate</i>	microalgae	Open raceway	52	15	3	[32]
9	<i>Scenedesmus obliquus</i>	microalgae	Raceway	50–56	10–17	12–14	[32]
10	<i>Prymnesium parvum</i>	microalgae	Open Raceway	28–45	25–33	22–39	[32]
11	<i>Bracteacoccus grandis</i>	microalgae	Open Raceway	40	2	33	[32]
12	<i>Dunaliella bioculata</i>	microalgae	Flask	49	4	8	[32]
13	<i>Dunaliella salina</i>	microalgae	Open Ponds	57	32	6	[32]
14	<i>Chlamydomonas reinhardtii</i>	microalgae	–	48	17	21	[32]
15	<i>Synechococcus</i> spp.	microalgae	–	63	15	11	[32]
16	<i>Chlorella vulgaris</i>	microalgae	Open Ponds and PBR	41–58	12–17	10–12	[32]
17	<i>Porphyridium cruentum</i>	microalgae	PBR	28–39	40–57	9–14	[32]
18	<i>Chlorella pyrenoidosa</i>	microalgae	–	57	26	2	[32]
19	<i>Botryococcus braunii</i> AP103	microalgae	Raceway	18	33	19	[34]
20	<i>Chlorella vulgaris</i> LEB-104	microalgae	BioFlo reactor	40.95	16.74	9.95	[37]
21	<i>Botryococcus braunii</i> SAG-30.81	microalgae	BioFlo reactor	39.61	2.38	33	[37]
22	<i>Chlorella emersonii</i>	microalgae	–	9.03	37.9	29.3	[38]
23	<i>Chlorella vulgaris</i>	microalgae	–	10.4	12.7	58	[38]
24	<i>Chlorella zofingiensis</i>	microalgae	–	11.2	11.5	56.7	[38]
25	<i>Chlorogloeopsis fritschii</i>	microalgae	PBR	41.8	37.8	8.2	[38]
26	<i>Chlorella</i> FC2 IITG	microalgae	–	10.4	24.5	37.3	[38]
27	<i>Dunaliella tertiolecta</i>	microalgae	PBR	50.8	–	23.4	[6]
28	<i>Phaeodactylum tricorputum</i>	microalgae	PBR	38	16	22	[6]
29	<i>Chlorella vulgaris</i>	microalgae	PBR	41.2	–	20.4	[6]
30	<i>Chlorella vulgaris</i>	microalgae	–	36.56	42.13	28.68	[39]
31	<i>Gelidiella acerosa</i>	macroalgae	–	9.18	14.34	3.83	[35]
32	<i>Lola capillaris</i>	macroalgae	–	40.87	22.32	4.05	[35]
33	<i>Enteromorpha intestinalis</i>	macroalgae	–	6.15	30.58	7.13	[35]
34	<i>Ulva lactuca</i>	macroalgae	–	8.44	35.27	4.36	[35]
35	<i>Rhizoclonium riparium</i>	macroalgae	–	21.09	15.34	3.37	[35]
36	<i>Polysiphonia mollis</i>	macroalgae	–	16.59	25.81	5.79	[35]
37	<i>Catenella repens</i>	macroalgae	–	8.42	28.96	5.29	[35]
38	<i>Dictyota ceylanica</i>	macroalgae	–	3.33	18.52	2.61	[35]
39	<i>Dunaliella tertiolecta</i>	microalgae	–	34	21	23	[40]
40	<i>Dunaliella tertiolecta</i> SAG-13.86	microalgae	BioFlo reactor	29.41	13.95	11.44	[37]
41	<i>Spirulina platensis</i> LEB-52	microalgae	BioFlo reactor	42.33	11	11	[37]
42	<i>Nannochloropsis gaditana</i>	microalgae	PBR	43.9	–	25.1	[6]
43	<i>Porphyridium purpureum</i>	microalgae	PBR	45.6	–	12.1	[6]
44	<i>Scenedesmus almeriensis</i>	microalgae	PBR	51.7	–	21.8	[6]
45	<i>Scenedesmus obliquus</i>	microalgae	PBR	28	–	16.8	[6]
46	<i>Pseudochoricystis ellipsoidea</i>	microalgae	Flask	27.5	19.3	45.4	[38]
47	<i>Scenedesmus obliquus</i>	microalgae	Raceway	11.1	40.7	25.7	[38]
48	<i>Spirulina fusiformis</i>	microalgae	Flask	38–58.2	18.5–36.4	7.5–19.6	[36]
49	<i>Tetraselmi suecica</i>	microalgae	Flask	44	21	20	[30]
50	<i>Nannochloropsis</i> spp.	microalgae	Flask	52	27	14	[30]

products i.e., CO₂, CH₄ and H₂, and solid waste i.e., bio-char) of the microalgae biomass and the composition and quantity of the HTL products. It also affects the distribution and chemical contents of HTL products.

6. Effect of temperature variation on HTL of algal biomass

Hydrothermal liquefaction represents the transformation of carbonaceous biomass into bio-oils in a hot pressurized aqueous environment. In this, the bio-molecular composition of the biomass disintegrates into various organic components due to complex reaction mechanisms. The hydrothermal liquefaction mechanism follows the reaction path that mainly comprises 3 steps; (1) decomposition, (2) recombination, and (3) depolymerization. In this, the biomass constituents decompose into small compounds and due to their highly reactive nature, polymerize and essentially form bio-crudes, gaseous compounds, and solid compounds. In the HTL process, the biomass supplemented with water under high

pressure disintegrates into the small molecules fragment and forms three-phase i.e. predominantly CO₂ and small amount of CH₄, CO, and H₂, a solid residue (i.e. char), and a water phase having a high organic carbon content. As biomass materials composed of complex mixtures of carbohydrates, lipids and proteins, the mechanism and reaction chemistry for the liquefaction of biomass is consequently also a complex system. Critical process parameters such as temperature, residence time, re-polymerization process, condensation, and component breakdown have key influences on reaction mechanisms and product compositions [105,106].

In addition to the presence or absence of a catalyst, the temperature is another crucial factor influencing the process and the productivity of the HTL process. Temperature is the most important parameter: an increase in temperature leads to an increase in bio-oil yields up to a limit value for which the contrasting performance arises due to the incidence of cracking reactions of the bio-oil to form light gas species and re-polymerization reactions to form bio-chars. The influence of temperature and biomass composition on

the yield and quality of the bio-oil has been investigated [107,108].

It is considered that the temperature in the range of 240–370 °C (Fig. 4) is the most suitable for producing bio-oils from algal biomass with a marginal variation in the minimum and maximum value of the temperature range depending on the characteristics of the feedstock. Fig. 4 shows the findings of several studies carried out to analyze the impact of temperature on the yield of bio-oil; the interpretation of the results reported in most studies indicates that the temperature of 240–370 °C is the optimal range to achieve the maximum bio-oil yield. The HTL of *Spirulina platensis* has been performed at three different temperatures: 280 °C, 320 °C, and 350 °C, with different reaction times (15, 30 and 45 min) at each temperature that resulted in the highest ($44.8 \pm 1.9\%$) and the lowest average yield ($29.6 \pm 1.6\%$) was reached at 280 °C and 350 °C, respectively. A higher bio-crude oils yield was achieved at 280 °C compared to the yield obtained at 300 °C and 350 °C in all the reaction times analyzed (15, 30 and 45 min). In addition, the study reported a marginal difference in mass yield when the process was carried out at 320 °C and 350 °C. It was explained that the observation was the resultant of the thermal conversion of bio-crude into gaseous molecules at high temperatures, which indicates that polymerization is not a favorable reaction at high temperatures [109]. Comparative HTL of *Nannochloropsis gaditana* and *Chlorella* sp. carried out at a temperature of 180–330 °C (with a reaction time of 30 min) resulted in a maximum yield of bio-crude of 47.5% of *N. gaditana* and 32.5% of *Chlorella* sp. at 300 °C [110]. It is not only the yield of the bio-oil, which is influenced by the variation in temperature at which liquefaction occurs; Temperature also simultaneously affects the characteristics of the oil. High heating value (HHV) is a desirable characteristic for any fuel product. Villaver et al. (2018) reported that a maximum HHV of 36.99 MJ/kg has been reported at the highest temperature (300 °C) used in the

study and at the longest reaction time (45 min) [109]. HTL of biomass-derived from culturing *S. obliquus* in municipal wastewater in a photobioreactor resulted in a maximum bio-oil yield of 24.57% [111]. In another study, HHV was reported to rise to a temperature cutoff of 330 °C (20 min reaction time) after a decrease in HHV when the temperature was further increased [110]. Patrick (2013) subjected *Chlorella* OZ to HTL at variable temperatures of 200, 225, 250, 275, 300 and 350 °C (with a reaction time of 15 min) and reported a yield of 3.5, 5.3% at low temperatures 200 and 225 °C, respectively [112]. When the process temperature was increased to 250 °C, the yields increased to 20.8%, further increasing the temperature to 350 °C, a much higher yield of 41.5% was achieved. The results obtained were explained by citing the fact that only lipids are extracted at low temperatures, while at higher temperatures together with lipids, non-lipid biomolecules (proteins, carbohydrates) are simultaneously liquefied resulting in a general increase in the content of bio-oils. Table 4 summarizes several studies that were carried out to study the effect of temperatures on the yield of bio-oils from algal biomass as feedstock.

7. Challenges associated with HTL and recommendations

There are some challenges associated with HTL that must be addressed for a successful scale-up of the method. Microalgae HTL bio-oil sometimes contains heteroatoms such as N, O, and S. Therefore, optimization of temperature and catalyst is necessary to decrease heteroatom production. Before installing an HTL pilot plant, a thorough analysis of the complexities of critical parameters such as temperature, pressure, HTL residence time, and the wet biomass conversion efficiency of a given feedstock is essential. Examine possible pathways for optimized conversion through HTL (both wet and dry biomass feedstock and their mixtures). Explore

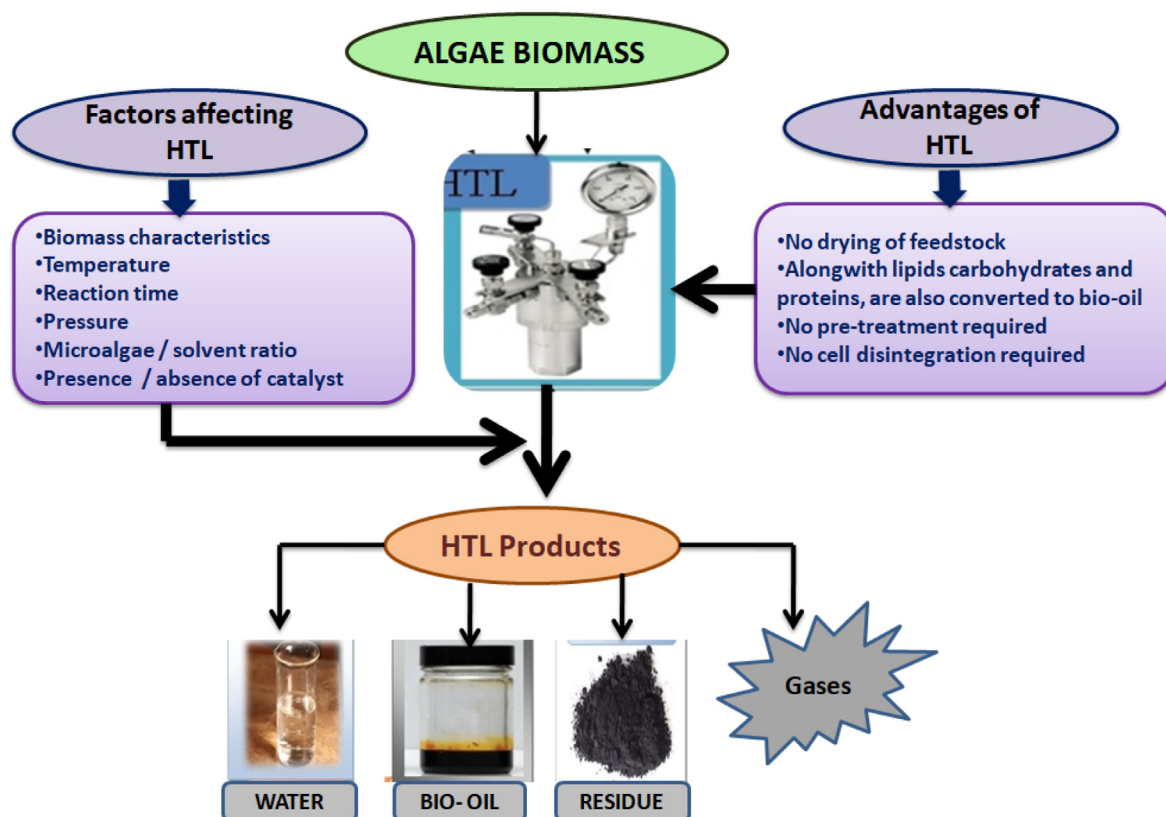


Fig. 2. Summary of different aspects of the HTL process of algae feedstock.

Table 2
Summary of hydrothermal liquefaction of wet and dry algal biomass.

Substrate	HTL process	Bio-oil yields (%)	Properties/Compositions	References
<i>Dunaliella</i> sp.	360 °C, 50 min, 5% Na ₂ CO ₃	25.8	HHV: 30.7 MJ/kg	[62]
<i>Tertiolecta</i> sp.			C: 63.55%, H: 7.66%, N: 3.71%, O: 25.08%	
<i>Chlorella</i> sp.	350 °C, 20 MPa,	5–25	HHV: 22.8–36.9 MJ/kg	[64]
<i>Nannochloropsis</i> sp.	1 h, 1M Na ₂ CO ₃ ,		C: 66–83%, H: 5–11%, N: 0–11.9%, O: 8–27%, and S: 0–1%	
<i>Porphyridium</i> sp.	1 M formic acid, or distilled water			
<i>Spirulina</i> sp.				
<i>Botryococcus braunii</i>	Dichloromethane	58	HHV: 48 MJ/kg	[68]
<i>Chaetomorpha linum</i>	350 °C	9.7	HHV: 32.5 MJ/kg	[69]
<i>Chlorella</i> sp.	350 °C, 3 min residence time and 200 bar	41.7	HHV: 33.8 MJ/kg	[67]
<i>Spirulina</i> sp.	300 °C, 3 min residence time and 200 bar	18	HHV: 32.0 MJ/kg	[67]
<i>Cladophora coelothrix</i>	350 °C	13.5	HHV: 33.3 MJ/kg	[69]
<i>Cladophora vagabunda</i>	350 °C	19.7	HHV: 33.5 MJ/kg	
<i>Derbesia tenuissima</i>	350 °C	19.7	HHV: 33.2 MJ/kg	
<i>Dunaliella tertiolecta</i>	—	37	HHV: 36 MJ/kg	[68]
<i>Spirulina platensis</i>	—	38	HHV: 34 MJ/kg	[68]
			C: 30.2%; P: 48.4%; F: 13.3%	
<i>Nannochloropsis salina</i>	310 °C for 30 min	46	HHV: 38.1 MJ/kg	[70]
<i>Nannochloropsis</i> sp.	350 °C for 60 min,		—	[66]
	Hexane	32		
	Chloroform	35		
	Dichloromethane	30		
	Methoxycyclopentane	32		
	Hexadecane	38		
	Decane	39		
	Cyclohexane	34		
<i>Oedogonium</i> sp.	350 °C	26.2	HHV: 33.7 MJ/kg	[69]
<i>Scenedesmus</i> sp.	Dichloromethane	34	HHV: 36 MJ/kg	[68]
<i>Spirulina platensis</i>	310 °C for 30 min	38	HHV: 35.2 MJ/kg	[70]
<i>Ulvaohnoi</i> sp.	350 °C	18.7	HHV: 33.8 MJ/kg	[69]

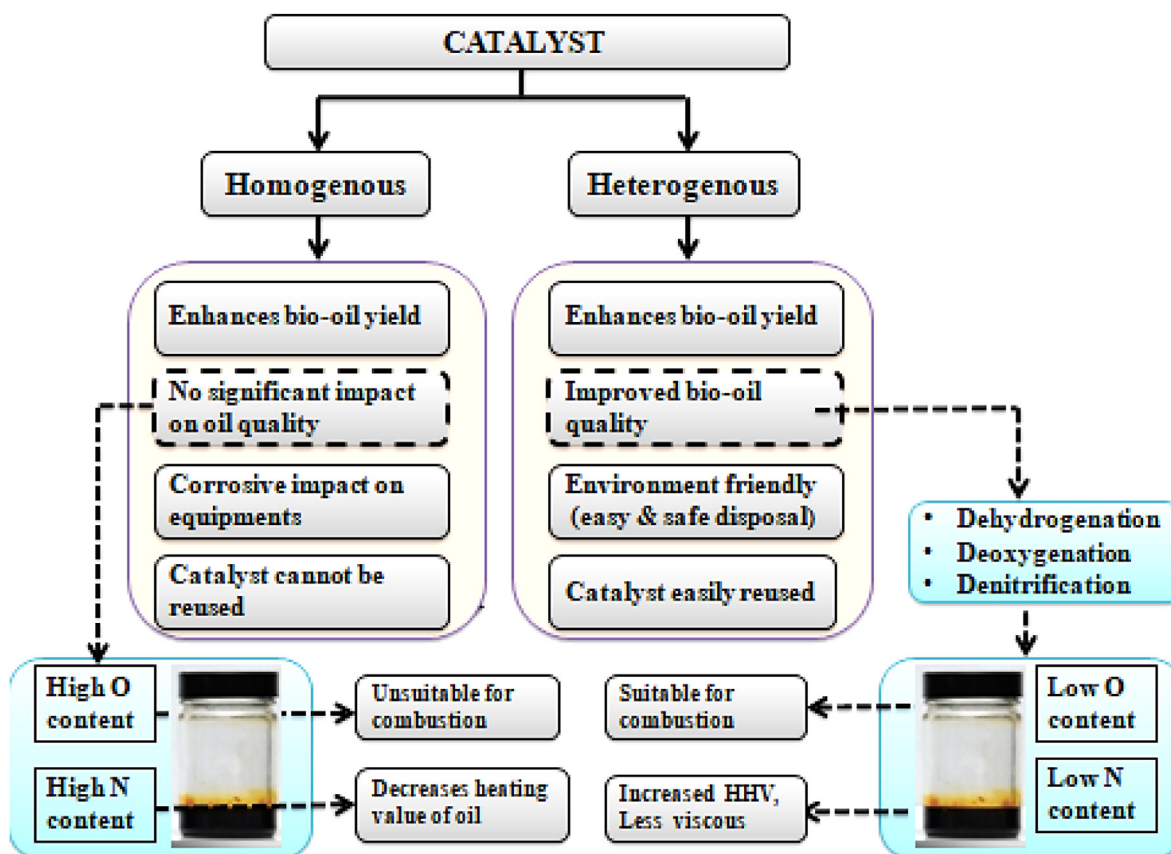


Fig. 3. Summary of the impact of the homogeneous and heterogeneous catalyst on the bio-oil obtained by the HTL process.

Table 3
Effect of homogeneous and heterogeneous catalysts on bio-crude oil.

Algae Species	Homogeneous catalysts	Heterogeneous catalysts	Bio crude yield (wt %)	Reference
<i>Nannochloropsis</i>	—	Ni/TiO ₂	48.23	[50]
<i>Spirulina</i>	Montmorillonite		39.67	[92]
	Kaolin		39.71	
	Dolomitic limestone		40.19	
<i>Nannochloropsis</i> , <i>Chlorella</i>	—	Pt/Al, CoMo/Al, Ni/Al, H ₂ O	18–40	[84]
<i>Nannochloropsis</i>	—	Co/Mo	34.3	[84]
		Ni/Al	25.5	
		Pt/Al	18.1	
<i>Chlorella</i>	—	H ₂ O	30.2	
		Co/Mo	35.8	
		Ni/Al	38.7	
		Pt/Al	30.0	
<i>Chlorella vulgaris</i>	Na	—	38.9	
	NaOH		32.9–48.2	[93]
	KOH		27.1–46.8	
	H ₂ SO ₄		26.2–46	
<i>Rhizoclonium hieroglyphicum</i>		—	26–47.2	
			29–47.7	
			26.1–44.9	
			28.5–45.7	
Co-culture of algae (<i>Microspora</i> spp., <i>Navicula</i> spp., <i>Lyngbya</i> spp., <i>Cladophora</i> spp., <i>Spirogyra</i> spp., and <i>Rhizoclonium</i> spp.)		—	29–46.7	
			30.1–47	
			30–46.3	
			28–45.2	
			28.1–47.1	
<i>Spirulina</i>	KOH	—	20	[94]
<i>Chlorella</i>	Na ₂ CO ₃		15.2	
	CH ₃ COOH		14.2	
	HCOOH		16.6	
		—	27.3	
			22.4	
			19.1	
			20.4	
<i>Chlorella vulgaris</i>	NaOH or KOH	—	85	[95]
	LiOH		85	
			55	
<i>Dunaliella tertiolecta</i>	Na ₂ CO ₃	—	25.8	[62]
<i>Enteromorpha prolifera</i>	Na ₂ CO ₃	—	25	[86]
<i>Nannochloropsis</i> spp.	—	Pd/C, Pt,C, Ru/C, Ni/SiO ₂ –Al ₂ O ₃ , CoMo/ Al ₂ O ₃ , Zeolite	35–57	[81]
<i>Nannochloropsis oculata</i>	—	CaO/Al ₂ O ₃	97.5	[96]
<i>Microcystis viridis</i>	Na ₂ CO ₃	—	25–34	[97]
<i>Spirulina platensis</i>	Na ₂ CO ₃ , Ca ₃ (PO ₄) ₂ , NiO	—	30–52	[98]
<i>Dinoflagellate</i>	KOH, NaOH or KOCH ₃	—	44.98	[99]
<i>Scenedesmus</i> sp. and <i>Nannochloropsis</i> sp.			96.6	
			91.6	
<i>C. sorokiniana</i>	KOH, H ₂ SO ₄ and Amberlyst-15	—		[100]
		Zirconia, Titania	90.20	[101]
		NiO, MoO ₃ /alumina	–	[102]
		Pt-SAPO-11	83	
		NiO, MoO ₃ /HZSM-5	–	
		Microporous titania	94.70	
		(HY-340) niobium oxide	94.27	
		Hierarchical h-Beta zeolites	–	
		Amberlyst-15	–	[100]
<i>Spirulina platensis</i>	CeO ₂		26	[103]
<i>Botryococcus braunii</i>	Na ₂ CO ₃ h-zeolite	Ni–Mo, Co–Mo	78	[104]
<i>Chlorella protothecoides</i>	HCl, NaOH in MeOH	—	80	
<i>Dunaliella tertiolecta</i>	Na ₂ CO ₃	—	42	
<i>Nannochloropsis</i>	H-ZSM5	—	55	
<i>Spirulina</i>	Fe(CO) ₅ –S	—	78	
<i>Ulva prolifera</i>	KOH		26.7%	[87]
	NaOH		25.2%	
	Na ₂ CO ₃		22.8%	

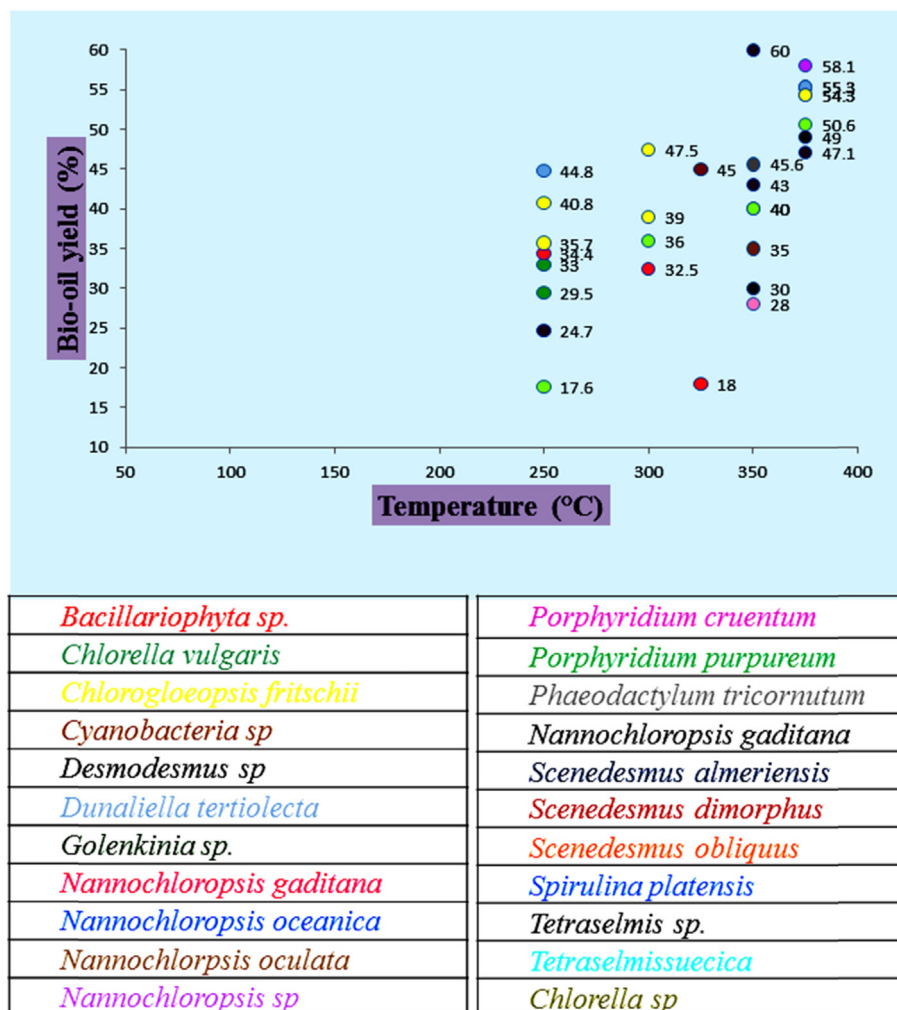


Fig. 4. Variation of the percentage of oil production with temperature.

the relationships between bio-crude oil yields, value-added chemical species and study the effects of the catalyst on the production of specific chemical compounds for each individual. Investigate the reaction pathways of the HTL process of the model compounds, as well as the total biomass. The development of theoretical models, especially computational, based on fluid dynamics is necessary to analyze the complex inherent properties, such as the thermodynamic properties of the bio-crude, the effects of viscosity, etc., to optimize the processing parameters.

Another, catalyst deactivation has been observed and attributed to fouling phenomena due to phenolic oligomers. However, simple aromatic compounds (such as guaiacol and phenol) and inorganic compounds have been reported not to be the reason for catalyst deactivation. The degree of deactivation can be assessed by aqueous-phase reforming of glycolic acid as an ideal reaction test. Furthermore, phenolic oligomers have been reported to deactivate catalysts, an important requirement for liquid-liquid extraction with an organic solvent in pretreatment. Also, it has been described that the temperature that influences the formation of high molecular weight compounds is responsible for the deactivation of the catalysts [119]. In addition to process parameters, the biomolecular compositions of the microalgae biomass (i.e. carbohydrates, proteins, and lipids) also influence the performance and quality of HTL products. The transformation of proteins and lipids in the HTL process has been reported to be more efficient than

carbohydrates. The transformation of the model lipid has shown the highest product yield followed by proteins and carbohydrates. Furthermore, strain-specific parameters, such as cell structure, biochemical composition, and growth environment, have also been evaluated on the performance and characteristics of the product [120]. Therefore, the influence of different types of algal species, different biochemical compositions can be important parameters to evaluate hydrothermal liquefaction. Therefore, this work recommendation deepens the different critical perspectives in the case of hydrothermal liquefaction of microalgae biomass to optimize and improve in consideration of the specific parameters of the strain, cell composition, suitable homogeneous/heterogeneous catalysts, temperatures, reduction of the catalyst deactivation, environmental factors to commercialize algal bio-refineries.

8. Conclusion

Owing to the inherent potential to produce biofuel along with the simplified cultivation process, microalgae have been established the algal biomass as a cost-effective, eco-friendly, and efficient feedstock to be processed as an alternative source of energy. Based on the interpretations made and inferences drawn from the results of various investigations carried out to optimize the cultivation and processing of algae biomass, techniques to produce bio-oil through HTL have been strongly supported. The HTL technique

Table 4

Effect of temperature on element composition of bio-crude oil.

Algae species	Temperature (°C)	Yield	C	H	O	N	S	Reference
<i>Bacillariophyta</i> sp.	325	18	73.4	9.5	10.4	5.3	1.3	[113]
<i>Chlorella vulgaris</i>	250	33.0	70.6	9.2	12.3	5.5	0.4	[6]
	375	55.3	72.5	8.7	8.6	7.1	0.5	
<i>Chlorogloeopsis fritschii</i>	300	39	66.5	7.2	19.0	6.8	0.4	[114]
<i>Cyanobacteria</i> sp.	325	45	74.6	8.5	8.7	6.9	1.3	[113]
<i>Desmodesmus</i> sp.	375	49	74.5	8.6	10.5	6.3	–	[115]
<i>Dunaliella tertiolecta</i>	250	44.8	71.3	9.1	12.2	5.3	0.4	[6]
	375	55.3	72.0	8.8	9.9	6.2	0.3	
<i>Golenkinia</i> sp.	350	30	76.6	9.0	5.9	6.6	0.2	[97]
<i>Nannochloropsis gaditana</i>	250	34.4	71.5	9.7	11.5	3.7	0.2	[6]
	375	54.3	74.7	9.9	8.5	5.2	0.4	
<i>Nannochloropsis oceanica</i>	350	40	76.2	10.2	7.3	6.1	0.2	[116]
<i>Nannochloropsis oculata</i>	350	35	68.1	8.8	18.9	4.1	0	[114]
<i>Nannochloropsis</i> sp.	350	43	76.0	10.3	9.0	3.9	0.8	[117]
<i>Porphyridium cruentum</i>	350	60	46.1	5.6	13.3	3.2	0.2	[64]
<i>Porphyridium purpureum</i>	250	24.7	69.1	8.4	15.2	5.0	0.5	[6]
	375	47.1	73.9	8.2	8.7	6.8	0.7	
<i>Phaeodactylum tricornutum</i>	250	40.8	62.9	8.0	12.0	4.7	0.3	[6]
	375	54.3	73.4	9.1	7.8	5.8	1.0	
<i>Scenedesmus almeriensis</i>	250	35.7	72.6	9.4	12.5	4.1	0.3	[6]
	375	58.1	74.3	9.1	8.4	6.1	0.4	
<i>Scenedesmus dimorphus</i>	350	28	73.0	8.2	12.6	5.7	0.5	[114]
<i>Scenedesmus obliquus</i>	250	17.6	69.3	9.1	12.9	5.1	0.2	[6]
	375	50.6	73.2	8.9	8.1	6.3	0.3	
<i>Spirulina platensis</i>	300	36	72.7	8.8	11.5	6.3	0.6	[114]
	350	40	73.7	8.9	10.1	6.3	0.9	
<i>Tetraselmis</i> sp.	350	65	71.0	9.4	14	5.0	0.6	[118]
<i>Tetraselmis suecica</i>	250	29.5	62.6	7.4	14.0	4.8	0.4	[6]
	350	45.6	74.0	9.4	7.7	6.1	0.9	

can be used commercially to produce bio-oil from algal biomass, although efforts are required to accelerate the scaling-up of several reported laboratory protocols to achieve large-scale commercial cultivation of microalgae. Temperature and catalyst utilization are among the crucial factors that directly influence algal biomass production, and these can be optimized to achieve maximum productivity of the algal species.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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