

Review

Catalytic Thermochemical Conversion of Algae and Upgrading of Algal Oil for the Production of High-Grade Liquid Fuel: A Review

Yingdong Zhou and Changwei Hu *

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China; yingdong_zhou@163.com

* Correspondence: changwei.hu@scu.edu.cn; Tel.: +86-28-85411105

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Abstract: The depletion of fossil fuel has drawn growing attention towards the utilization of renewable biomass for sustainable energy production. Technologies for the production of algae derived biofuel has attracted wide attention in recent years. Direct thermochemical conversion of algae obtained biocrude oil with poor fuel quality due to the complex composition of algae. Thus, catalysts are required in such process to remove the heteroatoms such as oxygen, nitrogen, and sulfur. This article reviews the recent advances in catalytic systems for the direct catalytic conversion of algae, as well as catalytic upgrading of algae-derived oil or biocrude into liquid fuels with high quality. Heterogeneous catalysts with high activity in deoxygenation and denitrogenation are preferable for the conversion of algae oil to high-grade liquid fuel. The paper summarized the influence of reaction parameters and reaction routes for the catalytic conversion process of algae from critical literature. The development of new catalysts, conversion conditions, and efficiency indicators (yields and selectivity) from different literature are presented and compared. The future prospect and challenges in general utilization of algae are also proposed.

Keywords: algae; bio-oil; thermochemical conversion; catalytic upgrading; high-grade liquid fuel

1. Introduction

The development of renewable and sustainable fuels is heavily required worldwide due to the depletion of finite fossil fuels [1,2]. In addition, the combustion of fossil fuels has caused several environmental problems, including global warming and environmental pollution [3]. Consequently, much of the attention has been drawn to alternatives such as biofuels from renewable biomass resources, which are able to mitigate CO₂ emission [4,5]. Usually, sugar or oil crops, and non-edible lignocellulosic feedstocks are applied for the production of the first- and second-generation liquid biofuels [6–9]. Different from terrestrial crops, algae are also attractive feedstock due to the advantages such as high lipid accumulation, short growth cycle, and the ability to grow in aquatic environments [5,10,11]. Generally, algal biomass accumulates about 20–50 wt % lipids based on the dry weight of biomass, and some species even have more than 60% lipids content [12–15]. In addition, some kind of natural algae can fix nitrogen, phosphorus, and heavy metals in waste water and polluted lakes [12,16,17]. Thus, algae cultivation cooperating with waste water treatment not only relieves the environmental pollution, but also offers the resource for the generation of renewable energy.

Varieties of technologies for algal biofuel production have been developed in recent decades. As shown in Figure 1, the methods of utilization of algae generally include bio-chemical conversion, lipid extraction, transesterification, and thermochemical conversion. Biochemical conversion mainly produces bioethanol from the fermentation of algal sugar [18,19]. Macroalgae with high saccharides

content are preferred in such process [20]. However, different kinds of algae need different enzymes for their conversion. Since algae contain considerable amount of lipids, extraction techniques are used to produce algal oil, which mainly consists of triglycerides and free fatty acids [21]. The extracted oil can be transesterified to biodiesel (defined as fatty acid alkyl esters, FFAE) over acid or base catalysts [22,23]. The traditional acid/base catalysts might corrode the equipment and cost a lot. Another way to produce biodiesel from algae is through *in situ* transesterification of algal feedstock with the aid of solvent. Technologies such as microwave, ultrasound, or supercritical fluid are usually applied in this process to enhance the biodiesel yield [24–28]. Biodiesel has the advantages of high biodegradability and renewability. Nonetheless, the extraction–transesterification process only utilizes the lipid fraction of algae, leaving the other parts (i.e., sugars and proteins) still remaining in algal cells [29]. In addition, not all kinds of algae have high lipid content. Some species of low-lipid algae contain lipid less than 15 wt % [5,11,16,17,30]. Moreover, in order to increase the content of lipids in algae, many researchers focused on the cultivation of algae, which required suitable temperature, pH, nutrient, some rigorous conditions and so on, resulting in extra expense [31–33].

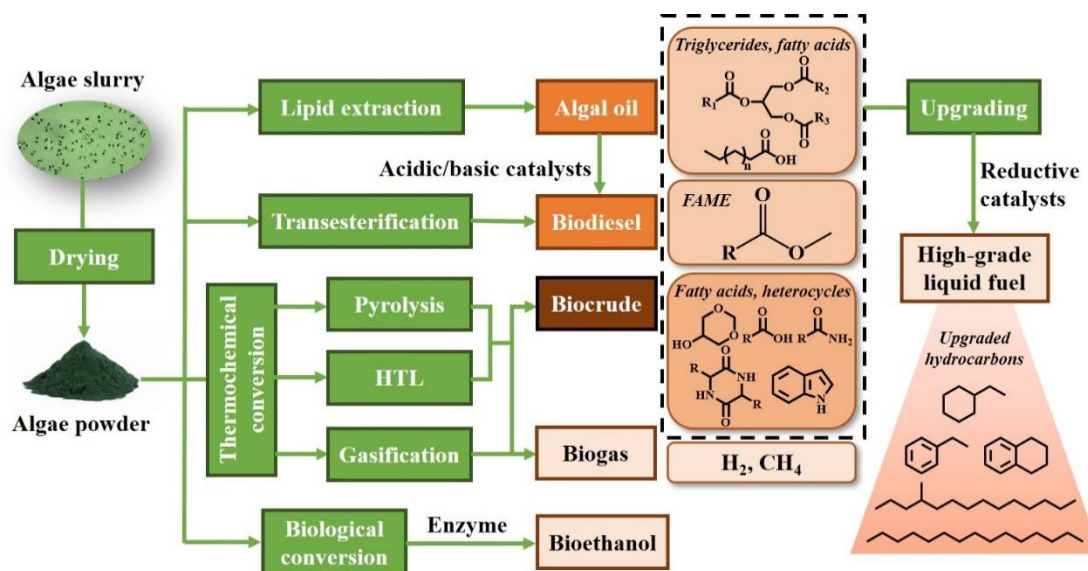


Figure 1. Schematic diagram for conversion of algae into biofuel.

Researchers have been seeking for the method to fully utilize the components in algae. Among the technologies, thermochemical routes are viable for the utilization of the entire algal cell, including lipids, sugars, and proteins. Thermochemical conversion can be classified to pyrolysis, hydrothermal liquefaction (HTL) and gasification [10,34]. Gasification produces mainly gas fuels (CH_4 and H_2) at high temperatures, while liquid bio-oil is obtained via pyrolysis and HTL [35]. Pyrolysis of dried algae produces bio-oil, biochar, and gas products via thermal degradation of feedstock at relatively high temperatures (300–700 °C) [36]. The HTL process usually conducts at mild temperatures (200–450 °C) but high pressure (4–22 MPa), which requires high-pressure resistant equipment [37,38]. Since dehydration of algae feedstock requires energy, hydrothermal liquefaction is favorable for wet biomass conversion. Thus, a great deal of studies focused on the thermochemical conversion of algae, in an attempt to convert the whole algae into a mixture of gases, liquid, and solids. The higher heating value (HHV) of bio-oil obtained from thermochemical conversion is around 30 MJ/kg, higher than the algae material itself [39–42].

However, the problem is that the composition of bio-oil obtained from direct thermochemical conversion of algae is complex, containing hydrocarbons, aromatics, organic oxygenates, and nitrogenous compounds, because of the complexity of algae [5,43–45]. The high oxygen content reduces the heating value of bio-oil, while the high nitrogen content makes the bio-oil not suitable for

combustion. In addition, biodiesel obtained from transesterification and bio-oil from thermochemical conversion have drawbacks such as poorer chemical stability, higher viscosity, and lower energy density compared with petroleum-based liquid fuel [46–48]. In order to improve the selectivity of target products and the quality of biofuel, thermochemical conversion of algae and the upgrading process in the presence of catalysts are developed. On the one hand, one-step catalytic thermochemical conversion of algae is able to increase the bio-oil yield and reduce the content of oxygen and heteroatoms with a proper catalyst. Usually, heterogeneous catalysts such as zeolite are employed in the thermochemical process. The obtained bio-oil has higher energy density and lower oxygen content, as well as a much higher aromatic hydrocarbon content [49–51]. On the other hand, the extracted algal oil, biodiesel, and biocrude obtained from direct thermochemical conversion can go through an upgrading process (hydroprocessing) for obtaining high-grade liquid fuels (mainly hydrocarbons) [52–54]. Therefore, catalysts with high activity in deoxygenation and denitrogenation are highly preferred in algae biorefinery.

This article focuses on the catalytic thermochemical conversion (pyrolysis and HTL) of algae as well as the catalytic upgrading of algal oil or biocrude to high-grade liquid fuels. In this review, the characteristics of biofuels from direct thermochemical conversion in recent research, the catalytic performances of catalysts on algae feedstock and bio-oil conversion are overviewed systematically, and the selection of catalysts is summarized in detail.

2. Production of Biofuel from Direct Conversion of Algae

2.1. Algal Oil from Lipid Extraction and Transformation to Biodiesel

Algal lipids are regarded as a renewable source for the production of the third-generation biofuel [55]. The methods of lipid extraction from algae have been studied for decades, which are classified into mechanical and chemical methods [56]. Chemical methods are generally solvent assisted extraction, including Soxhlet extraction and supercritical fluid extraction, while mechanical methods include grinding, bead beating, ultrasound, and microwave [57–60]. Organic solvents such as chloroform and methanol (Bligh and Dyer method) are frequently used [61], most of which are harmful to the environment and human health [62]. In addition, the lipids in algal cells can hardly be fully extracted when a single method is applied. Since algae have multi-layered cell walls, the mechanical methods combined with chemical methods are used in the extraction process for the disruption of algal cell walls and enhancing the lipid yield. However, the cost and energy-intensive mechanical methods for cell disruption and lipids extraction make the process less attractive and limit its industrialization.

Nevertheless, the selectivity of extracted lipids becomes poor when the lipid yield enhances, due to the fact that the solvents with high extraction efficiency usually extract more compositions from algae, containing neutral lipids (triglycerides), glycolipids, phospholipids, chlorophyll, carotenoid, and sterol [13,63]. For example, lipids extracted from algae by hexane contained a high fraction of neutral lipids, while chloroform/methanol and hexane/isopropanol mixture gave a higher composition of polar lipids [63]. According to the US Department of energy's standard, the N, O and S content in upgraded algal fuels should be <0.05%, <1% and 0, respectively [64]. Due to the high oxygen content and existence of nitrogen and sulfur, algal derived oil is unsuitable to directly use in diesel engines. Consequently, the extracted lipids need to be hydrotreated to high-grade hydrocarbons. Technologies developed in the petroleum refinery for deoxygenation, denitrogenation, and desulfurization can be directly applied in hydrotreatment of algal lipids [12].

Furthermore, triglycerides and free fatty acid in algal lipids can be transformed into biodiesel via transesterification with alcohol, which exhibits better performance in diesel engines [22]. However, the oxygen content of biodiesel is still high, resulting in many drawbacks such as low stability and poor flow property at low temperature. Thus, biodiesel itself is only used as an additive in diesel engines [2,12]. In order to get algae-derived high-grade liquid fuels, which can be directly combusted

in diesel engines, the upgrading process is needed to remove the heteroatoms in algal oil or algae derived biodiesel, and convert them into diesel-range hydrocarbons.

2.2. Bio-Oil from Direct Pyrolysis

Heating biomass in the absence of air or oxygen for thermal degradation at relatively high temperatures is called pyrolysis. Usually, temperature between 300–700 °C is applied [2]. In some cases, the pyrolysis temperature is over 800 °C or below 300 °C [65]. Bio-oil, biochar, and gaseous products are obtained via pyrolysis. Direct pyrolysis can be classified into slow pyrolysis (SP), fast pyrolysis (FP), and microwave assisted pyrolysis (MAP). In slow pyrolysis, the heating rate is relatively slow (between 0.1–1 °C·s^{−1}) so that the process of heating cannot be ignored [65]. It is reported that the heating rate had an influence on the yields and distribution of oil products from the slow pyrolysis of lignocellulosic biomass [66,67]. In fast pyrolysis, the temperature rises to the designated temperature within seconds (>100 °C·s^{−1}). The bio-oil yields from fast pyrolysis are usually higher than slow pyrolysis because the high heating rate makes the vapor products stay in the reactor within only seconds [65,68]. Recently, microwave pyrolysis is considered as an efficient way for biomass conversion. Microwaves can be controlled easily with instantaneous start-up and shut-off with high heating efficiency [17]. The pyrolysis atmosphere is reported to have an influence on the pyrolytic products [17,69]. Because algae are poor absorbers of microwaves, suitable absorbers such as activated carbon are mixed with the feedstock [65]. There are several parameters influencing the yields and properties of pyrolysis products. Expected heating rate and pyrolysis atmosphere, pyrolysis temperature, time, and particle size of feedstock have shown influence on pyrolysis products [65]. For example, high temperature and residence time usually resulted in high bio-oil yield and complex composition of bio-oil, while higher yield of oil was obtained from microalgae with a larger particle size in MAP [17,70].

However, the residue (%) from pyrolysis of algae is usually over 30%, which indicates that pyrolysis of algae is not able to convert the whole algal cell. Even at 700 °C, fast pyrolysis of *Chlorella vulgaris*, *Schizochytrium limacinum*, *Arthrospira platensis*, and *Nannochloropsis oculata* yielded residue of 39%, 48%, 36%, and 48%, respectively [71]. Since pyrolysis at a relatively high temperature cannot selectively degrade only one component (i.e., lipids, sugars or proteins) from algae, the composition of bio-oil is complex. Recent research on direct (non-catalytic) pyrolysis of algae are summarized and listed in Table 1. It can be seen that, whatever the method of pyrolysis is applied, the oxygen and nitrogen content of bio-oil are too high to be directly used in diesel engines. The high oxygen content of pyrolytic bio-oil results in low HHV and poor stability, and the combustion of the high nitrogen content bio-oil may generate NO_x and cause air pollution [2,5]. Therefore, developing strategies for improving the quality of pyrolytic bio-oil becomes a hot topic. Since different components of algae have different thermal stability, the degradation temperature influences the selectivity of products in bio-oil. Recently, researchers have developed fractional pyrolysis of algae, which is separate conversion of the three main components (lipids, carbohydrates and proteins) by controlling the pyrolytic temperature and to realize the multistep conversion. Fractional pyrolysis of cyanobacteria from water booms was studied, and it was found that fractional pyrolysis separated the degradation of different components in algae and improved the selectivity of products in bio-oil [72,73]. However, the stepwise pyrolysis made the process complex and might require extra energy consumption, which increased the cost. Thus, one-step catalytic pyrolysis to remove O and N during the thermal degradation process is favorable for the production of high-grade green diesel.

Table 1. Properties of bio-oil from non-catalytic pyrolysis.

Feedstock	Method	T (°C)	Bio-Oil Yield (wt %)	Elemental Composition (wt %)				HHV (MJ·kg ⁻¹)	Ref.
				C	H	O	N		
<i>Nannochloropsis oculata</i>	FP	500	-	-	-	-	-	33.4	[74]
<i>Nannochloropsis</i> sp. residue	SP	400	31.1	56.1	7.6	30.1	5.3	24.4	[75]
<i>Scenedesmus dimorphus</i>	SP	500	40.0	74.7	10.6	8.3	5.8	28.5	[76]
Cyanobacteria	SP	300	9.8	66.0	8.6	14.8	10.7	32.0	[73]
<i>C. vulgaris</i> remnants	FP	500	53	51.4	8.3	27.5	12.8	24.6	[77]
<i>C. vulgaris</i>	FP	400	72	61.0	8.2	24.8	6.0	28.9	[78]
<i>Chlorella</i> sp.	MAP	490	28.6	65.4	7.8	16.5	10.3	30.7	[79]
<i>Chlorella</i> sp.	MAP	550	57	65.7	9.3	15.8	8.5	32.4	[80]

2.3. Biocrude from Direct Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) of algae is usually conducted in a pressurized water environment (4–28 MPa) at a relatively moderate temperature (200–450 °C) [3,37,38,81,82]. At elevated temperature and pressure, the properties (e.g., solubility) of water change, which promote the degradation of macromolecules in algae to small molecular compounds [5,37]. HTL is considered to be a favorable technique for the conversion of wet algae due to no need for the dewatering process. Like pyrolysis, HTL also has the ability to utilize all of the algae including lipids, carbohydrates, and proteins. After HTL, liquid products, solid residues and gas products are obtained. The water-insoluble phase of liquid products can be recovered by extraction using organic solvents, and the obtained oil-like products are called biocrude. The water-soluble phase separated from liquid products containing nutrients (e.g., N, P, Mg and K) makes up a large fraction, which can be recycled for microalgae cultivation and anaerobic digestion [81,83–86].

Compared with pyrolysis, the yield of solid residue from HTL of algae was around 20% at 350 °C [87–89]. In other words, the conversion of algae via HTL is higher than pyrolysis even when HTL is conducted at relative mild temperatures. This is probably due to the high solubility of some components in water. A summary of the yields and properties of biocrude from direct (non-catalytic) HTL of algae is given in Table 2. In general, the biocrude obtained from HTL has higher HHV compared with pyrolysis oil. The nitrogen content of biocrude is relatively low because some fraction of nitrogen remains in aqueous products. Despite the advantages of HTL, the biocrude composition from HTL of algae is also complex. To gain a high biocrude yield, HTL treatment usually conducts at high temperatures (>300 °C) [89,90]. The dissolution of proteins or saccharides which contain a high proportion of N and O makes the quality of biocrude reduced and limits its commercialization [91]. Therefore, strategies for improving the biocrude yield and quality have drawn lots of researchers' attention. With a proper catalyst, the yield of biocrude can be increased to a certain amount, whereas the content of heteroatoms decreases via denitrogenation or deoxygenation [92,93]. In addition, HTL of algae usually couples with the catalytic upgrading process for the production of high-quality biofuel containing low oxygen and nitrogen.

Table 2. Properties of biocrude from non-catalytic HTL.

Feedstock	Condition	Biocrude Yield (wt %)	Elemental Composition (wt %)				HHV (MJ·kg ⁻¹)	Ref.
			C	H	O	N		
<i>Scenedesmus</i> sp.	250 °C, 7 min	20	66.1	8.6	20.8	4.5	31.2	[90]
<i>Scenedesmus</i> sp.	350 °C, 30 min	36	72.5	9.1	12.9	5.5	35.0	[90]
<i>G. sulphuraria</i>	350 °C, 6 min	28.1	78.2	11.4	4.2	4.6	38.2	[94]
<i>L. digitata</i>	350 °C, 15 min	17.6	70.5	7.8	17	4.0	32	[88]
<i>L. hyperborea</i>	350 °C, 15 min	9.8	72.8	7.7	14.9	3.7	33	[88]
<i>Kirchneriella</i> sp.	300 °C, 30 min	45.4	76.6	9.0	7.9	5.2	37.5	[89]
Algal blooms	300 °C, 60 min	18.4	73.5	9.0	10.9	6.6	35.5	[95]
<i>Tetraselmis</i> sp.	350 °C, 30 min	31.0	75.6	9.9	12.7	5.2	33.3	[96]

3. Catalytic Thermochemical Conversion of Algae

3.1. Catalytic Pyrolysis of Algae

The quality of bio-oil can be improved by using catalysts in pyrolysis. The oxygen content of pyrolytic bio-oil needs to be reduced in order to improve the stability and heating value. In addition, the high proportion of N atoms in the bio-oil should also be removed to meet the standard of combustion fuel. With the aid of an appropriate catalyst, the pyrolytic pathway can be changed, and consequently the selectivity of products is influenced [97]. Generally, catalysts such as zeolite are frequently applied in catalytic pyrolysis, due to the high activity in deoxygenation, cracking, and dehydration [68,98]. Moreover, metal oxides and supported metal catalysts have also been explored for catalytic pyrolysis of algae. This part overviews the performance of different types of catalysts on catalytic pyrolysis of algae.

3.1.1. Zeolites

Zeolites are regarded as highly efficient catalysts for upgrading bio-oil from algae, due to the suitable acidity, resistance of carbon deposition, and the ability to eliminate oxygen atoms without hydrogen [98–100]. Of the zeolite catalysts, ZSM-5 is commonly used because of its adjustable acidity and high performance in deoxygenation, decarboxylation, and decarbonylation [68]. Its acidity can be controlled by varying the Si/Al ratio. High Si/Al ratio results in low acidity of the zeolite [68,101]. The acid sites on zeolites make the macromolecules of algae degrade to compounds with small molecular size. Subsequently, the formed compounds pass through deoxygenation or aromatization forming reduced compounds such as hydrocarbons.

The performance of a catalyst on catalytic pyrolysis of algae can be evaluated by the bio-oil yield, the oxygen and nitrogen content of bio-oil. Pyrolysis of macroalgae *Enteromorpha clathrata* over metal modified Mg-Ce/ZSM-5 catalysts at 550 °C produced bio-oil with high quality [99]. The 1 mmol Mg-Ce/ZSM-5 showed the ability to increase bio-oil yield from 33.77% (without catalyst) to 37.45% and decrease the acid content. In addition, the average molecular weight of bio-oil obtained over such catalyst seemed to decrease, with the content of gasoline-like (C₅–C₇) compounds increased. Primary cracking and decarboxylation might occur due to the presence of 1 mmol Mg-Ce/ZSM-5. Catalytic fast pyrolysis of *spirulina* sp. over different types of zeolites (ZSM-5, zeolite-β and zeolite-Y) was performed [45]. The HHV of pyrolysate ranged over 30–37 MJ·kg⁻¹, which was much higher than that of algae feedstock. All types of zeolites facilitated the formation of aromatics (monoaromatics, PAHs, and indoles). Cycloalkanes were formed over ZY and Zβ, while C₂–C₄ nitriles formed over high acidity zeolites. Anash et al. studied the pyrolysis behavior of *Chlamydomonas debaryana* with and without β-zeolite or activated carbon (AC) [102]. The yields of total hydrocarbons were highest over β-zeolite than that over AC and without catalyst. The combination of hydrothermally carbonized pretreatment and catalytic pyrolysis could effectively reduce nitrogen content of bio-oil, and produce more hydrocarbons, including aromatics. It was found that AC catalyst was more likely to form coke than β-zeolite. More detailed results of catalytic pyrolysis over zeolites were listed in Table 3.

Table 3. Catalytic pyrolysis of algae over zeolites.

Feedstock	Catalyst	Condition	Catalytic Performance	Ref.
<i>Spirulina</i>	Fe/HMS-ZSM5	500 °C, catalyst/algae = 0.5	Highest bio-oil yield: 37.8 %, hydrocarbon yield: 33.04 %	[98]
<i>Tetraselmis suecica</i>	CBV zeolite	400 °C, catalyst/algae = 0.2	Zeolite (Si/Al=30) showed good activity in deoxygenation.	[100]
Cyanobacteria	MgAl4-LDO/ZSM-5	550 °C, catalyst/algae = 0.75	Maximum liquid yield: 41.1%, O/C: 0.09, HHV: 37.164 MJ·kg ⁻¹	[51]
<i>Spirulina</i>	HZSM-5 and H-β with different Si/Al ratio	450 °C, 30 s catalyst/algae = 0.75	Maximum of aromatic (6.54%) hydrocarbons were obtained over HZSM-5 (Si/Al=23), but lower acidity catalysts increased the production of aliphatic hydrocarbons.	[101]
<i>Isochrysis</i> sp.	Li-LSX-zeolite	500 °C, catalyst/algae = 0.5	Bio-oil yield: 29%11.8% aromatics and 23.1% aliphatics	[103]

To summarize, catalysts applied for pyrolysis of algae usually have high activity in deoxygenation. The deoxygenation performance of zeolites can be adjusted by changing the Si/Al ratio of the zeolite. In addition, aromatization of pyrolytic products can be observed, generating abundant aromatics in bio-oil. The increasing acidity of catalysts (low Si/Al ratio) results in promotion of aromatization [98,101]. After catalytic pyrolysis with zeolites, bio-oil with high HHV and low O/C ratio was obtained, but the nitrogen content could hardly be reduced to meet the standard of commercial transportation fuel. The bio-oil obtained from catalytic pyrolysis contained about 5% of N content [51,98,100,101,103]. To produce high-quality biofuel with low N content, catalysts with the ability to remove N in bio-oil need to be developed. The bio-oil obtained from catalytic pyrolysis needs to be further upgraded by catalysts such as sulfide CoMo/Al₂O₃ or NiMo/Al₂O₃, which have high activity in hydrodenitrogenation (HDN) [2].

3.1.2. Other Catalysts

Except zeolites, other catalysts such as metal oxides and supported metal catalysts are applied in catalytic pyrolysis. Transition metal such as nickel has high activity in C-C and C-O bonds cleavage, resulting in high performance for decarbonylation and decarboxylation [12]. Furthermore, reducible metal oxides are considered as a favorable support or catalyst because of their superior redox properties and low carbon deposition rate [104]. It was found that the pyrolysis of *Tetraselmis* sp. and *Isochrysis* sp. over Ni-Ce/Al₂O₃ and Ni-Ce/ZrO₂ produced a higher yield of bio-oil (26 wt %) [105]. The catalysts exhibited strong deoxygenation and denitrogenation ability, with only 9–15% oxygen remained and removal of 15–20% nitrogen from bio-oil. In addition, pyrolysis of Pavlova sp. over Ce/Al₂O₃-based catalysts produced bio-oil with a low O/C ratio (0.1–0.15). MgCe/Al₂O₃ exhibited the best performance on the reduction of oxygen content from 14.1 to 9.8 wt %, while NiCe/Al₂O₃ produced the highest hydrocarbon fraction [106]. Catalytic fast pyrolysis of *Nannochloropsis oculata* over Co-Mo/γ-Al₂O₃ was carried out in an analytical microreactor coupled with a gas chromatograph/mass spectrometer (py-GC-MS) [74]. It was found that aliphatic alkanes and alkenes, aromatic hydrocarbons, and long-chain nitriles were the main products in bio-oil. Co-Mo/γ-Al₂O₃ catalyst could promote the formation of 1-isocyanobutane and dimethylketene with 35% selectivity. In addition, catalytic pyrolysis over Co-Mo/γ-Al₂O₃ produced pyrolysates with higher calorific value (33–39 MJ·kg⁻¹) compared with that of algal feedstock (18 MJ·kg⁻¹).

3.2. Catalytic HTL of Algae

3.2.1. Catalytic HTL with Homogeneous Catalysts

Because HTL is conducted in aqueous phase, water-soluble homogeneous catalysts can be used. They commonly have the ability to improve biocrude yield or produce target compounds with high selectivity. Generally, the homogeneous catalysts include acid catalysts (HCl, H₂SO₄ and other organic acids), alkali catalysts (Na₂CO₃), or other inorganic salts. These catalysts usually promote bonds cleavage, so the degradation of components in algae to small molecular compounds is facilitated. In the presence of homogeneous catalysts, the dissolution of components from algae is facilitated and hence the biocrude yield enhances. However, the homogeneous catalysts can hardly improve the quality of biocrude. In other words, they have a weak influence on deoxygenation and denitrogenation of algal biocrude [3]. A summary of recent works on catalytic HTL on homogeneous catalysts is displayed in Table 4.

In general, the homogeneous catalysts used in HTL are catalysts with proper acidity or basicity. Koley et al. studied the catalytic and non-catalytic HTL of wet *Scenedesmus obliquus* (Table 4) [107]. The optimizations of HTL temperature, pressure, and residence time were conducted on both catalytic and non-catalytic HTL. They found that 300 °C, 200 bar, and 60 min was the optimum condition for obtaining the maximum yield of biocrude (35.7 wt %). By adding catalysts, the biocrude yield increased and followed the order: acidic catalyst CH₃COOH (45%) > HCOOH (40%) > HCl (39%) > H₂SO₄ (38%) > H₃BO₃ (37%), and basic catalyst Na₂CO₃ (40%) > NaOH (38%) > Ca(OH)₂ (37%) > KOH (37%) > K₂CO₃ (36%). In addition, the acetic acid had the ability to reduce the oxygen content of biocrude, resulting in a considerable HHV of 40.2 MJ·kg^{−1}. However, the composition of biocrude in the presence of CH₃COOH was still complex, containing fatty acids, phenols, indoles, monoaromatics, and N-heterocycles.

The effect of acidic, neutral and basic catalysts on the conversion of microalgae (*Spirulina platensis*) by HTL at various temperatures was studied by Zhang et al. [108]. HCl and acetic acid were used to create acidic condition, while KCl for neutral, and K₂CO₃ and KOH for basic conditions. Among these catalysts, only acetic acid and KOH are found to positively influence the biocrude yield, which was more obvious at lower temperatures. The acid and base catalysts promoted the degradation of components in microalgae and suppressed the condensation reaction, resulting in lower average molecular weight of biocrude. However, the distribution of compounds detected by GC-MS showed little change even with the aid of acid or base catalysts.

Typically, Na₂CO₃ is a commonly-used homogeneous catalyst for HTL because of its ability to enhance the biocrude yield. Shakya et al. studied the effect of temperature on the HTL of three kinds of algal species *Nannochloropsis*, *Pavlova*, and *Isochrysis* over Na₂CO₃ [109]. It can be concluded that the biocrude yield increased with the rise of temperature from 250 to 350 °C. The maximum biocrude yields from HTL of three algae species followed the order: *Nannochloropsis* (48.67 wt %) > *Isochrysis* (40.69 wt %) > *Pavlova* (39.96 wt %). When using Na₂CO₃ as the catalyst, the biocrude yield changed to the order of *Pavlova* > *Isochrysis* > *Nannochloropsis*. The biocrude yields of algae with high carbohydrates content (*Pavlova* and *Isochrysis*) increased at higher temperatures (300–350 °C) with the aid of Na₂CO₃, whereas the high-protein-containing algae (*Nannochloropsis*) showed higher yield of biocrude at lower temperature (i.e., 250 °C). However, the conversion of algae with Na₂CO₃ did not significantly improve biocrude properties. The biocrudes obtained were still not suitable for application in transportation.

Overall, homogeneous catalysts have a strong impact on the products yields, especially enhancing the biocrude yields. This is probably ascribed to the degradation ability of these catalysts to create an acid or basic condition. There were few reports about the deoxygenation and denitrogenation ability of homogeneous catalysts. Thus, the quality of biocrude from HTL can hardly be improved by homogeneous catalysts. The biocrude obtained cannot meet the standard for transportation fuel. Furthermore, the acidity and basicity of catalysts might influence the pH value of biocrude and lead to corrosion to the equipment. The homogeneous catalysts can hardly be recovered after reaction,

and this leads to further expense [3,82]. Therefore, finding catalysts with good reusability and highly efficient for deoxygenation and denitrogenation is pressing required.

Table 4. Catalytic HTL of algae with homogeneous catalysts.

Catalyst	Algae Feedstock	Condition	Biocrude Yield (wt %)	Performance	Ref.
Without catalyst	<i>Scenedesmus obliquus</i>	300 °C, 200 bar, 1 h	35.7	HHV: 39.4 MJ·kg ⁻¹	[107]
CH ₃ COOH	<i>Scenedesmus obliquus</i>	300 °C, 200 bar, 1 h	45.1	HHV: 39.1 MJ·kg ⁻¹ , O%: 8.9%	[107]
Na ₂ CO ₃	<i>Scenedesmus obliquus</i>	300 °C, 200 bar, 1 h	40.2	HHV: 40.2 MJ·kg ⁻¹ , N%: 4.7%	[107]
KOH	<i>Spirulina platensis</i>	300 °C, 35 min	30.1	Positive effect on biocrude yield, more ketone and amides formed, lighter volatiles generated	[108]
K ₂ CO ₃	defatted <i>Cryptococcus curvatus</i>	350 °C, 1 h	68.9	The highest biocrude yield, HHV: 38.2 MJ·kg ⁻¹	[110]
K ₂ CO ₃	defatted <i>Cryptococcus curvatus</i>	300 °C, 1 h	63.9	The best biocrude quality, HHV: 36.9 MJ·kg ⁻¹ , lowest nitrogen (0.77%)	[110]
KOH	<i>Cyanidioschyzon merolae</i>	300 °C, 0.5 h, 120 bar	22.67	HHV: 33.66 MJ·kg ⁻¹	[111]
CH ₃ COOH	<i>Cyanidioschyzon merolae</i>	300 °C, 0.5 h, 120 bar	21.23	HHV: 33.36 MJ·kg ⁻¹	[111]
KOH	<i>Ulva prolifera</i>	290 °C, 10 min	26.7	Biocrude yield increased from 12.0 wt % to 26.7 wt % with KOH; Higher HHV: 33.6 MJ·kg ⁻¹	[112]
Na ₂ CO ₃	Green macroalgal blooms	270 °C, 45 min	20.1	The highest bio-oil yield was achieved over Na ₂ CO ₃	[113]

3.2.2. Catalytic HTL with Heterogeneous Catalysts

The heterogeneous catalysts, which exist in different phases with the reaction media, are usually solid catalysts [114]. Heterogeneous catalysts can be easily recovered after reaction, therefore reducing the cost of the process [115,116]. Conversion of algae in the presence of heterogeneous catalysts might cover the deficiency of homogeneous catalysts. Commonly, heterogeneous catalysts include zeolites (e.g., H-ZSM-5), supported metal catalysts (Pt/C), and other metal oxide supported catalysts (e.g., sulfide CoMo/Al₂O₃ and Ni/TiO₂) [117–119]. These materials have strong activity for bonds cleavage, resulting in facilitation of macromolecule degradation and conversion of oxygenates and nitrogenates to high-grade hydrocarbons. As a result, biocrude with low viscosity, high HHV, and low N content is produced in the presence of heterogeneous catalysts.

The effects of heterogeneous catalysts on the yield and quality of biocrude are summarized in Table 5. After screening, the majority of the catalysts listed in the table are supported metal catalysts and can be recycled several times. For example, magnetic nanoparticles (MNPs) were synthesized for microalgae separation and catalytic HTL by Egesa et al. [115]. Firstly, the MNPs were used for separation of algae from the culture medium, with a separation efficiency of 99% achieved. Then, the MNPs were applied in catalytic HTL for the production of biocrude from microalgae. The biocrude yield significantly increased from 23.2% (without catalyst) to 37.1% in the presence of Zn/Mg-ferrite MNPs. Moreover, the percentage of hydrocarbons increased by 26.4%, and the percentage of heptadecane increased by 27.8%, while the percentage of oxygenates and N-containing compounds decreased. This indicated the catalysts had activity in deoxygenation and denitrogenation. In addition, the MNPs could be easily recovered and recycled several times.

Additionally, noble metal catalysts such as commercial Pd/C, Ru/C and Pt/C are widely used in algae conversion and show excellent catalytic performance. Liu et al. reported a two-step catalytic conversion of algae (*Spirulina*) via solvent extraction followed by catalytic HTL of the extracted

residue [120]. In the extraction process, ethanol was found to be the best solvent with the highest extraction efficiency, and the introduction of MgSO_4 could produce ethyl esters from fatty acids. The lipid extracted residue was treated by HTL in the presence of commercial Pd/C, Pt/C, Ru/C, Rh/C, and Pd/HZSM-5. Among all catalysts, Rh/C exhibited the best performance in catalytic conversion of algae, producing 50.98% yield of biocrude with $30.7 \text{ MJ}\cdot\text{kg}^{-1}$ HHV. The O and N content of biocrude obtained from HTL over Rh/C decreased significantly from 32.2% and 7.1% to 23.6% and 4.4%, respectively. In addition, the percentage of hydrocarbons in biocrude obtained over Rh/C based on GC-MS results was 55.7%. Xu et al. studied the catalytic effects of Pt/C, Ru/C and Pt/C + Ru/C on the HTL of *Chlorella* in the presence of H_2 (Table 5) [117]. They divided the biocrude into water-soluble biocrude (WSB) and water-insoluble biocrude (WISB). The addition of catalysts could decrease the fraction of WSB but increase WISB fraction. At optimized conditions, Pt/C and Ru/C led to the highest carbon (63.6% and 74.2%) and hydrogen (7.3% and 8.4%) contents but lowest oxygen (14.1% and 9.2%) and nitrogen (12.2% and 7.1%) contents, and the highest HHV (29.7 and $35.6 \text{ MJ}\cdot\text{kg}^{-1}$) for WSB and WISB fraction, respectively. The water insoluble biocrude obtained from HTL of algae over Pt/C contained amides (48.2%), hydrocarbons (17.7%), acids (12.8%), and phenols (7.7%). In addition, catalytic HTL produced biocrude with more low boiling point fractions.

Apart from noble metal catalysts, the application of non-noble metal catalysts in algae HTL has drawn lots of attention due to their low cost and high activity in bonds cleavage. Among the non-noble metals, nickel, cobalt, iron, and molybdenum are proved to be active in deoxygenation and denitrogenation [2]. Kohansal et al. conducted the HTL of *Scenedesmus obliquus* in the presence of Ni-based catalysts (Ni/AC, Ni/AC- CeO_2 nanorods and Ni/ CeO_2 nanorods) [121]. The optimum condition for the catalytic HTL of microalgae over the catalysts was to set at 324.12°C , 43.52 min, and 19.90 wt % feedstock. With the addition of heterogeneous catalysts, the biocrude yields over three catalysts were higher than that from a non-catalytic process. The highest biocrude yield of 41.87% was achieved over Ni/AC- CeO_2 nanorods, with the HHV of $38.57 \text{ MJ}\cdot\text{kg}^{-1}$. In the presence of Ni-based catalysts, the percentage of hydrocarbons in biocrude was higher than that of the non-catalytic biocrude, but the content of nitrogen-containing compounds was also higher.

Overall, heterogeneous catalysts perform better than homogeneous catalysts in terms of the improvement of algal biocrude quality. In addition, the yield of biocrude can be improved in the presence of heterogeneous catalysts. The catalysts can be easily recovered and reused after HTL, but the coke formation is still the major problem during catalytic HTL. However, in the previous literature, the contents of oxygen and nitrogen in the obtained biocrude are still too high to satisfy the standard of transportation fuel. Therefore, the technologies for production of high-quality liquid fuel with extremely low O and N content from algae need to be further developed.

Table 5. Catalytic HTL of algae with heterogeneous catalysts.

Catalyst	Algae Feedstock	Condition	Biocrude Yield (wt %)	Performance	Ref.
Co/CNTs	<i>Dunaliella tertiolecta</i>	320 °C, 30 min, catalyst/algae = 0.1	40.25	Higher percentage of hydrocarbons, lower content of fatty acid and lower N-compounds	[122]
nano-Ni/SiO ₂	<i>Nannochloropsis</i> sp.	250 °C, 60 min, catalyst/algae = 0.05	30.5	Bio-oil with lower O and N content, catalyst recovery 2–3 times	[123]
Pd/HZSM-5@MS	<i>Spirulina</i>	380 °C, 2 h, HCOOH, catalyst/algae = 0.02	37.3	Promotion of HDO for bio-oil, HHV: 32.65 MJ·kg ^{−1} , catalyst recovery for 5 times	[116]
Ni/TiO ₂	<i>Spirulina</i>	250 °C, 30 min, catalyst/algae = 0.05	43.1	Promoting the formation of hydrocarbons (14%) and esters (15%), and decreasing oxygenates and nitrogenates.	[124]
Ru/C	<i>Nannochloropsis</i> sp.	350 °C, 20 min, H ₂ , catalyst/algae = 0.2	43.5	Increasing the yield of water-insoluble biocrude, decreasing O (7.95%) and N (4.95%) content	[125]
Ru/C	<i>Chlorella</i>	350 °C, 30 min, 0.3 MPa H ₂ , catalyst/algae = 0.2	27	Water insoluble biocrude with highest C (74.2%) and H (8.4%) contents, the lowest O (9.15%) and N (7.1%) and highest the HHV (35.6 MJ·kg ^{−1})	[117]
ZSM-5	<i>Ulva prolifera</i>	280 °C, 10 min, catalyst/algae = 0.15	29.3	HHV of biocrude was 34.8 MJ·kg ^{−1} (non-catalytic was 21.2 MJ·kg ^{−1}); Biocrude with lower viscosity, more light fractions, HHV: 35 MJ·kg ^{−1} , reproduction for at least 10 times	[118]
Ni/TiO ₂	<i>Nannochloropsis</i>	300 °C, 30 min, catalyst/algae = 0.1	48.23	Increase of carbon into biocrude, nitrogen into aqueous phase	[119]
Fe/HZSM-5	<i>Nannochloropsis</i>	365 °C, 60 min	38.1	The percentage of hydrocarbons (46.5%), heptadecane (37.8%), HHV: 35.4 MJ·kg ^{−1}	[126]
Zn/Mg-ferrite MNPs	<i>Scenedesmus obliquus</i>	320 °C, 60 min, catalyst/algae = 0.12	37.1		[115]

4. Catalytic Conversion of Oil Derived from Algae

4.1. Catalytic Hydroprocessing of Extracted Algal Oil

Generally, the oil recovered from algal cell consists of different types of triglycerides. The fatty acids fraction of triglycerides usually contains palmitic, palmitoleic acid, stearic acid, and oleic acid. Some algal species also contain polyunsaturated fatty acids (PUFA) such as eicosapentaenoic acid (EPA), arachidonic acid (AA), and docosahexaenoic acid (DHA), which are value-added health care products [12,127]. The algae derived triglycerides can be hydrotreated by catalysts to fuel-like hydrocarbons with the aid of a proper catalyst. Since hydrogen could be obtained from a wealth of sources, including water splitting, especially by electrolysis of water with renewable electricity such as wind power or solar power, the consumption of hydrogen in the hydroprocessing can be ignored. A summary of recent works on hydroprocessing of algal oil is listed in Table 6.

Conventional NiMo sulfide catalyst has been widely used in hydrogenation of natural oil into fuel-ranged hydrocarbons. Liu et al. investigated the hydrocracking of algal oil from *Botryococcus braunii* (C_nH_{2n−10}, n = 29–34) with sulfide NiMo into fuel-ranged hydrocarbons [128]. The support effect on the selectivity of products was studied under the conditions of 300 °C for 6 h under 4 MPa H₂. For the hydrotreating of the model compound (squalene C₃₀H₅₀), the main product was squalane (C₃₀H₆₂) over NiMo/SiO₂, C₁–C₄ gas hydrocarbons over NiMo/HZSM-5, C₅–C₉ gasoline-ranged hydrocarbons over NiMo/HY and NiMo/SiO₂-Al₂O₃, and C₁₀–C₁₅ aviation fuel-ranged hydrocarbons over NiMo/Al₁₃-Mont, respectively. The hydrocracking of algal oil over NiMo/Al₁₃-Mont gave aviation fuel-ranged hydrocarbons (C₁₀–C₁₅) with a yield of 52%. The sulfide NiMo catalyst acted as a

bifunctional catalyst for hydrogenation of squalene to squalane followed by cracking of the formed squalane to shorter-chain hydrocarbons. Zhao et al. explored the hydrotreating of extracted algal lipids from *Nannochloropsis* for the production of aviation fuel [129]. The effect of hydrotreating temperature (270–350 °C) and catalyst loading (10–30%) was investigated. The optimum condition for hydrotreating reaction was 350 °C and 30% catalyst loading. The main components of biofuel were C₈–C₁₆ hydrocarbons and aromatics. The two-step hydrotreating process obtained biofuels with oxygen content below 0.3% and nitrogen content below 0.007% and HHV of 46.24 MJ·kg^{−1}.

In addition, noble metal catalysts such as Pt, Pd and Ru, which have high activity in hydrodeoxygenation, are also suitable for conversion of algal oil into high-grade hydrocarbons [130,131]. Xu et al. explored a technology for selective extraction of neutral lipid from algae *Scenedesmus dimorphus* and subsequently conversion into jet fuel [132]. Hexane and ethanol solvent mixture was used for selective extraction of neutral lipids. Then, the extracted lipid was hydrogenated over the Pt/Meso-ZSM-5 catalyst. The obtained product oil (38%) mainly contained branched paraffin with C₉–C₁₅ chain length. The jet fuel product satisfied the ASTM 7566 standard with the desired freeze point (−57 °C), flash point (42 °C), heating value (45 MJ·kg^{−1}), and aromatics content (<1%).

Although metal sulfides and noble metals are highly active in deoxygenation of algal lipid/oil, the sulfur leaching of metal sulfides and high-cost noble metal make these process not environmentally and economically friendly [47,133]. Except for metal sulfides and noble metal catalysts, the sulfur-free non-noble metal catalysts are promising in heterogeneous catalysis. It is found that non-noble metals (e.g., Ni, Co, Cu) are active in deoxygenation of fatty acids and natural oil to hydrocarbons [47,134,135]. Santillan-Jimenez et al. investigated the continuous catalytic hydrogenation of model compound and algal lipids to fuel-like hydrocarbons using Ni–Al layered double hydroxide [136]. In addition, Ni/Al₂O₃, Ni/ZrO₂, and Ni/La–CeO₂ were applied for the comparison experiments. Of all Ni-based catalysts, Ni–Al LDH showed the best results for conversion of tristearin to C₁₀–C₁₇ hydrocarbons at 260 °C. Higher temperatures favored the cracking reaction to form lighter alkanes, while lower H₂ pressure favored the formation of heavier hydrocarbons. For the hydrogenation of algal oil, ~50% yield of hydrocarbons was obtained over Ni–Al LDH.

Table 6. Catalytic hydroprocessing of algal oil.

Catalyst	Feedstock	Condition	Conversion (%)	Performance	Ref.
Ni/meso-Y	Microalgae biodiesel	275 °C, injection rate: 0.02 mL·min ^{−1}	91.5	Hydrocarbon selectivity: 56.2%, isomer ratio: 46.4%	[137]
Ni-Cu/Al ₂ O ₃	Extracted algal lipids	260 °C and 580 psi	-	Diesel-ranged hydrocarbons content: 83%	[138]
Ni-Al LDH	Extracted algal lipids	300 °C, 4 h stream	100	Hydrocarbon content: 99 wt %, diesel-like hydrocarbons: 76 wt %	[139]
Co/clay	Algae DHA oil	260 °C, 8 h, 40 bar H ₂	100	Hydrocarbon yield: 85.5 wt %	[47]
Ce/Zeo-β	Algal oil	400 °C, 6 h	98	Selectivity for C ₁₀ –C ₁₄ hydrocarbons: 85%	[140]

Generally, extracted algal oil/lipids have the potential to be converted to high-grade, fuel-like hydrocarbons. The nitrogen and oxygen content of algal-lipid derived fuel are low enough to satisfy the standard for transportation fuel due to the low nitrogen content and easily editable oxygen of algal lipids. However, due to the limited lipid content of algae, the yield of algal lipids derived green fuel based on the whole algal cell is also low. Based on the concept of “waste-free biorefinery”, the utilization of other components of algae except for lipids needs to be explored.

4.2. Catalytic Upgrading of Biocrude Oil from Thermochemical Conversion of Algae

Another way for production of fuel-ranged hydrocarbons from algae is the upgrading of the biocrude oil from thermochemical conversion. The biocrude oil obtained at high temperatures contains the components derived from saccharides and proteins apart from lipid. Some of the oxygenates and nitrogenates cause the undesired properties of biocrude oil [141]. Therefore, the large proportion of oxygen and nitrogen of bio-oil needs to be removed for obtaining high-quality biofuel. This process involved the use of a proper heterogeneous catalyst with high activity in deoxygenation and denitrogenation. Generally, the upgrading process also needs H_2 to remove the heteroatoms (O, N, and S), for improving the heating value and reducing the O, N, and S content of product oil. The resulted biofuel should have low viscosity, high stability, and high HHV [68,82]. A summary of recent works on catalytic upgrading of algal biocrude oil is presented in Table 7.

4.2.1. Catalytic Upgrading of Pyrolysis Bio-Oil

As mentioned in the previous section, the bio-oil from direct pyrolysis of algae contains high proportion of O and N due to the degradation of the whole algae cell at high temperatures. The quality of pyrolytic bio-oil needs to be upgraded via catalytic process before utilization as transportation fuel. Elkasabi et al. investigated one-step hydrotreating and aqueous extraction of O and N-containing compounds, for the production of fuel-range hydrocarbons from *Spirulina* pyrolysis bio-oil [142]. The catalytic hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN) were conducted over commercial Ru/C catalyst. The upgrading at 385 °C resulted in organic oil with low N and O content (<1 wt %). The selectivity of products could be controlled by varying reaction conditions. More paraffins were obtained at higher temperature (~400 °C), while lower temperature (350 °C) resulted in more phenolics. The remaining oxygen and nitrogen-containing compounds in the upgraded oil could be removed through aqueous extraction with HCl.

Guo et al. reported an approach to get high-quality liquid fuel from catalytic HDO of pyrolysis oil from *Chlorella* and *Nannochloropsis* by using Ni-Cu/ZrO₂ bimetallic catalysts [143]. The highest HDO activity was obtained over 15.71 wt % Ni 6.29 wt % Cu supported on ZrO₂, with the HDO efficiency of 82% for the upgrading of bio-oil from *Chlorella*. The Ni-Cu/ZrO₂ catalyst showed excellent stability after reaction, with low sintering and coking. In addition, the heating value, viscosity, and the water content of the upgraded oil were improved. Particularly, the cetane number of the product oil from *Nannochloropsis* satisfied the standard of EN 590-09.

Overall, catalytic upgrading of pyrolytic oil from algae can successfully remove the O and N content to a low level. In addition, the remaining N and O can possibly be removed using physical adsorption or the extraction method. The resulting liquid biofuel can meet the standard of transportation fuel. However, the mentioned works did not study much on the recyclability and regeneration of the catalysts, and the mechanism of upgrading process for a better understanding of catalyst design.

4.2.2. Catalytic Upgrading of HTL Biocrude

Like pyrolysis, direct HTL of algae produces biocrude oil with poor quality, especially for its high O and N content, and the physical properties that do not suit the fuel standards [141]. Patel et al. explored a method for catalytic upgrading of biocrude from fast HTL of algae over Pt, Pd, Ru supported on C and Al₂O₃, and sulfide NiMo/Al₂O₃ [144]. The highest oil yield (60 wt %) and highest denitrogenation ability (2.05 wt %) were obtained over NiMo/Al₂O₃, but the effect of deoxygenation was poor. The oxygen content of the upgraded biocrude ranged from 1.60–6.07 wt %, while the nitrogen content ranged from 2.05–3.47 wt %. The decrease of O content resulted in the increase of HHV to 38.36–45.40 MJ·kg^{−1}. The boiling point distribution of upgraded biocrude decreased from the gas oil fraction (271–343 °C) to the kerosene fraction (<271 °C). In addition, the abundant components in upgraded biocrude were branched alkanes and straight-chain alkanes.

Shakya et al. studied the catalytic upgrading of biocrude oil from HTL of *Nannochloropsis* [145]. Five different catalysts (Pt/C, Ru/C, Ni/C, ZSM-5 and Ni/ZSM-5) were used as the upgrading catalysts. Upgrading at 300 °C showed higher oil yield, while higher temperature at 350 °C resulted in bio-oil with higher quality. The maximum upgraded oil yield was obtained over Ni/C at 350 °C, whereas upgraded oil with higher HHV, lower acidity, and nitrogen content was achieved over Ru/C and Pt/C. The HHVs of upgraded biocrude ranged from 40–44 MJ·kg⁻¹, which were highly improved compared with biocrude feedstock (36.44 MJ·kg⁻¹). The catalytic upgrading produced upgraded oil with a 65–75% decrease in nitrogen content, and 95–98% decrease in oil acidity.

Biller et al. investigated the hydroprocessing of biocrude on sulfide CoMo and NiMo catalysts from continuous HTL of *Chlorella* [146]. In the non-catalytic HTL step, 40 wt % yield of biocrude was obtained with 6% nitrogen, 11% oxygen, and HHV of 35 MJ·kg⁻¹. The upgrading of biocrude over both NiMo and CoMo catalysts was conducted at 405 °C and 350 °C. The two catalysts showed similar performance on the improvement of hydroprocessed oil. The upgraded oil with the highest HHV (45.4 MJ·kg⁻¹) was achieved over CoMo catalyst at 405 °C, with the oil yield of 69.4 wt %, nitrogen content of 2.7%, and oxygen content of 1.0%. Hydroprocessing at high temperature (405 °C) resulted in upgraded oil with higher gasoline and diesel #1 fractions. Moreover, hydrocarbons (C₉–C₂₆) were the main products in upgraded bio-oil.

Table 7. Catalytic upgrading of biocrude oil from thermochemical conversion.

Catalyst	Feedstock	Condition	Yield (wt %)	Performance	Ref.
H β	Pretreated algal bio-oil	400 °C, 4 h, 6 MPa H ₂	44.8	HHV: 44.3 MJ·kg ⁻¹ , O: 2.3% N: 2.1%, total hydrocarbons: 75.4%	[147]
MCM-41 (100%Si)	Pretreated algal bio-oil	400 °C, 4 h, 6 MPa H ₂	54.5	HHV: 45.2 MJ·kg ⁻¹ , O: 1.9% N: 1.7%, total hydrocarbons: 81.5%	[147]
HY (5%Na ₂ O)	Pretreated algal bio-oil	400 °C, 4 h, 6 MPa H ₂	48.1	HHV: 44.9 MJ·kg ⁻¹ , O: 1.9% N: 1.7%, total hydrocarbons: 80.5%	[147]
HZSM-5 (Si/Al=25)	Pretreated algal bio-oil	400 °C, 4 h, 6 MPa H ₂	52.3	HHV: 44.5 MJ·kg ⁻¹ , O: 2.0% N: 1.8%, total hydrocarbons: 60.8%	[147]
NiMo/Al ₂ O ₃	HTL biocrude from <i>Spirulina</i>	400 °C, 4 h, 8 MPa H ₂	70.4	Hydrocarbons: 78%, reduced boiling point	[148]
Ru/C+alumina	Pretreated algal oil	400 °C, 4 h, 6 MPa H ₂	70	HHV: 47.0 MJ·kg ⁻¹ , O: 0.4% N: 2.5%, total hydrocarbons: 43.2%	
Ru/C+Mo ₂ C	Pretreated algal oil	400 °C, 4 h, 6 MPa H ₂	77	HHV: 46.8 MJ·kg ⁻¹ , O: 0.1% N: 3.1%, total hydrocarbons: 36.7%	[149]

In the previous section, catalytic HTL can improve the quality of biocrude, but the characteristics of biocrude still cannot meet the ideal standard. In comparison to one-step catalytic HTL, the upgrading of biocrude from HTL obtained biofuel with higher quality, with low boiling point, low viscosity, high HHV over 40 MJ·kg⁻¹, and low oxygen and nitrogen content, which is more preferable than the one-step catalytic HTL.

5. Conclusions and Outlook

Algae is considered as a potential feedstock for the production of biofuel. The common approaches for utilization of algae are lipid extraction and transesterification, pyrolysis, and hydrothermal liquefaction. The extraction–transesterification of algae only utilizes the lipid fraction of algae, leaving other parts (i.e., saccharides and proteins) as waste. Thermochemical conversion of algae is a viable method to fully utilize algae. However, the percentage of solid residue via pyrolysis of algae is usually high (30–50%) even at high temperatures (e.g., 700 °C), indicating the low conversion of algae [71]. The conversion of algae via HTL is usually high, with about 10% yield of solid residue at relatively mild temperatures [87–89]. However, the yield of biocrude oil recovered from the organic fraction is relatively low, leaving much of the water-soluble fraction remaining in aqueous products. In addition, the produced bio-oil or biocrude has some unwanted properties such as high viscosity, high acidity, high oxygen content, high nitrogen content, and low energy density. In order to improve the

yield and quality of algal biofuel, catalysts are employed in the conversion process. Homogeneous catalysts (e.g., HCOOH , KOH and Na_2CO_3) enhance the biocrude yield via HTL, but these catalysts show little effect on improving the biocrude quality. In the presence of heterogeneous catalysts (zeolites, metal oxides, supported metal catalysts, etc.), the thermochemical conversion produces bio-oil with higher yield, lower oxygen content, and higher energy density, but the nitrogen content (~5%) and some properties (such as viscosity and boiling point) can hardly be improved by the one-step catalytic conversion.

Another way to improve algal bio-oil quality is upgrading of the obtained bio-oil with heterogeneous catalysts and hydrogen. Catalysts with high activity in deoxygenation and denitrogenation are employed in this process. Generally, commercial metal sulfides (sulfide CoMo and NiMo), commercial noble metal catalysts (Pt/C, Ru/C), and non-noble metal catalysts (Ni, Co, Fe) show excellent performance in the upgrading of algae-based biocrude oil. Usually in this process, higher temperature results in higher yield of hydrocarbons. The upgrading process reduces the oxygen and nitrogen content (<1%), oil acidity, boiling point, and enhances the hydrocarbons content up to 80%. The remaining nitrogen can be removed by using physical adsorption or extraction. Possibly, by catalytic pyrolysis or HTL of algae cooperating with catalytic upgrading of the obtained oil product, the oxygen and nitrogen content might be reduced to a very low level.

According to the recent advances on algal biorefinery, we have proposed the following six aspects of the future prospect and challenges in utilization of algae.

- (1) The denitrogenation of algal bio-oil should be further studied. There are many research works focusing on the catalytic deoxygenation of algal based molecules. The technology of deoxygenation process is relatively mature. However, few studies have focused on the denitrogenation of algal biocrude oil. The N-containing compounds in bio-oil might cause the emission of NO_x during combustion. Hence, developing technology for lowering the N-containing compounds is essential. In general, denitrogenation is more difficult than deoxygenation due to the less reactive organic nitrogenates than oxygenates [68]. Denitrogenation of algal oil requires more energy, making the process costly. The mechanism needs to be further studied, for better understanding of the insight into denitrogenation and design of the denitrogenation catalysts. Therefore, searching for an effective catalyst, which is highly active in denitrogenation, is pressing required.
- (2) The characterization of oil products from algae conversion, including quantification of monomers and identification of oligomers should be improved and further developed. Until now, the composition of products obtained by thermochemical conversion is usually analyzed by GC-MS because of the lack of authentic samples. The percentage of compounds in biocrude oil is determined by the relative area of total ion peaks. Based on the fundamental knowledge of GC, the response factors of different compounds are different, so the response factors must be introduced to quantify the absolute concentration of each compound accurately. However, the exact structure of the compounds should be accurately analyzed for quantification, so some other techniques should be involved. In addition, the polysaccharides and proteins from algae are macromolecules, and the full degradation of them to monomers or compounds with small molecular size is difficult. The existence of oligomers in the liquid products from the thermochemical conversion is unavoidable. Biocrude with high fraction of oligomers usually has undesired properties such as high viscosity and boiling point, so the content of oligomers in algal biofuel should be minimized, for obtaining high-quality bio-oil. However, oligomeric products usually cannot be detected by GC-MS, so the development of other techniques, such as ESI-MS and MALDI-TOF MS, is needed. By identifying the structure of oligomers, it is easier to design a specific catalyst for efficient degradation of oligomers or even algae-derived polymers (polysaccharides and proteins) and their further conversion to small-molecule fuel chemicals.
- (3) Converting algae through fractional route might be preferable. For improving the selectivity of target products from starting materials with complex components, the concept of fractional conversion has been proposed and accepted for lignocellulosic biomass, which is defined as

a selective in situ conversion of biomacromolecules to desired products [5,11,72,73]. Due to the complexity of algae, the fractional conversion, in other words, selective conversion of one specific component in algae, needs to be developed for the full utilization of algae. With the multi-step conversion, the feedstock of each step is simplified and it becomes possible to obtain high-grade biofuel or high selectivity to target products. For example, the lipid fraction can be extracted and hydrogenated to hydrocarbons. The saccharides in lipid extracted algae could be converted to value-added chemicals, and the protein component might be converted to amino acids or N-containing compounds. In this way, the algae feedstock can be fully utilized to avoid generating waste, which might do harm to the environment. In addition, the strategy for algae fractionation by simultaneous separating and converting needs to be developed—for example, simultaneously separating algal lipid and catalytic converting it to hydrocarbons. Thus, finding a method to selectively convert one component of algae without destroying the others is also a way to obtain products with high selectivity.

- (4) The utilization of algal sugar to produce valuable chemicals might be a potential research goal. It is well-known that polysaccharides can be hydrolyzed and further converted to valuable platform molecules—for example, monosaccharides, 5-HMF, levulinic acid, lactic acid, etc. However, only a few research works have focused on the conversion of sugars in algae to value-added chemicals, taking advantage of the oxygen content of the algae feedstock itself. Generally, carbohydrates from algae are suitable for the conversion into platform molecules. Hydrolysis of algal polysaccharides is usually carried out in the presence of acidic catalyst, such as Brønsted acid, metal chlorides, and heterogeneous catalysts such as HZSM-5 and Sn-Beta. Over these catalysts, highly selective chemicals such as rhamnose, 5-HMF, levulinic acid or lactic acid are formed [150–154].
- (5) The research of algal biorefinery should also focus on improvement of the process, in order to realize the commercialization and industrialization. Although high-quality algae-based liquid fuel can be obtained via catalytic upgrading process, the operating conditions are severe. Usually, high temperature (400 °C), high pressure (6 MPa), and long reaction time (4 h) are required in the upgrading of algal oil. This causes high costs in energy consumption and equipment. In addition, the selection of the catalyst should not only focus on the activity, but also on the reusability, and the selectivity of products. Except for activity in deoxygenation and denitrogenation, the catalyst should also be active in degradation of the oligomers from bio-oil. The catalyst with good reusability should have high thermal stability and resistance to coke in the upgrading process. Due to catalytic HTL conducts in aqueous environments, the catalyst should also be resistant to water. In addition, the upgrading process also needs to be performed on a large scale with low costs, to make it possible for commercialization and industrialization.

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