Chinese Chemical Letters 37 (2026) 112441

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Parametric study of hydrothermal liquefaction of macroalgae for bio-oil production upgrading: A review

Zhaoying Li[a,b], Wanlong Zhao[b], Chenyu Yang[b], Yingnan Duan[c], Xianghao Zha[a,*], Zhurui Shen[a,c,*]

[a] Xinjiang Biomass Solid Waste Resources Technology and Engineering Center, College of Chemistry and Environmental Science, Kashi University, Kashi 844000, China
[b] College of Mechanical and Electrical Engineering, Qingdao University, Qingdao 266071, China
[c] School of Materials Science and Engineering, Nankai University, Tianjin 300350, China

ARTICLE INFO

Article history:
Received 22 August 2025
Revised 15 January 2026
Accepted 21 January 2026
Available online 22 January 2026

Keywords:
Macroalgae
Hydrothermal liquefaction
Bio-oil
Reaction conditions
Elemental migration

ABSTRACT

Macroalgae, as the third-generation biomass energy source, is considered the most promising form of renewable energy to replace fossil-based energy resources. Hydrothermal liquefaction (HTL) is a low-carbon conversion technology that transforms macroalgae into liquid biofuels by decomposing and converting macroalgal biomass. This review, based on a summary of recent literature, first outlines the environmental risks associated with macroalgae blooms and highlights the benefits of utilizing hydrothermal liquefaction technology for macroalgae treatment. Subsequently, it elaborates on the key factors influencing the hydrothermal liquefaction of macroalgae, including reaction temperature, reaction time, catalyst type, and solution conditions. The results indicate that bio-oil production and consumption occur concurrently during the hydrothermal liquefaction of macroalgae. As reaction temperature and time increase, the bio-oil yield exhibits a trend of first increasing and then decreasing. When the reaction temperature is excessively high or the reaction time is prolonged, the bio-oil consuming reactions gradually dominate, resulting in reduced bio-oil yields. Compared to homogeneous catalysts, heterogeneous catalysts have garnered greater attention due to their superior catalytic performance and recyclability. The findings demonstrate that mixed solutions are more conducive to bio-oil production than aqueous solutions. Furthermore, this review examines the latest advancements in hydrothermal liquefaction technologies, as well as the elemental migration occurring during the process. The current challenges associated with bio-oils include their high production costs and complex compositions, necessitating further investigation and forming the cornerstone of future research endeavors.

© 2026 Published by Elsevier B.V. on behalf of Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.

1. Introduction

As the global economy expands rapidly, energy demand is correspondingly increasing. To date, fossil energy has been the most widely utilized energy source. However, fossil energy is finite, and its depletion is becoming one of the most significant global challenges in contemporary times [1]. The utilization of fossil energy invariably results in significant CO_2 emissions. Global efforts are intensifying, and numerous nations are implementing policies aimed at controlling carbon emissions [2]. Thus, replacing fossil energy with renewable alternatives has emerged as a feasible solution to address the energy crisis [3]. Currently, the utilized renewable energy sources include biomass energy, solar energy, wind energy, hydro energy, and tidal energy. Notably, biomass energy is primarily derived from diverse waste sources such as algae, crops, and wood [4]. Contrary to traditional fossil energy, the carbon in biomass is recyclable. For instance, algae fix atmospheric carbon dioxide through photosynthesis, thereby facilitating carbon recycling. This process also contributes to reducing greenhouse gas emissions, subsequently mitigating the severe global greenhouse effect [5]. The production of high-quality liquid fuels (bio-oil) from biomass, owing to its accessibility and low cost, has become a focal point of research in recent years [6]. Algae, classified as third-generation biomass [7], differ from first and second-generation biomass in that they grow independently of arable land [8] and exhibit lower requirements for growth environments, such as the ability to thrive in wastewater (Fig. 1).

* Corresponding authors.
E-mail addresses: zhaxianghao@163.com (X. Zha), shenzhurui@nankai.edu.cn (Z. Shen).

https://doi.org/10.1016/j.cclet.2026.112441
1001-8417/© 2026 Published by Elsevier B.V. on behalf of Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.

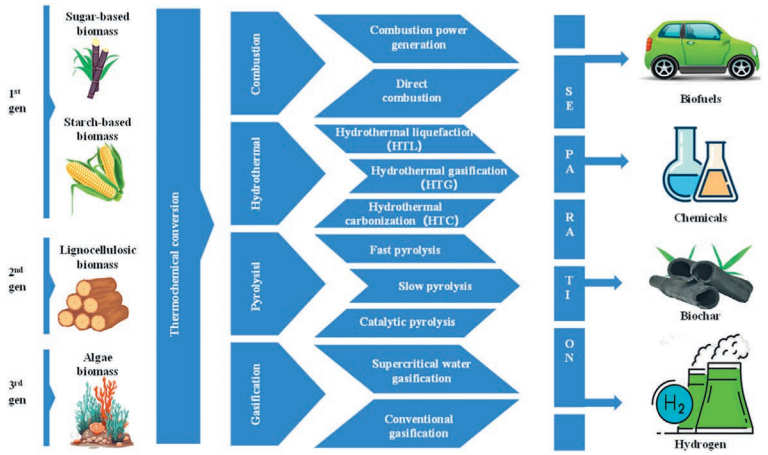


Fig. 1. Development course of biomass energy and thermochemical transformation method.

Algae can be classified into two main categories: microalgae and macroalgae [9]. Bio-oil derived from algae exhibits significant compositional similarity to fossil energy sources, comprising a variety of hydrocarbons. This bio-oil, after undergoing further refining and bioconversion processes, can be directly employed as a liquid fuel [10]. Thermochemical conversion [11] and bioconversion form the two cardinal methods of transforming biomass into bio-oil. Bioconversion entails using microorganisms for biomass fermentation, thereby generating liquid or gaseous fuels along with carbon dioxide. Currently, this method is widely utilized in the production of ethanol and biogas [12]. However, it is characterized by low fuel yields [13] and high pretreatment costs [14], which limit its suitability for large-scale application. Thermochemical conversion of biomass can be further classified into combustion, hydrothermal liquefaction (HTL), pyrolysis, and gasification. Fig. 1 illustrates the thermochemical conversion methods and their classification. High pretreatment costs rendering it unsuitable for widespread application.

HTL and pyrolysis are two widely adopted technologies for producing bio-oil from macroalgae. Pyrolysis refers to the process of heating biomass using an external heat source under an inert atmosphere, which induces the breakdown of macromolecules in the biomass and forms a three-phase product comprising solid char, bio-oil, and gaseous products [15]. HTL is a method wherein biomass is converted into liquid fuel by applying high temperatures and pressures in a sub-supercritical water solution environment [16]. The pyrolysis temperature generally ranges from 400 °C to 900 °C [17], with macroalgae pyrolysis typically being conducted at approximately 550 °C [18]. In comparison to pyrolysis, HTL usually occurs at temperatures below 400 °C, under relatively mild reaction conditions. This leads to a lower tar content and higher energy efficiency. Additionally, HTL eliminates the need for drying macroalgae, enabling direct processing and thereby reducing energy consumption. Consequently, employing the HTL method for processing macroalgae to produce high-quality bio-oil represents a feasible alternative to conventional fossil energy [19], taking into account both economic and environmental considerations. The HTL of macroalgae enables the separation of gas-liquid-solid three-phase products [20], with this review specifically focusing on bio-oil production. In recent years, there has been a growing body of research focused on the production of high-quality bio-oil using HTL of macroalgae, indicating broader development prospects for bio-oil production *via* algal HTL [21].

This review summarizes the current findings on the HTL of macroalgae, assessing the impact of various reaction conditions, such as temperature, duration, catalysts, and solution environments, on the yield and composition of bio-oil. Furthermore, with the development of HTL technology, a variety of emerging technologies have been introduced. This article provides a summary of three innovative technologies: two-stage HTL, fast HTL, and hydrotreatment. The bio-oil produced by existing technologies often contains high levels of nitrogen compounds, which can significantly affect its quality. Therefore, this paper discusses the migration of nitrogen during the HTL process.

2. Hydrothermal liquefaction of macroalgae

Macroalgae are large, multicellular aquatic plants that typically contain only 1 %-6 % of the total lipid content found in microalgae. The increasing pollution of seawater has exacerbated eutrophication, resulting in significant algal blooms in recent years. If left untreated, the subsequent decomposition of these blooms can release unpleasant odors, thereby affecting local air quality, residents, and potentially harming the tourism industry. Enteromorpha prolifera, a common species of macroalgae, can trigger a "green tide" phenomenon when it floats abundantly on the sea surface. Its accumulation along coastlines can adversely impact adjacent water bodies, terrestrial ecosystems, and local flora and fauna [22]. Major algal blooms predominantly occur along the coastlines of industrialized cities, with “green tides” primarily caused by green macroalgae accounting for approximately 60 % of all occurrences. These events are notable for their large-scale outbreaks and potentially hazardous impacts. Brown macroalgae, red macroalgae, and mixed macroalgae blooms together constitute less than 40 % of such phenomena [23]. However, the most extensive macroalgae bloom on record occurred in 2019 with the Atlantic Sargassum bloom, during which approximately 20 million tons of Sargassum were distributed across an 8000 km stretch from the Mexican coast to the west coast of Africa [24]. Consequently, it is imperative to develop an effective macroalgae management strategy. Analysis of macroalgae reveals that, compared to terrestrial plants, their composition is relatively simple, primarily consisting of organic components such as proteins, lipids, and carbohydrates. Table S1 (Supporting information) provides a detailed overview of the compound composition of several macroalgae species [25–28].

A comparative analysis conducted by Aresta *et al.* evaluated the efficiency of HTL and supercritical CO_2 extraction for bio-oil production from macroalgae, revealing that HTL yielded significantly higher bio-oil outputs [29]. Furthermore, Anastasakis *et al.* reported the successful production of catalyst-free bio-oil (19.3 % w/w) with a calorific value of up to 36.5 MJ/kg *via* HTL using Laminaria saccharina (a kind of brown macroalgae) [30]. Similarly,

Elliott *et al.* demonstrated the potential of continuous thermal liquefaction for producing high-quality bio-oils from sucrose algae [31]. These findings collectively indicate that high-temperature catalytic cracking, particularly through HTL, represents an effective approach for converting macroalgae into high-calorific-value bio-oils, thereby facilitating their efficient utilization.

3. Factors affecting hydrothermal liquefaction of macroalgae

HTL is conducted in a high-pressure reactor using sub- or supercritical water, as well as other substances, as solvents. Macroalgae exhibit a complex composition, with their lipids consisting of intricate components, primarily triglycerides formed by fatty acids and glycerol [32]. During the HTL process, heating and pressurization predominantly convert fatty acids into bio-oils, while glycerol is transformed into a liquid-phase product [33]. Proteins in macroalgae exhibit a complex structure, consisting of peptide chains polymerized through dehydration condensation. During HTL, these proteins undergo reactions such as decarboxylation and deamidation [34], leading to the formation of small molecules [35], which are subsequently re-polymerized into target products. Carbohydrates, including starch, cellulose, and hemicellulose, present in macroalgae, are hydrolyzed to form compounds such as glucose, which further decompose into smaller molecules [36]. Given the intricately complex nature of the HTL reaction mechanism, process parameters such as reaction temperature, duration, catalyst type, and solution environment play a critical role in determining the yield of bio-oil [37]. This section therefore synthesizes recent research findings regarding the influence of reaction conditions on the yield and composition of bio-oil produced *via* HTL.

3.1. The effect of Reaction temperature in hydrothermal liquefaction of macroalgae

The energy required for HTL primarily originates from the need to elevate the temperature to a specific value to achieve the activation energy threshold necessary for initiating the reaction [38]. It has been demonstrated that temperature is a decisive factor in determining both the yield and quality of bio-oil [39]. Fig. S1 (Supporting information) illustrates the distribution of optimal temperatures for the HTL of macroalgae across various studies. The optimal temperature range is generally centered around 300 ± 50 °C, with variations depending on the type of feedstock and reaction conditions [40]. A decrease in bio-oil yield is observed when temperatures exceeded the optimum range due to an increase in gaseous reactions which resulted in a surge of gaseous products [41]. In a study, Fragile Forked Knotweed was utilized as feedstock for HTL experiments conducted within a temperature range of 220-340 °C. The results demonstrated that both bio-oil yield and overall biomass conversion increased with rising temperature, peaking at 320 °C after a reaction time of 60 min, with a bio-oil yield of 28.9 wt%. The primary constituents of the bio-oil were identified as hydrocarbons, lipids, and aromatic hydrocarbons. Elemental analysis of the bio-oil obtained *via* HTL revealed carbon content of 66.2 %, hydrogen content of 4.2 %, and oxygen content of 28.6 %, corresponding to a calorific value of 23.3 MJ/kg. However, further increases in reaction temperature led to a decline in bio-oil yield due to enhanced decomposition reactions of low molecular weight compounds, which subsequently transitioned into gas-phase products and solid residues [42].

Biswas *et al.* conducted an experiment with a reaction time of 15 min to evaluate the influence of reaction temperature on the HTL of Sargassum. The reaction temperatures were set at 260, 280, and 300 °C. An increase in bio-oil yield was observed as the temperature rose, with the highest yield of 16.3 wt% achieved at 280 °C [43]. However, further increases in temperature resulted in a decline in bio-oil yield, accompanied by a significant reduction in solid residue content. These findings indicate that elevated temperatures enhance the feedstock conversion rate, reduce the organic acid content in bio-oil, and generally contribute to improved bio-oil quality. In a similar study, Yan *et al.* conducted HTL experiments on Ulva prolifera at temperatures of 270, 290, and 310 °C. As the temperature increased from 270 °C to 290 °C, both the bio-oil yield and calorific value improved, with the bio-oil yield peaking at 26.7 wt% and the calorific value reaching 33.6 MJ/kg. However, further increasing the temperature to 310 °C resulted in a decline in bio-oil production due to the conversion of certain short-chain compounds in the bio-oil into non-condensable gases at temperatures exceeding 290 °C. This observation also confirms that as bio-oil production decreases, gas production increases. The experimental results confirmed the optimal temperature range for HTL, while exceeding this threshold led to the decomposition of bio-oil, thereby reducing its yield [44]. Currently, HTL predominantly employs the electric heating method, which involves heating the reaction vessel to transfer heat to the raw materials through conduction. This approach often results in higher energy consumption. Microwave technology, as a novel heating method, can accelerate organic reactions while reducing energy consumption. This is because microwave heating directly transfers energy to the biomass materials, thereby enhancing efficiency and minimizing energy loss. Ong *et al.* [45] conducted HTL experiments using microwave-assisted heating with the marine macroalgae *Chaetomorpha* sp. as the feedstock. The optimal reaction conditions were determined through response surface methodology, and a series of experiments were performed. The bio-oil yield was observed to increase with rising reaction temperature, peaking at 21.47 wt% at an optimal temperature of 226 °C. When the reaction temperature exceeded this optimal value, the bio-oil yield began to decline due to the occurrence of secondary reactions at higher temperatures, which diverted intermediate products toward gas-phase and solid residue formation, thereby reducing the overall bio-oil yield.

3.2. The effect of reaction time in hydrothermal liquefaction of macroalgae

In HTL processes, reaction duration significantly influences bio-oil yield, demonstrating time-dependent optimization characteristics. Below the optimal timeframe, bio-oil yield is positively correlated with reaction time due to the progressive depolymerization of biomass macromolecules into smaller compounds [38]. However, beyond this critical threshold, yield degradation occurs *via* two primary mechanisms: (1) Re-polymerization of reactive bio-oil intermediates into tar-like substances, which subsequently undergo martensitic condensation reactions to form biochar [46]; (2) formation of gas-phase products through secondary cleavage of unstable constituents, particularly under prolonged subcritical conditions [47]. Consequently, determining the optimal reaction time in HTL processes is essential for maximizing bio-oil yield.

Chen *et al.* conducted a systematic investigation into the influence of varying residence times (15, 30, 45, and 60 min) on the bio-oil yield and elemental distribution during the HTL of duckweed at 370 °C. Their findings revealed that the maximum bio-oil yield (35.6 wt%) was achieved at a residence time of 45 min. Furthermore, the resulting bio-oil exhibited a calorific value of 40.85 MJ/kg, a heat/carbon ratio ranging from 1.72 to 1.98 (comparable to that of petroleum at 1.84), and a significant presence of valuable compounds such as 3-pyridinol and 2-pyridone in its composition [48]. Yuan *et al.* conducted an experimental study on the co-HTL of *Enteromorpha tertiolecta* and rice husk at various reaction times (15, 30, 45, 60, and 75 min) to investigate the

influence of reaction time on bio-oil yield. The results revealed a growth-decline trend in bio-oil yield over time, with the maximum yield achieved at 45 min. The resulting bio-oil exhibited a calorific value of 33.05 MJ/kg, with long-chain compounds (C14-C20) accounting for 28 % and short-chain compounds (C5-C12) comprising 72 %. However, extending the reaction time beyond 45 min resulted in a decrease in bio-oil yield and an increase in biochar content [49]. This phenomenon can be attributed to the polymerization of bio-oil components, leading to the formation of solid-phase products due to prolonged residence times. In the study conducted by Ma *et al.*, a high-temperature HTL reaction of *Ulva prolifera* was performed without catalysts at 280 °C for reaction times of 15, 30, and 45 min. The highest bio-oil yield (16.6 wt%) was achieved at a reaction time of 15 min. Conversely, extending the reaction time to 30 and 45 min resulted in a decrease in bio-oil yield and an increase in biochar content [50]. This phenomenon can be attributed to the fact that longer reaction times promote the re-polymerization of monomers in the bio-oil into biochar. The HTL of Enteromorpha clathrata exhibits distinct time-dependent product distribution patterns, as demonstrated by Yuan *et al.* [51]. Increasing the reaction duration from 15 to 45 min enhanced bio-oil yield from 24.25 % to 45.00 %, reflecting progressive biomass depolymerization. However, extending the reaction time to 75 min triggered a yield reduction to 35.75 %, accompanied by a concomitant increase in gaseous products from 49.75 % to 57.50 %. Solid residue content displayed nonlinear temporal evolution: peaking at 15 min (45.00 %), decreasing to a minimum at 45 min (5.25 %), followed by a gradual rise to 75 min (9.80 %). This kinetic equilibrium shift—from primary decomposition to secondary cracking pathways—highlights the critical role of reaction temperature in determining optimal durations. Specifically, elevated temperatures accelerate reaction kinetics, thereby reducing the time required to achieve maximum bio-oil yield [52].

3.3. The effect of catalysts in hydrothermal liquefaction of macroalgae

Catalysts play a pivotal role in enhancing the yield of bio-oil during HTL. The use of catalysts not only increases the bio-oil yield but also reduces energy consumption compared to conventional HTL methods [53]. Furthermore, catalysts significantly contribute to improving the overall HTL process by enhancing the quality of bio-oil [54]. The selection of appropriate catalysts is often determined by the type of biomass feedstock. For macroalgae HTL, determining the most suitable catalyst is essential. The catalysts used in the HTL of various types of algae and their effects on bio-oil characteristics are summarized in Table 1 [55–66].

Various catalysts have been shown to positively influence both the yield and quality of bio-oil in HTL processes. Currently, popular catalysts can be classified into homogeneous and heterogeneous categories based on their physical state. From the perspective of acidity or alkalinity, catalysts can further be divided into basic and acidic types. It is evident that the acidity or alkalinity of a catalyst significantly affects the HTL process. Fig. 2 illustrates several commonly used catalysts in the HTL process along with their typical representatives. The catalytic performance and underlying mechanisms vary significantly across different catalyst types. As shown in Figs. 2b-g, SEM images reveal distinct structural features of various catalysts. The 50 % Ni/SiO_2·MgO catalyst (Fig. 2b) derives its catalytic activity primarily from metallic nanoparticles dispersed on the support surface [67]. In contrast, the zeolite catalysts depicted in Figs. 2c-e exhibit catalytic behavior driven by acidic sites. These materials possess well-defined, uniform pore architectures that provide a high specific surface area. Moreover, their pore dimensions are comparable to the kinetic diameters of many organic molecules, thereby enhancing reaction selectivity [68–70]. The metal oxide catalyst in Fig. 2f operates through basic sites as

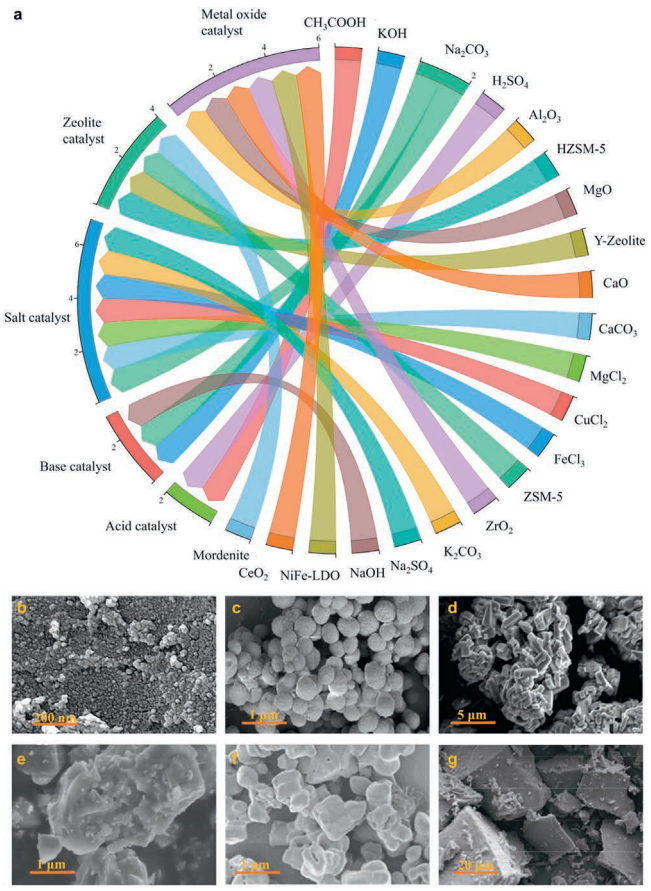


Fig. 2. Some catalysts used in HTL. (a) Classification of catalysts. (b) SEM of 50 % Ni/SiO_2·MgO. Copied with permission [67]. Copyright 2024, Elsevier. (c) SEM of ZSM-5. Copied with permission [68]. Copyright 2025, Elsevier. (d) SEM of HZSM-5. Copied with permission [69]. Copyright 2022, Elsevier. (e) SEM of Mn/Y-Zeolite. Copied with permission [70]. Copyright 2025, Elsevier. (f) SEM of CaO. Copied with permission [71]. Copyright 2024, Elsevier. (g) SEM of SO_4^{2-}/ZrO_2. Copied with permission [72]. Copyright 2022, Springer.

active centers [71]. Finally, Fig. 2g presents the solid acid catalyst SO_4^{2-}/ZrO_2, whose performance originates from surface superacid sites. By modulating the concentration and strength of these acid sites, its catalytic properties can be effectively tuned [72].

3.3.1. Homogeneous catalysts

Standard homogeneous catalysts can be classified into acidic catalysts (*e.g.*, H_3PO_4, HCOOH, and H_2SO_4) and alkaline catalysts (*e.g.*, KOH, NaOH, and Na_2CO_3). These catalysts primarily function through acid-base or ionic mechanisms, influencing reaction pathways such as hydrolysis, dehydration, and esterification.

Nallasivam *et al.* conducted experiments using alkaline catalysts (Na_2CO_3, K_2CO_3, KOH, NaOH) in the HTL of two marine macroalgae species. The results demonstrated that Na_2CO_3 yielded the highest bio-oil production for *Kappaphycus alvarezii* (KA), while KOH yielded the highest bio-oil production for *Eucheuma denticulatum* (ED). Furthermore, the use of KOH as a catalyst resulted in a higher hydrocarbon content in the bio-oil for both macroalgae compared to other catalysts, achieving hydrocarbon contents of 4.2 % for KA and 24.4 % for ED [73]. These findings indicate that KOH exhibits high selectivity for hydrocarbon production, likely *via* enhanced decarboxylation and deoxygenation pathways. Yan *et al.* conducted experiments on the HTL of *Ulva prolifera* macroalgae using three different alkaline catalysts (KOH, NaOH, and Na_2CO_3). At a reaction temperature of 290 °C for 10 min, the presence of KOH (0.1 g) resulted in the highest bio-oil yield of 26.7 wt%. This

Table 1
The catalysts used in the hydrothermal liquefaction of different algae and their effects on bio-oil.

Catalyst	Types of algae	Impact on bio-oil	Ref.
KOH	*Saccharina latissima*	The generation of solid residue was reduced by only 5 wt%, and the yield of bio-oil was increased from 12.9 wt% to 20.2 wt%	[64]
Na_2CO_3	*Saccharina latissima*	Promotes the decomposition of carbohydrates into ketones and esters.	[64]
Organic acid (formic acid and acetic acid)	*Chlorella*	Catalytic conversion of macromolecules into small molecules increased the yield of bio-oil from 20.3 wt% under non-catalytic conditions to 38.0 wt% (formic acid) and 32.6 wt% (acetic acid), respectively.	[66]
Inorganic acid (HCl and H_2SO_4)	*Chlorella*	Hydrochloric acid leads to an increase in the yield of bio-oil from 20.3 wt% to 22.1 wt%, while sulfuric acid leads to a decrease in the yield of bio-oil to 12.6 wt%	[66]
YCl_3	*Ulva prolifera*	Promote the conversion of rhamnose into valuable products such as lactic acid. When YCl_3 at a concentration of 26 mmol/L was used, the yield of lactic acid was 30.4 wt%.	[65]
ZSM-5	*Kappaphucus alverizii*	The yield of bio-oil increased from 18.3 wt% to 28.4 wt%, while the output of biochar decreased from 40.3 wt% to 34.5 wt%	[58]
Biochar	*Chlorella sp.* (*microalgae)*	The calorific value increased from 35.8 MJ/kg to 37.7 MJ/kg. The oxygen content in the bio-oil (10.7 %) was lower than that in the raw materials (31.3 %)	[59]
Ce/HZSM-5	*Saccharina latissima*	The degree of bond breaking and depolymerization was increased, and the yield of bio-oil increased from 12.9 wt% to 23.6 wt%	[64]
W/MCM-41	*Enteromorpha clathrata* and *Chlorella vulgaris*	The carbon content in bio-oil reaches 72.1 %, promoting the decomposition of proteins into small molecule substances.	[55]
Ni/MCM-41	*Enteromorpha clathrata* and *Chlorella vulgaris*	Compared with the absence of catalysis, the carbon content in the bio-oil increased significantly to 72.3 %, and the calorific value of the bio-oil reached 35.0 MJ/kg	[55]
Mo/MCM-41	*Enteromorpha clathrata* and *Chlorella vulgaris*	Promote esterification reactions to generate esters, with lipid content reaching 40.5 %. The content of acidic substances is only 1.7 %	[55]
$NiFe_2O_4$	*Sargassum sp.*	After the use of the catalyst, the carbon content increased from 68.3 % to 78.2 %, the bio-oil contained no sulfur, and the nitrogen content decreased to 4 %	[57]
Ni/MTi_xO_y (M = K, Ca, Sr, Ba)	*Saccharina japonica*	It is conducive to catalytic hydrogenation reaction. The minimum content of biochar using $Ni/MTiO_3$ catalyst is 5.6 wt%	[61]
$NiMo/Al_2O_3$ Pt/Al_2O_3 Pb/Al_2O_3	*Nannochloropsis sp. (microalgae)*	All three catalysts increased the calorific value of bio-oil. Among them, Pt/Al_2O_3 had the greatest increase in the calorific value of bio-oil, from 36.5 MJ/kg to 45.4 MJ/kg	[63]
Pd/C and Ni/SiO_2-Al_2O_3	*Saccharina latissima*	Decomposition of macromolecular structures to improve bio-oil yield.	[64]
5GaNiFe-LDO/AC	*Gracilaria corticata*	Compared with the absence of a catalyst, the maximum yield of bio-oil increased from 38.8 wt% to 56.2 wt%, and the catalyst exhibited an increased heptane selectivity	[60]
Functionalized graphene oxide/polyurethane (F-GO-PU)	*Cladophora glomerata*	Compared with the working condition without a catalyst, the content of bio-oil has increased by approximately 54 %. The addition of a catalyst is beneficial for removing oxygen-containing compounds and cracking long-chain compounds into low-molecular-weight compounds	[62]
Ni, Zn, Cd and Cu	*Chlorella vulgaris, Arthrospira platensis, Ulva lactuca* and *Sargassum muticum*	The catalyst increases the calorific value of bio-oil. Zn has the greatest increase in calorific value for the other three types of algae except Sargassum: spirulina (increased from 32.6 MJ/kg to 34.3 MJ/kg), Chlorella (increased from 33.5 MJ/kg to 34.5 MJ/kg), and Ulva (increased from 31.9 MJ/kg to 33.1 MJ/kg). The maximum effect of Cu on Sargassum has increased from 33.4 MJ/kg to 33.9 MJ/kg	[56]

bio-oil also exhibited a higher calorific value compared to those obtained using other catalysts. The GC-MS analysis revealed that the alkaline catalysts participated in the HTL process, thereby enhancing the selectivity of specific compounds. Notably, the content of hexadecanoic acid in the bio-oil demonstrated selectivity, with significantly higher values observed when alkaline catalysts were used (KOH: 19.4 %, NaOH: 18.6 %, Na_2CO_3: 11.2 %) compared to the uncatalyzed condition (4.5 %). Additionally, the content of heptadecane in the bio-oil was 7.5 % when KOH was employed as a catalyst, which was markedly higher than the values of 1.3 %-3.2 % observed under no-catalyst conditions or when using other catalysts. These findings indicate that KOH exhibits high selectivity for specific compounds during the HTL process, promoting deoxygenation and hydrocarbon formation [44].

Yang *et al.* conducted HTL of *Enteromorpha prolifera* using H_2SO_4 and CH_3COOH as acid catalysts to investigate the effects of organic and inorganic acids on the process. Their findings demonstrated that the primary constituents of bio-oil include fatty acids, ketones, olefins, and 5-methyl furfural. Furthermore, the study revealed a reduction in the total bio-oil yield when employing both acid catalysts. However, the nitrogen content in the bio-oil decreased compared to the uncatalyzed condition, while the oxygen content increased due to esterification reactions. Additionally, the contents of ketone and 5-methyl furfural were enhanced in the presence of acid catalysts, thereby improving the flowability of the bio-oil [74]. This suggests acid catalysts favor dehydration and cyclization reactions. Saber *et al.* conducted acidic catalysts (synthetic zeolite) in the HTL process, achieving a peak bio-oil yield of 24.0 wt% with zeolite at 250 °C. They also found that the use of catalysts reduced the nitrogen and oxygen content in bio-oils, thereby enhancing their calorific value [75].

Performance and limitations: Homogeneous catalysts often achieve high selectivity for specific compounds (*e.g.*, hydrocarbons, esters) and can significantly improve bio-oil quality metrics such as calorific value and deoxygenation. However, they are typically corrosive, negatively impacting the life expectancy of equipment. Additionally, the solubility of homogeneous catalysts in water significantly decreases under HTL conditions, potentially causing issues with equipment. Crucially, homogeneous catalysts exhibit poor performance for large-scale applications due to their high mixing with the feedstock, which results in increased recovery costs and challenges in separation [7].

3.3.2. Heterogeneous catalysts

Heterogeneous catalysts have garnered significant attention globally owing to their advantages, including high catalytic activity, ease of separation, and reusability. Their mechanisms often involve surface reactions, promoting key pathways such as deoxygenation, decarboxylation, denitrification, and hydrogenation, which significantly improve the yield and quality of bio-oil during the HTL process. The following will explain alkali metal catalysts, molecular sieve catalysts, and bifunctional catalysts.

Nguyen *et al.* conducted experiments using heterogeneous catalysts (Fe catalyst) in the HTL of Cladophora socialis, followed by a comparative analysis of the results. The study concluded that the highest bio-oil yield of 36.2 % was achieved with the Fe catalyst. The incorporation of the iron-based catalyst promotes the formation of hydrocarbons (*e.g.*, cyclopentadiene, undecane, heptadecane) within the bio-oil while facilitating the decarboxylation reaction for deoxygenation. Additionally, the iron-based catalyst was found to play a critical role in reducing carbonyl compounds, such as five-membered cyclic ketones, in the bio-oil, thereby enhancing its stability, highlighting its efficacy in hydrodeoxygenation [76–78]. Li *et al.* conducted a study on the effects of nickel-iron layered double oxide (Ni Fe-LDO) catalysts, supported on activated biochar, during the HTL of Gracilaria corticata (GC) macroalgae at a temperature of 280 °C. Their research findings demonstrated that the use of 5 % Ga/Ni Fe-LDO/AC catalysts led to a significant increase in bio-oil yield, achieving a peak yield of 56.2 wt%. Regarding the bio-oil composition analysis, enhanced selectivity for heptadecane compounds was identified when employing the Ga/Ni Fe-LDO/AC catalyst [60]. Xu *et al.* employed basic metal oxide catalysts (MgO, CaO, $CaCO_3$) during the HTL of *Ulva prolifera*. The results demonstrated that basic metal oxide catalysts yielded higher bio-oil production, ranging from 24.5-35.1 wt%. Notably, the highest biomass conversion and bio-oil yield of 35.1 wt% were achieved using MgO catalysts, which significantly enhanced the content of phenolic compounds and cyclic compounds in the bio-oil. Bio-oil obtained from catalytic HTL exhibited a carbon content of 66.2 % and a calorific value of 34.2 MJ/kg, surpassing the calorific value of 30.2 MJ/kg observed in non-catalytic reactions [79]. The effective denitrification capacity of MgO catalysts enhanced selectivity towards ester compounds, underscoring the role of basic sites in promoting deoxygenation and condensation reactions.

Molecular sieve catalysts, particularly HZSM-5, have become a hot topic in HTL research due to their unique pore structure, acidity, and excellent catalytic performance, traditionally employed in the petrochemical industry and for the catalytic pyrolysis of biomass [80]. HZSM-5 molecular sieve catalyst exhibits excellent decarboxylation and denitrification effects in the HTL process, significantly reducing the oxygen and nitrogen content in bio-oil, thereby improving its quality. Ma *et al.* examined the impact of three zeolite-based catalysts (ZSM-5, Y-zeolite, and mercerized zeolite) at dosages of 10, 15, and 20 wt% on the HTL of *Ulva prolifera* macroalgae. The best bio-oil yields were 29.3 wt% (ZSM-5) and 24.1 wt% (mercerized zeolite) at 15 wt% catalyst concentration, while Y-zeolite achieved 23.4 wt% at 20 wt%. All catalysts outperformed the 16.6 wt% yield without catalysts. The zeolite catalysts enhanced hydrocarbon selectivity, reduced oxygen content, and ZSM-5 showed superior deracemization and denitrification effects, attributed to its shape selectivity and strong acidity. Jazie *et al.* converted Fucus vesiculosus into bio-oil *via* catalytic HTL, utilizing Hβ molecular sieve catalysts during the experimental process. Under optimal reaction conditions, a maximum biocrude oil yield of 27.6 % was achieved, with the bio-oil exhibiting a high calorific value of 38.47 MJ/kg. Given that *Fucus vesiculosus* contains low lipid content and high carbohydrate content, the resulting bio-oil primarily consisted of ketones (43 %) and nitrogenous heterocyclic compounds (19 %), indicating the catalyst's role in ketonization and dehydration pathways [81].

Dual functional catalysts can enhance catalytic activity through synergistic effects, primarily by improving the catalyst's hydrogenation, deoxygenation, and denitrification capabilities, thereby significantly increasing the calorific value and stability of bio-oil. Liu *et al.* developed a Pd/HZSM-5 bifunctional catalyst, which exhibited superior hydrogenation and denitrogenation effects. The study demonstrated that incorporating metal elements into molecular sieve catalysts could significantly enhance the hydrogen content of bio-oils while effectively reducing their nitrogen content, thereby improving the quality of bio-oils [82]. In a similar vein, Cheng *et al.* employed Zn/HZSM-5, Co/HZSM-5, and bimetallic Co-Zn/HZSM-5 catalysts in HTL and observed that each catalyst significantly enhanced the bio-oil yield. Notably, the bimetallic Co-Zn/HZSM-5 catalyst not only increased the hydrocarbon content of the bio-oil to 18.59 % but also reduced the oxygenated compounds, thereby improving the higher heating value (HHV) of the bio-oil [83]. Hierarchical zeolites (dual functional catalysts), with their diverse pore structures and high surface areas, are used to effectively anchor metals and enhance coke tolerance. Yang *et al.* synthesized meso-microporous zeolite carriers and loaded them with Co species for propane dehydrogenation catalysts using alkaline solution post-treatment. The results showed that the alkali solution modification produced carriers with larger mesopore volumes and richer hydroxyl nests. The mesopores in the microporous zeolite support help disperse the active Co metal and facilitate coke removal during dehydrogenation, effectively preventing deactivation from sintering and coke coverage, a principle applicable to HTL catalyst design [84]. In contrast, non-catalytic HTL bio-oil exhibited high oxygen content, high nitrogen content, high viscosity, and high acidity, rendering it unsuitable for direct use as fuel. The introduction of catalysts effectively promotes the hydrogenation, deoxygenation, and denitrification processes. Graded zeolites possess distinct pore structures and high surface areas, enabling efficient metal anchoring and enhanced coke resistance, thus contributing to the development of high-performance bifunctional catalysts.

Comparative performance summary: Heterogeneous catalysts generally offer superior recyclability and easier separation compared to homogeneous counterparts. They effectively enhance key bio-oil quality metrics such as yield, hydrocarbon content, HHV, and reduce O/N content *via* mechanisms like deoxygenation and denitrification. Molecular sieves, particularly metal-loaded bifunctional catalysts, show significant promise due to their tunable acidity and shape selectivity. However, their stability and anti-coking performance in high-temperature and high-pressure environments still need further optimization. Future research should prioritize optimizing catalyst design and synthesis protocols, exploring novel catalyst architectures and loading strategies. Enhancing catalyst stability and coke resistance while reducing costs is crucial to facilitate the industrial implementation of HTL technology.

3.4. The effect of solution environment in hydrothermal liquefaction of macroalgae

The HTL process, carried out under high-pressure conditions, enables the solution environment to uniformly disperse the macroalgae, thereby facilitating solvent access for the decomposition of macromolecules within the macroalgae structure [85]. Researchers have observed variations in yield and bio-oil composition when different solvents are employed in the HTL process. Common solution environments for HTL include water and organic solutions, notably alcohols such as methanol and ethanol [86]. Owing to its low cost, HTL is predominantly conducted under sub- or supercritical water. However, the use of water as a solution environment has several drawbacks, including relatively high boiling and criti-

cal points, as well as a low calorific value for the resultant bio-oil. The utilization of an ethanol-water co-solution environment in HTL reactions enhances bio-oil yield [87]. Moreover, the critical point and dielectric constant of an ethanol-water co-solution environment are lower than those of water, enabling milder reaction conditions and more complete decomposition of larger molecules. Additionally, when ethanol is used as the solution environment in HTL, it can provide hydrogen to stabilize free radicals, thereby improving bio-oil quality [88]. Reaction solution environments based on alcohols interact with acidic compounds to generate ester compounds. This dual process not only reduces the acid content in bio-oil, thereby improving its stability, but also enhances bio-oil quality through an increased lipid content. Yuan *et al.* conducted HTL of the macroalgae Enteromorpha clathrata using ethanol-water mixtures with varying ethanol concentrations. The maximum bio-oil yield (46.75 %) and minimum solid residue (4.5 %) were achieved at an ethanol concentration of 75 % [51]. Analysis of the bio-oil compounds revealed that the use of ethanol as a reaction solution environment increased the ester compound content. Furthermore, the acceleration of the transesterification reaction by a catalyst resulted in 43.48 % ester compounds.

In the study by Biswas *et al.*, the effects of different solution environments on the HTL of *Sargassum tenerrimum* were investigated. A bio-oil yield of 16.33 % was achieved when water was used as a solvent at 280 °C, with the main bio-oil components being 3-pyridinyl and *p*-hydroxyphenyl compounds. Under similar temperature conditions, higher bio-oil yields were obtained when methanol and ethanol were used as solvents (22.8 % and 23.8 %, respectively). When methanol was employed, the primary bio-oil components were hexadecanoic acid-methyl ester and tetradecanoic acid-methyl ester, whereas hexadecanoic acid-ethyl ester and oleic acid-ethyl ester were the predominant components when ethanol was utilized [89]. Alcohol-based solution environments significantly enhanced the bio-oil yield and exerted distinct influences on the bio-oil composition. In the study by Chen *et al.*, it was found that employing an ethanol-water co-solution environment under subcritical conditions is advantageous for enhancing bio-oil yield and lipid content [90]. The ratio of the ethanol-water co-solution environment plays a critical role in influencing bio-oil yield and reducing solid residues. A competitive interplay exists between hydrolysis and re-polymerization within the co-solution environment. Excessive ethanol may lead to a reduction in free radical presence, thereby promoting re-polymerization and inhibiting hydrolysis, ultimately resulting in increased solid residue. Consequently, selecting an appropriate ratio of the co-solution environment becomes particularly significant. Wang *et al.* employed four different concentrations of ethanol-water co-solution environments in their experiments. The bio-oil yield increased with the ethanol content. Although this trend persisted beyond an ethanol content of 50 %, the increase was marginal, rising only from 35.17 % to 38.20 %. Consequently, higher ethanol concentrations do not lead to a significant enhancement in bio-oil yield but instead result in increased costs due to the rising ethanol content [91].

The interaction among multiple factors plays a crucial role in HTL. Uzoejinwa *et al.* researched that the main and interaction effects of three effective parameters (pyrolysis temperature, feedstock blending ratio, and heating rate) were also modeled and simulated to determine the yield rates of bio-oil. Optimization studies were performed to predict the optimal conditions for maximum yields using the central composite circumscribed experimental design [92]. In addition, Zhu *et al.* converted wet Southern green algae (NA) biomass waste into high-quality bio-oil and investigated the coupling effects of catalysts and solvents, using ethanol, methanol (54.0 wt%), and water (43.8 wt%) as solvent systems to evaluate bio-oil yield [93]. Similarly, Gong *et al.* selected two types of algae, fresh algal biomass (HS) and desalinated biomass (TH and CH), to investigate the interactive effects of temperature and reaction time on bio-oil production. The observed bio-oil yield exhibited an initial increase followed by a decrease with increasing reaction temperature and duration [94]. In addition, the reasons for catalyst deactivation and regeneration strategies are listed in Fig. S2 (Supporting information).

3.5. Technical economic analysis of hydrothermal liquefaction of macroalgae

Key factors such as catalysts, raw material processing, and reaction temperature (reflecting energy consumption) are major cost drivers in catalytic processes. Although precious metal catalysts like Pt and Pd exhibit high catalytic activity, their high cost and susceptibility to deactivation through sintering and carbon deposition significantly increase operational expenses. In contrast, non-precious metal catalysts such as $NiMo/Al_2O_3$ or alkaline catalysts like KOH offer lower initial costs, but their economic viability depends critically on lifespan, stability, and regeneration frequency. Catalyst recyclability and regeneration cost thus constitute pivotal determinants of overall process economics [40]. Reaction temperature and pressure represent the primary contributors to energy consumption. While elevated temperatures and extended residence times can enhance conversion rates, they lead to an exponential increase in energy input costs [95]. Therefore, optimizing reaction conditions to achieve an optimal balance between product yield and energy expenditure is critical for process efficiency. Additionally, energy-intensive steps such as the drying and size reduction of macroalgae, followed by hydrogenation and refining of bio-oil to remove oxygen and nitrogen impurities, constitute significant cost factors in the overall process.

Compared to non-recyclable homogeneous catalysts, the use of recyclable heterogeneous catalysts, such as nickel-based catalysts, can reduce operating costs by approximately 15 % -20 %. However, this cost advantage must offset the higher initial investment and periodic regeneration expenses associated with such catalysts. While two-stage HTL can lower nitrogen content and enhance bio-oil quality through low-temperature pretreatment, it entails additional reactor units and increased operational complexity, leading to corresponding rises in capital expenditure and operating costs. Technical and economic analysis requires balancing the premiums and additional costs associated with product upgrades. The processing scale of an HTL facility significantly influences the unit production cost. Expanding the scale from a few tons per day to hundreds of tons per day can substantially reduce the unit production cost of bio-oil through economies of scale. Masoumi *et al.* reported an activated minimum fuel selling price (MFSP) of 2.2 $/L to achieve break-even operating costs, which is approximately 10 % lower than that of combustion-based systems. The estimated greenhouse gas emission performance is −1.13 g CO_2-eq/MJ, indicating a significant reduction in greenhouse gas emissions compared to petroleum-based fuel production [96]. Mishra *et al.* utilized wet biomass directly, eliminating the need for drying equipment and thereby reducing capital and operational expenditures. The conversion of biomass into solid and liquid fuels was achieved at moderate temperatures (250-400 °C) and pressures (10-35 MPa), further contributing to lower overall costs [97]. Subhash *et al.* provided a comprehensive overview of the challenges associated with microalgae production for bioenergy and discussed biorefining approaches that can valorize by-products to enhance the technical and economic viability of the process [98].

These studies consistently emphasize that reducing raw material costs, improving energy efficiency, optimizing catalyst performance and longevity, and enabling process integration are key strategies for enhancing the economic feasibility of HTL.

4. Recent advances in hydrothermal liquefaction

4.1. Advances in traditional hydrothermal liquefaction techniques

Two-stage HTL, fast HTL, and hydrotreatment are recognized as innovative approaches to enhance the quality and yield of HTL bio-oil. One-step HTL typically produces bio-oils with a high concentration of nitrogenous compounds, primarily resulting from protein hydrolysis. Pre-treatments aimed at removing and recovering proteins and carbohydrates from macroalgae can significantly improve the quality of bio-oils. In recent years, two-step HTL methods for bio-oil production have attracted substantial attention (as shown in Table 2 [25,48,91,99–101]). The first stage involves conducting HTL of macroalgae at a lower temperature, which causes several nitrogenous compounds to migrate into the aqueous phase product. The second stage entails performing HTL at a higher temperature to produce the final product. Fig. 3a illustrates the fundamental process of two-step HTL. Fig. 3d [102] depicts a traditional 'black box' batch reactor, which is the workhorse for foundational HTL reaction screening but provides limited process insight. In contrast, Fig. 3e shows an advanced interactive reactor equipped with *in-situ* sampling and monitoring capabilities, which is crucial for understanding real-time reaction kinetics and mechanisms [102].

Depending on the ex-post cultivation of the algal species, the algal base can be pre-treated in several stages to make it suitable for biodiesel production (Fig. 3b) [102–105]. Advanced methodologies, including machine learning, are increasingly being applied to the study of algal hydrothermal liquefaction, enhancing analytical precision and process optimization [106]. Jazrawi *et al.* performed an initial stage of HTL at 200 °C, demonstrating that approximately 50 % of the nitrogen was transferred to the liquid phase [107]. This resulted in a 55 % reduction in nitrogen content in the final bio-oil compared to that obtained *via* one-step HTL. Nevertheless, the consumption of macroalgae during pre-treatment led to a minor decrease in the bio-oil yield in the subsequent stage. Notably, while current research on two-step HTL predominantly centers on microalgae [108], investigations into macroalgae remain in their nascent stages.

In experimental comparisons between traditional one-step HTL and two-step HTL of macroalgae, Wang *et al.* obtained and analyzed bio-oil under varying conditions. Low-temperature HTL was performed at 200 °C for one hour, while high-temperature HTL was conducted at 300 °C for the same duration. In the two-step HTL process, the first step was carried out at 200 °C for 30 min, followed by the second step at 300 °C for an additional 30 min. The results indicated that the bio-oil yield from low-temperature HTL was lower due to incomplete conversion of macroalgae under these conditions. However, the bio-oil yields from high-temperature HTL and two-step HTL were observed to be comparable, with both exceeding the yield obtained from low-temperature HTL. Notably, the two-step process generated fewer solid residues. Upon analyzing the composition of the bio-oil, it was found that the hydrocarbon content in the bio-oil derived from the two-step reaction was approximately 45.46 %. The content of nitrogen-containing compounds was 16.08 %, significantly lower than the 28.64 % recorded after the high-temperature reaction [91]. Based on these findings, it was concluded that the bio-oil obtained from the two-step HTL process exhibited superior quality.

In conventional HTL, the heating rate is typically slower, often requiring more than ten minutes to reach the predetermined temperature. The extended heating time can induce additional reactions, thereby reducing the conversion efficiency of biomass into bio-oil. In contrast, rapid HTL features a faster heating rate, enabling the predetermined temperature to be achieved within tens of seconds to a few minutes. Fast HTL has been applied to macroalgae, though research remains relatively limited compared to other feedstocks [108].

Bio-oils derived from macroalgae exhibit disadvantages such as high viscosity and acidity compared to petroleum, along with a complex composition that poses challenges for storage. Consequently, they require further hydrotreating before being utilized as fuel. Hydrotreating involves the removal of oxygen from oxygenated compounds in bio-oil through a hydrodeoxygenation reaction, producing hydrocarbons and water. This process reduces the oxygen content of the bio-oil, thereby enhancing its calorific value. Hydrotreating is achieved by introducing hydrogen into the reaction vessel in the presence of a metal or metal/carrier catalyst. Various types of catalysts are employed in bio-oil hydrotreating, with noble metal catalysts (Ru, Rh, Pd, Pt, Re) demonstrating superior performance. However, their high cost significantly increases expenses and restricts large-scale application [109]. In contrast, transition metal-based catalysts, such as $NiMo/Al_2O_3$ [110] and $CoMo/Al_2O_3$ [111], are widely used due to their relatively low cost and favorable catalytic properties.

Table 2
Raw materials and working conditions of two-step hydrothermal liquefaction of microalgae and macroalgae.

Classify	Raw material	Pretreatment condition	Second stage	Implications for bio-oil	Ref.
Microalgae	*Chlorella vulgaris*	100-200 °C, 5-15 min	250-350 °C, 10 min	The nitrogen content in bio-oil has decreased by more than 55 %	[99]
	Nannochloropsis	180 °C, 30 min	240-300 °C, 30 min	The content of fatty acid esters increased by 61.9 % and the content of nitrogen-containing compounds was 2.3 %	[100]
	Scenedesmus/ Desmodemus	180-260 °C, 0.5-24 h	360 °C, 72 h	The nitrogen content in the second-stage HTL bio-oil decreased from 3.5 wt% to 1.3 wt%, and the oxygen content decreased from 16.3 wt% to 0.8 wt%	[101]
	Chlorella	200 °C, 15 min	300 °C, 15 min	The yields of bio-oil and hydrocarbons increased from 16.0 % and 2.9 % to 28.7 % and 5.7 %, respectively	[48]
Macroalgae	*Enteromorpha clathrata*	200 °C, 30 min	300 °C, 30 min	Under high-temperature conditions, compared with the first stage HTL, the yield of bio-oil in the second stage HTL changed little, but the amount of solid residue was significantly reduced	[91]
	Ulva prolifera	350 °C, 1 h	400 °C, 2 h	The carbon content increased from 76.4 % to 87.2 %, and the calorific value increased from 35.67 MJ/kg to 37.3 MJ/kg	[25]
	Saccharina japonica	350 °C, 1 h	400 °C, 2 h	The carbon content increased from 74.9 % to 87.3 %, and the calorific value increased from 36.0 MJ/kg to 41.2 MJ/kg	[25]
	Lemna minor	350 °C, 1 h	400 °C, 2 h	The carbon content increased from 73.9 % to 85.9 %, and the calorific value increased from 36.1 MJ/kg to 40.8 MJ/kg	[25]
	Pyropia yezoensis	350 °C, 1 h	400 °C, 2 h	The carbon content increased from 74.2 % to 87.2 %, and the calorific value increased from 35.7 MJ/kg to 41.5 MJ/kg	[25]

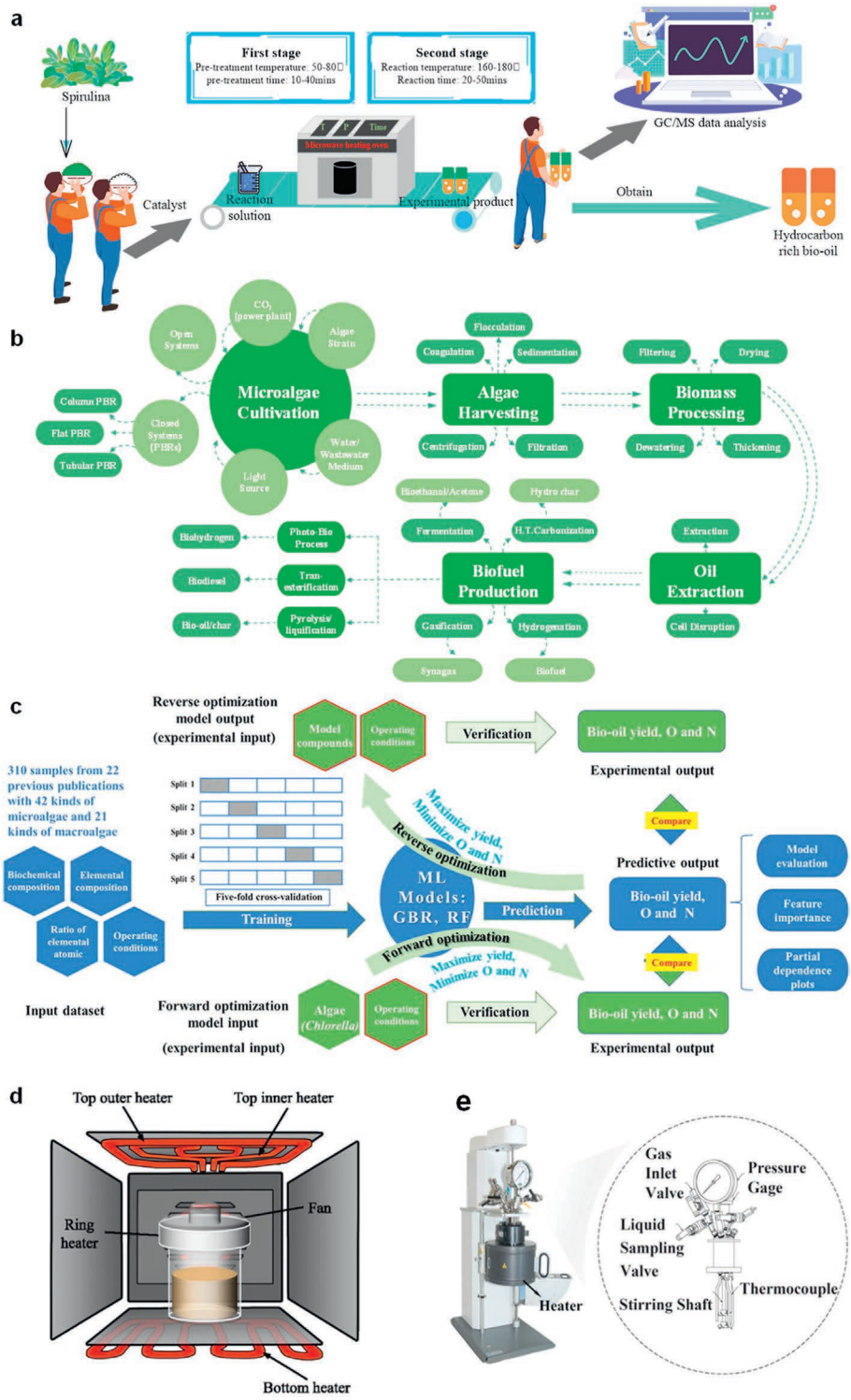


Fig. 3. (a) Experimental flow of two-stage HTL of algae. (b) Flow chart of the production of biofuel from microalgae. Copied with permission [103–105]. Copyright 2024, 2001, 2025, Elsevier. (c) Machine learning prediction and optimization of bio-oil production from the HTL of algae. Copied with permission [106]. Copyright 2021, Elsevier. (d) "Black box" batch reactor. (e) Interactive batch reactor. (d, e) Copied with permission [102]. Copyright 2023, American Chemical Society.

4.2. Emerging role of machine learning in HTL optimization

The complexity of HTL processes, involving numerous interdependent parameters (temperature, pressure, residence time, catalyst type, biomass composition, *etc.*), makes traditional optimization approaches challenging and time-consuming. Machine learning (ML) has emerged as a powerful tool for predicting and optimizing HTL outcomes, enabling data-driven insights that complement experimental research (Fig. 3c) [106]. Data requirements and preprocessing form the foundation of effective ML models. HTL datasets typically include biomass properties (elemental composition, biochemical components), process conditions, and product characteristics (bio-oil yield, composition, quality metrics) [112]. The quality and comprehensiveness of these datasets sig-

nificantly impact model performance. Recent efforts have focused on creating standardized databases to facilitate ML applications in HTL [112,113].

In terms of algorithm selection, tree-based methods have demonstrated particular effectiveness for HTL prediction tasks. Random Forest (RF) and Gradient Boosting Regression (GBR) algorithms have been widely employed for predicting bio-oil yield and quality parameters [112,114]. These algorithms can handle complex, non-linear relationships between process parameters and outcomes. Comparative studies indicate that GBR often outperforms RF for multi-target predictions, though optimal algorithm choice may depend on specific prediction objectives [115]. Key predictive variables identified through feature importance analysis consistently highlight the dominant role of process temperature, followed by residence time and biomass characteristics [114,116]. For instance, Zhang *et al.* [106] demonstrated that temperature was the most critical factor influencing bio-oil yield from algal HTL, with optimal predictions achieved using GBR models ($R^2 > 0.9$). Similarly, studies have successfully predicted nitrogen content in bio-oil [114,117] and energy recovery rates [118] with high accuracy using ML approaches. ML models have enabled the optimization of multiple objectives simultaneously, such as maximizing bio-oil yield while minimizing nitrogen content or production costs [119]. This multi-objective optimization capability represents a significant advancement over traditional single-parameter optimization. For example, recent work has integrated ML with experimental validation to design optimized microalgae biorefineries [119], demonstrating the practical utility of these approaches.

Despite promising results, challenges remain in ML applications for HTL. Data scarcity and inconsistency across studies limit model generalizability [113]. There is also a need for more comprehensive feature sets that include catalyst properties and detailed product compositions. Future directions should focus on developing larger, standardized datasets [112], exploring deep learning approaches for more complex predictions [113], and enhancing model interpretability to extract fundamental insights about reaction mechanisms [116]. As ML techniques continue to evolve alongside experimental research, they hold significant potential for accelerating the optimization and commercialization of HTL processes for macroalgae conversion.

5. Elemental transport in hydrothermal liquefaction of macroalgae

In recent years, extensive research has been conducted on the factors influencing HTL reaction conditions and catalysts, leading to significant improvements in bio-oil yields [51]. Bio-oil primarily consists of hydrocarbons (including cyclic, aliphatic, and aromatic hydrocarbons), oxygenated compounds (such as fatty acids, methyl esters, and alcohols), and nitrogenous compounds (*e.g.*, pyrroles, pyridines) [120,121]. The quality of bio-oil derived from HTL of macroalgae tends to improve with an increase in the content of hydrocarbons and specific oxygenated compounds.

Understanding the elemental migration during bio-oil conversion is of critical importance [121]. The main elements in macroalgae include carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S). As shown in Table S2 (Supporting information) [25,27,28,44,111], the content of these different elements varies across various species of macroalgae.

Notably, carbon, hydrogen, and oxygen together account for the majority of the total elemental composition in macroalgae. High concentrations of nitrogen and sulfur have adverse effects on bio-oil quality [16]. The combustion of sulfur-containing fuels generates sulfur oxides (SO_x), which are primary pollutants responsible for particulate matter pollution, acid rain, and significant health risks [107]. During the catalytic upgrading process of bio-oil, sulfur compounds adsorb onto the active centers of the hydrogenation catalyst, forming stable metal sulfides, which leads to catalyst deactivation [122]. When fuels containing these elements are combusted, they produce nitrogen oxides (NO_x) and SO_x, which are major pollutants responsible for smog, acid rain, and health risks. Additionally, many nitrogenous compounds in bio-oil, such as pyridine, exhibit toxicity and tend to induce detrimental free radical reactions that compromise the stability of bio-oil during storage. During HTL, the primary components of macroalgae, including proteins, lipids, and carbohydrates, undergo decomposition from macromolecules into corresponding monomers. The main transformation pathways for these components are illustrated in Fig. 4 [37,123–125].

Elemental balance analysis of the system reveals that the migration pathways and final distribution of carbon, hydrogen, and oxygen during HTL exhibit significant variation and are highly dependent on process conditions. Carbon is predominantly distributed between bio-oil and solid residue. In single-stage HTL, approximately 30%-60% of the feedstock carbon is recovered in the bio-oil fraction, 10%-25% is transferred to the aqueous phase as water-soluble organic compounds, and 15%-30% remains in the solid residue [126]. Elevated reaction temperatures generally enhance the decomposition of macromolecules, thereby promoting the transfer of carbon to the bio-oil phase. The distribution of hydrogen plays a critical role in determining bio-oil quality, with 40%-60% of the hydrogen incorporated into bio-oil, directly influencing its H/C ratio and calorific value; an additional 20%-35% is found in the aqueous phase, primarily in the form of water molecules [126,127]. Oxygen removal constitutes a primary objective of HTL, primarily facilitated through decarboxylation and dehydration reactions. A substantial portion of oxygen (40%-60%) migrates to the aqueous phase, while 10%-20% is released into the gas phase as CO_2, resulting in residual oxygen content in bio-oil being reduced to 10%-20% [128]. The use of catalysts significantly influences elemental partitioning. For instance, catalytic hydroprocessing with $NiMo/Al_2O_3$ can reduce the oxygen content in bio-oil from 20% to below 2.25%, while increasing the hydrogen content from 9.61% to 14.08%, thereby substantially enhancing fuel quality [128]. Temperature is a key operational parameter: higher temperatures favor deoxygenation and denitrogenation, but excessive temperatures may induce over-cracking, leading to increased gas formation and reduced liquid product yield [129].

In the HTL of biomass, the Maillard reaction is the primary pathway for the formation of nitrogen heterocycles (N-H compounds). During HTL, amino acids react with reducing sugars under high temperature and pressure to generate nitrogen heterocycles such as pyrazines and pyridines. Additionally, amino acids containing N-H structures can directly form indoles, imidazoles, and pyrrolidines through decarboxylation and deamination. Furthermore, due to the complexity of reactions in HTL, nitrogen-containing compounds in the organic, aqueous, and solid phases undergo mutual transformations.

During HTL, the majority of nitrogen transitions into the liquid phase [130]. In the liquid phase, nitrogen primarily exists in the forms of NH_4^+, NO_3^-, and NO_2^-. If released in large quantities, these compounds can significantly contribute to water eutrophication, leading to issues such as algal blooms [131]. To enhance bio-oil quality, it is crucial to increase its carbon and hydrogen content while minimizing the levels of nitrogen, oxygen, and sulfur [132]. The primary source of nitrogen in bio-oil is protein decomposition, which results in higher nitrogen content in bio-oil derived from high-protein biomass compared to macroalgal feedstocks that are rich in lipids and carbohydrates [133].

The regulation of nitrogen content in bio-oil mainly involves two approaches: Optimization of feedstock characteristics and pretreatment. Optimization of feedstock characteristics primarily in-

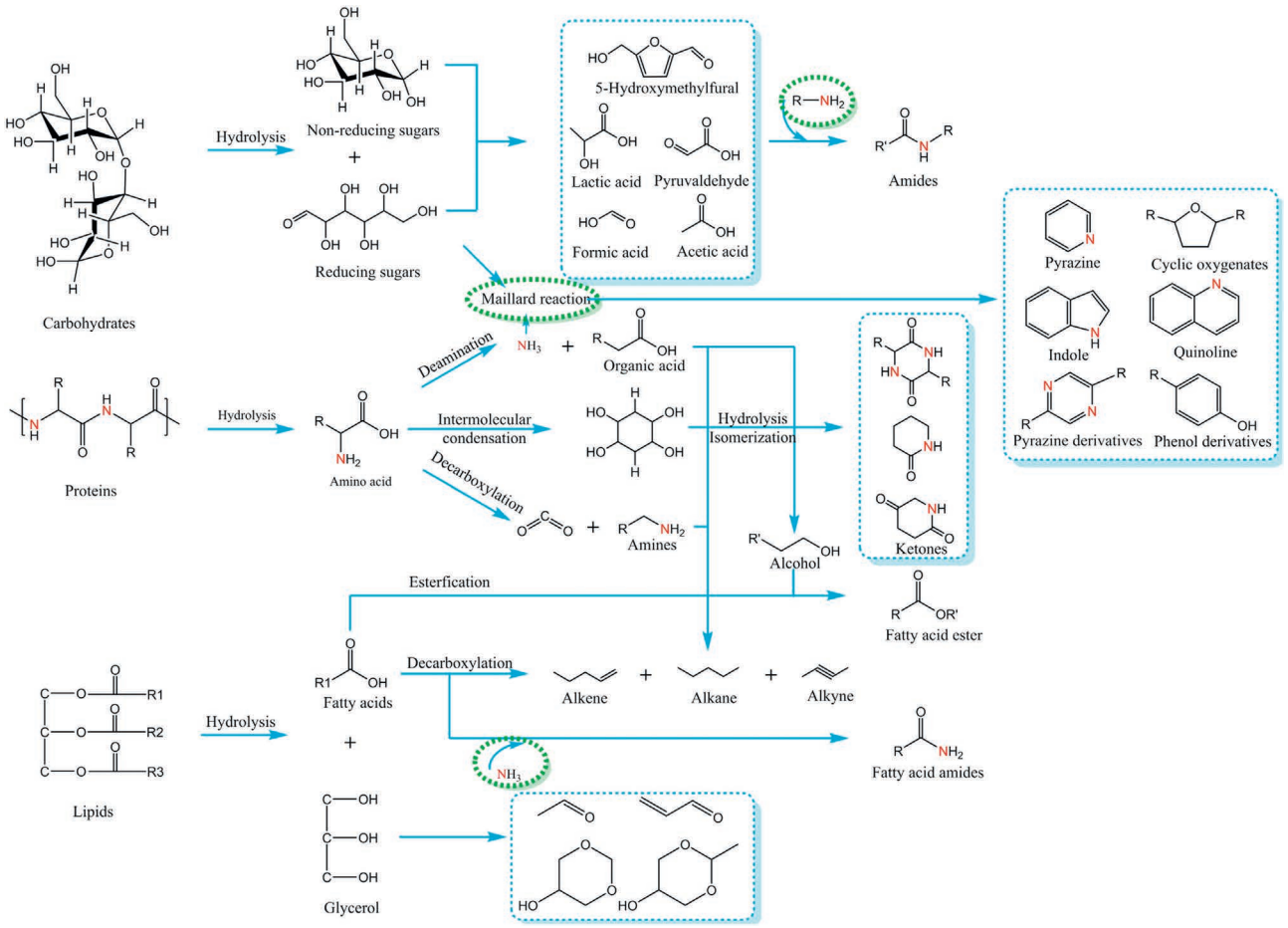


Fig. 4. Transformation of major compounds in macroalgae.

volves selecting biomass with high lipid content, low protein, and low carbohydrate levels during HTL. When lipid content is high, the co-hydrothermal liquefaction (Co-HTL) of lipids and proteins creates a dilution effect, thereby reducing the nitrogen content in bio-oil. Pretreatment, on the other hand, involves two-stage HTL and protein removal treatment of biomass to alter the biomass composition, reduce protein content in the biomass, and ultimately decrease nitrogen content in the bio-oil.

Raw material optimization strategies, particularly co-HTL, enable the quantitative and effective reduction of nitrogen content in bio-oil. Studies have demonstrated that co-liquefying protein-rich macroalgae with lipid-rich biomass significantly suppresses nitrogen transfer through both dilution effects and synergistic interactions. For example, one study reported that co-liquefying high-protein algae with lipid-rich feedstock at a 1:1 mass ratio reduced the nitrogen content in the resulting bio-crude from 5.2 % to 2.8 %, representing a 46 % reduction [134]. Two-stage HTL represents another efficient strategy for nitrogen mitigation. Singh and Mohanty provided quantitative evidence by subjecting the high-protein microalga Monoraphidium sp. KMC4 to a two-step process: Pre-treatment at 220 °C followed by liquefaction at 300 °C. Compared to single-stage HTL conducted directly at 350 °C, this approach reduced the nitrogen content in bio-crude from 4.6 % to 2.88 %, achieving a 37 % nitrogen removal efficiency [129]. Furthermore, catalytic hydroprocessing enables more profound denitrogenation. Zhao *et al.* demonstrated that under optimized two-stage catalytic hydroprocessing conditions using a $NiMo/Al_2O_3$ catalyst at 350 °C, the nitrogen content in the final upgraded biofuel was reduced to as low as 0.016 % [128]. These quantitative findings collectively demonstrate that nitrogen levels in bio-crude can be effectively controlled and substantially reduced through strategic approaches—including feedstock blending, two-stage processing, and catalytic upgrading—thereby facilitating subsequent refining and enabling its use as a high-quality renewable fuel.

Costanzo *et al.* used a two-step HTL process, in which low-temperature pretreatment can decompose nitrogen-containing organic matter, disrupt the cellular structure of biomass, and promote the dissolution of nitrogen-containing compounds, thus improving their migration efficiency in the aqueous phase. In addition, the low-temperature pretreatment can optimize the conditions of the subsequent high-temperature reaction, reduce the occurrence of side reactions, and further improve the nitrogen migration efficiency and the quality of bio-oil. Nitrogen removal in bio-oil from algae pretreated at 225 °C for 15 min was 45 % [135]. Algae with high lipid content generate bio-oils with higher hydrocarbon content and HHV, while those with high carbohydrate content produce bio-oils with lower levels of hydrocarbons and HHV. Algae with high protein content exhibit intermediate characteristics between these two extremes [136].

Notably, synergistic effects arise between different macroalgae components, leading to the formation of N-cyclic compounds *via* the Maillard reaction between proteins and carbohydrates [137] and the production of amides through the interaction between lipids and proteins [138]. System temperature has a substantial impact on bio-oil composition [139]. Higher reaction temperatures promote an increase in hydrocarbon content in bio-oil, while nitrogen content tends to rise within the temperature range of 175-275 °C [139]. In the temperature range of 270-330 °C, nitrogen

content reaches its peak and subsequently decreases from 4.7 % to 4 % as the temperature increases to 370 °C [94]. Although reaction time significantly affects bio-oil yield, its influence on nitrogen migration remains relatively minor [140]. A study investigating the HTL of six macroalgal species revealed variations in nitrogen content in the resulting bio-oil depending on the species. According to the findings, bio-oil derived from the marine macroalga Ulva exhibited the lowest observed nitrogen content at 5.8 %. In contrast, bio-oil obtained from the marine macroalga Cladophora demonstrated the highest recorded nitrogen content at 7.1 %. Notably, despite producing bio-oil with the highest nitrogen content, Cladophora itself contained the lowest nitrogen content among the six macroalgal species examined. The nitrogen content of bio-oils derived from the remaining four macroalgal species ranged between 6.3 % and 6.8 % [28].

6. Conclusions, challenges and outlook

HTL is a promising technology that efficiently converts macroalgae into usable liquid fuels. Due to its relatively mild reaction conditions compared to other conversion methods, it significantly reduces energy consumption, rendering it both technically and economically feasible for the transformation of macroalgae into bio-oil.

This review consolidates current research on the HTL of macroalgae, emphasizing how specific reaction conditions (reaction temperature, duration, catalyst type, and solution environment) influence the yield and quality of bio-oil. The key findings and perspectives of this review are summarized as follows:

(1) The optimal reaction temperature for HTL of macroalgae without catalysts generally falls within the range of 240-280 °C. At these temperatures, the bio-oil yield initially increases before gradually declining. This trend is attributed to incomplete reactions at lower temperature ranges and an increased tendency for products to convert into gas-phase and solid-phase states at higher temperatures.
(2) In the HTL process of macroalgae, the reaction duration typically spans from 15 min to 45 min. Extended reaction times enhance the interaction between bio-oil components, thereby promoting the formation of solid residues.
(3) Studies indicate that utilizing alcohols as the solution environment in HTL enhances both the yield and quality of bio-oil for the following reasons: (a) The alcohol-water mixture exhibits a lower critical point compared to pure water, enabling alcohol to function as an *in-situ* hydrogen donor; (b) alcohols can facilitate esterification reactions with acidic compounds in bio-oil.
(4) In HTL, the addition of catalysts accelerates the conversion process by reducing the activation energy and optimizing reaction conditions, while simultaneously enhancing the yield and quality of bio-oil. Heterogeneous catalysts, with their high catalytic activity and regenerative properties, demonstrate promising application prospects.
(5) The bio-crude oil produced *via* HTL currently contains a significant amount of elemental nitrogen (N). By regulating the feedstock characteristics and employing pretreatment methods, the nitrogen content in bio-oil can be effectively reduced, thereby improving the overall quality of the bio-oil.

Although HTL technology has garnered significant research attention, inherent challenges remain to be addressed, including:

(1) Reaction conditions: Since these conditions directly influence bio-oil yield, identifying optimal reaction conditions continues to be a critical research focus.
(2) Catalyst use: While catalysts generally improve bio-oil yields, further investigation into their enhancement mechanisms is necessary to identify suitable catalysts that exhibit both excellent catalytic activity and high stability (withstanding the high temperatures and pressures of HTL while ensuring recyclability).
(3) Production costs: The production costs of bio-oil *via* HTL technology remain significantly higher compared to fossil energy sources. Given that high costs hinder the market application of bio-oil, optimizing the process to reduce costs represents a key challenge that must be addressed.

To further advance the practical application and industrialization of HTL technology, future research should prioritize the following key areas:

(1) Although HTL has achieved significant progress at the laboratory scale, efforts must now shift toward multi-scale development to bridge the gap between microscopic reaction mechanisms and macroscopic process engineering. Through process simulation, energy integration, and life cycle assessment (LCA), more efficient and low-energy-consumption HTL systems can be designed. Integrating HTL with complementary processes, such as anaerobic digestion and algae cultivation, can enhance material and energy recycling, improving overall system sustainability.
(2) While the development of highly active and stable catalysts remains critical, equal emphasis should be placed on employing advanced analytical methods, such as machine learning, to gain deeper mechanistic understanding of catalyst deactivation during HTL. This knowledge will enable the design of *in-situ* regeneration strategies, supporting the long-term stability and continuous operation of HTL processes.
(3) Intensified research is needed to develop efficient bio-oil upgrading strategies tailored to its complex composition, particularly through hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN). Simultaneously, novel conversion pathways that transform nitrogen-containing compounds into high-value chemicals should be explored to improve product utility and economic viability.
(4) The transition of HTL from laboratory research to industrial commercialization demands strengthened interdisciplinary collaboration. A systematic evaluation of engineering challenges and economic feasibility at scale is essential. Moreover, innovative collaboration models involving government, industry, and academic institutions should be developed. Combining policy incentives with technological advancements will be crucial for reducing production costs and enhancing the market competitiveness of bio-oil.
(5) Establishing a publicly accessible HTL database-incorporating data on diverse catalysts, reactor configurations, feedstock properties, and operating conditions-alongside predictive models for product yield and quality, would provide vital support for process optimization and rational catalyst design.

CRediT authorship contribution statement

Zhaoying Li: Writing – original draft. **Wanlong Zhao:** Writing – original draft. **Chenyu Yang:** Writing – original draft. **Yingnan Duan:** Writing – review & editing. **Xianghao Zha:** Writing – review & editing. **Zhurui Shen:** Writing – review & editing.

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.

Acknowledgments

This work was supported by Kashi University Research Team for Low-Carbon Recycling of Biomass Wastes, Open Project Fund of Xinjiang Biomass Solid Waste Resources Technology and Engineering Center (No. KSUGCZX202301) and the Central Guide Local Science and Technology Development of Xinjiang Uygur Autonomous Region (No. ZYYD2023B16).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2026.112441.

References

[1] T.G. Liu, D.H. Xu, L.L. Qian, et al., Water Res. 289 (2026) 124945.
[2] Y.M. Wei, K. Chen, J.N. Kang, et al., Engineering 14 (2022) 52–63.
[3] S. Raikova, T.D.J Knowles, M.J. Allen, et al., ACS Sustainable Chem. Eng. 7 (2019) 6769–6781.
[4] K. Srirangan, L. Akawi, M. Moo-Young, et al., Appl. Energy 100 (2012) 172–186.
[5] H. Kargbo, J.S. Harris, A.N. Phan, Renew. Sust. Energy Rev. 135 (2021) 110168.
[6] J. Arun, P. Varshini, P.K. Prithvinath, et al., Bioresource Technol. 261 (2018) 182–187.
[7] P. Duan, Y. Xu, F. Wang, et al., Biochem. Eng. J. 116 (2016) 105–112.
[8] J. Kosinkova, A. Doshi, J. Maire, et al., Renew. Sust. Energ. Rev. 49 (2015) 1271–1285.
[9] Y.D. Chen, F. Liu, N.Q. Ren, et al., Chin. Chem. Lett. 31 (2020) 2591–2602.
[10] S.M.Z. Hossain, Chem. Eng. Technol. 42 (2019) 2594–2607.
[11] X. Chen, Y. Chen, H. Yang, et al., Bioresource Technol. 273 (2019) 153–158.
[12] K.M.V. Nogueira, V. Mendes, C.B. Carraro, et al., Renew. Sust. Energy Rev. 131 (2020) 109991.
[13] R.C. Rajak, S. Jacob, B.S. Kim, Sci. Total. Environ. 716 (2020) 137067.
[14] R.P. Brexó, A.S. Sant'Ana, Renew. Sust. Energy Rev. 73 (2017) 423–434.
[15] X. Gu, L. Yu, N. Pang, et al., Appl. Energy 259 (2020) 114115.
[16] J. Watson, T. Wang, B. Si, et al., Prog. Energy Combust. 77 (2020) 100819.
[17] W. Tian, R. Liu, W. Wang, et al., Bioresource Technol. 263 (2018) 569–575.
[18] P.N.Y. Yek, W.A.W. Mahari, S.H. Kong, et al., Bioresource Technol. 347 (2022) 126687.
[19] E.A. Ramos-Tercero, A. Bertucco, D.W.F. Brilman, Energy Fuels 29 (2015) 2422–2430.
[20] M.H. Marzbali, S. Kundu, P. Halder, et al., Chemosphere 279 (2021) 130557.
[21] D.C. Hietala, C.K. Koss, A. Narwani, et al., Algal Res. 26 (2017) 203–214.
[22] D.A. Lyons, C. Arvanitidis, A.J. Blight, et al., Global Change Bio. 20 (2014) 2712–2724.
[23] C.F.H. Joniver, A. Photiades, P.J. Moore, et al., Algal Res. 58 (2021) 102407.
[24] Y. Kulikova, S. Sukhikh, S. Ivanova, et al., Appl. SCI-Basel. 12 (2022) 569.
[25] Y.P. Xu, P.G. Duan, F. Wang, et al., Biotechnol. Biof. Biop. 11 (2018) 83.
[26] K. Balina, F. Romagnoli, L. Pastare, et al., Energy Procedia 113 (2017) 403–410.
[27] R.B. Madsen, R.Z.K. Bernberg, P. Biller, et al., Sustain. Energy Fuels 1 (4) (2017) 789–805.
[28] N. Neveux, A.K.L. Yuen, C. Jazrawi, et al., Bioresource Technol. 155 (2014) 334–341.
[29] M. Aresta, A. Dibenedetto, M. Carone, et al., Environ. Chem. Lett. 3 (2005) 136–139.
[30] K. Anastasakis, A.B. Ross, Bioresource Technol. 102 (2011) 4876–4883.
[31] D.C. Elliott, T.R. Hart, G.G. Neuenschwander, et al., ACS Sustain. Chem. Eng. 2 (2014) 207–215.
[32] R. Shakya, S. Adhikari, R. Mahadevan, et al., Bioresource Technol. 243 (2017) 1112–1120.
[33] V. Lehr, M. Sarlea, L. Ott, et al., Catal. Today 121 (2007) 121–129.
[34] N. Sudasinghe, B. Dungan, P. Lammers, et al., Fuel 119 (2014) 47–56.
[35] S. Ravikumar, I. Ganesh, M.K. Maruthamuthu, et al., Korean J. Chem. Eng. 32 (2015) 2073–2077.
[36] G. Konwar, R. Banik, S.R. Geed, Chem. Eng. J. 515 (2025) 163456.
[37] I.A. Basar, H. Liu, H. Carrere, et al., Green Chem. 23 (2021) 1404–1446.
[38] K.P.R. Dandamudi, T. Muppaneni, J.S. Markovski, et al., Biomass Bioenergy 120 (2019) 224–228.
[39] K. Brindhadevi, S. Anto, E.R. Rene, et al., Fuel 285 (2021) 119106.
[40] N. Sharma, K.K. Jaiswal, V. Kuma, et al., Renew. Energy 174 (2021) 810–822 74.
[41] H. Li, Z. Liu, M. Wang, et al., IET Renew. Power Gen. 13 (2019) 2215–2220.
[42] J. Arun, K.P. Gopinath, P.S. SundarRajan, et al., Bioresource Technol. Reports 11 (2020) 100465.
[43] B. Biswas, A.C. Fernandes, J. Kumar, et al., Fuel 222 (2018) 394–401.
[44] L. Yan, Y. Wang, J. Li, et al., Bioresource Technol. 292 (2019) 121286.
[45] M.Y. Ong, S. Nomanbhay, Energies 15 (2022) 3974.
[46] S. Raikova, M.J. Allen, C.J. Chuck, Biofuel. Bioprod. Bior. 13 (2019) 1483–1504.
[47] P.J. Valdez, M.C. Nelson, H.Y. Wang, et al., Biomass Bioenergy 46 (2012) 317–331.
[48] J. Chen, J. Zhang, W. Pan, et al., Energ. Convers. Manage. 255 (2022) 115330.
[49] C. Yuan, S. Wang, B. Cao, et al., Energy 173 (2019) 413–422.
[50] C. Ma, J. Geng, D. Zhang, et al., J. Energy Inst. 93 (2020) 581–590.
[51] C. Yuan, S. Wang, L. Qian, et al., Int. J. Energ. Res. 43 (2019) 8841–8851.
[52] C. Gai, Y. Li, N. Peng, et al., Bioresource Technol. 185 (2015) 240–245.
[53] N. Gao, K. Kamran, C. Quan, et al., Prog. Energ. Combust. 79 (2020) 100843.
[54] G. Haarlemmer, C. Guizani, S. Anouti, et al., Fuel 174 (2016) 180–188.
[55] Y. Hu, W. Zhang, J. Yan, et al., J. Energy Inst. 110 (2023) 101311.
[56] M. Piccini, S. Raikova, M.J. Allen, et al., Sustain. Energ. Fuels 3 (2019) 292–301.
[57] H. Rahbari, A. Akram, M. Pazoki, et al., J. Health Sci. 11 (2019) 1–6.
[58] V. Santhosh, S. Periyasamy, Biomass Convers. Bior. 13 (2023) 15295–15305.
[59] J. Lu, Z. Zhang, L. Zhang, et al., Catal. Commun. 149 (2021) 106236.
[60] Y. Li, C. Zhu, J. Jiang, et al., Bioresour Technol. 319 (2021) 124163.
[61] Y.B. Park, J.H. Choi, S.C. Lee, et al., Fuel Process. Technol. 238 (2022) 107486.
[62] O. Norouzi, S. Mazhkoo, S.A. Haddadi, et al., Catal. Today 404 (2022) 93–104.
[63] B. Patel, P. Arcelus-Arrillaga, A. Izadpanah, et al., Renew. Energy. 101 (2017) 1094–1101.
[64] M. Oke, F. Resende, Energy Fuels 37 (2023) 17345–17358.
[65] M. Li, Y. Zhou, C. Hu, Catalysts 13 (2023) 262.
[66] Y. Hu, L. Qi, S. Feng, et al., Fuel 238 (2019) 240–247.
[67] S. Karimi, F. Meshkani, M. Rezaei, et al., Fuel 372 (2024) 131945.
[68] Y. Mao, J. Zhu, H. Li, et al., J. Solid State Chem. 346 (2025) 125294.
[69] F. Nasution, H. Husin, F. Abnisa, et al., Energ. Convers. Manage. 273 (2022) 116440.
[70] H. Zhang, C. Xu, J. Bi, et al., Sep. Purif. Technol. 374 (2025) 133542.
[71] H. Lv, L. Zhang, H. Zhang, et al., J. Environ. Chem. Eng. 12 (2024) 114305.
[72] M. Liu, X. Yu, X. Yu, et al., J. Ocean U. China 21 (2022) 1214–1226.
[73] J. Nallasivam, P.F. Prashanth, S. Harisankar, et al., Bioresource Technol. 346 (2022) 126515.
[74] W. Yang, X. Li, S. Liu, et al., Energ. Convers. Manage. 87 (2014) 938–945.
[75] M. Saber, A. Golzary, M. Hosseinpour, et al., Appl. Energy 183 (2016) 566–576.
[76] Y. Guo, T. Yeh, W. Song, et al., Renew. Sust. Energy Rev. 48 (2015) 776–790.
[77] G. Deng, X. Tang, J. Li, et al., Fuel 390 (2025) 134709.
[78] J. Lu, J. Wu, L. Zhang, et al., Fuel 279 (2020) 118529.
[79] J. Xu, X. Dong, Y. Wang, Ind. Crop. Prod. 151 (2020) 112458.
[80] M.J.B. Fong, A.C.M. Loy, B.L.F. Chin, et al., Bioresource Technol. 289 (2019) 121689.
[81] A.A. Jazie, J. Haydary, S.A. Abed, et al., Algal Res. 61 (2022) 102596.
[82] C. Liu, L. Kong, Y. Wang, et al., Algal Res. 33 (2018) 156–164.
[83] S. Cheng, L. Wei, M. Rabnawaz, Fuel 223 (2018) 252–260.
[84] L. Zhou, A. Lawal, Catal. Sci. Technol. 6 (2016) 1442–1454.
[85] A. Yerrayya, A. Nikunj, P.F. Prashanth, et al., Energy 244 (2022) 123192.
[86] Z. Cui, F. Cheng, J.M. Jarvis, et al., Bioresource Technol. 310 (2020) 123454.
[87] X. Peng, X. Ma, Y. Lin, et al., Energ. Convers. Manage. 117 (2016) 43–53.
[88] X.Z. Yuan, H. Li, G.M. Zeng, et al., Energy 32 (2007) 2081–2088.
[89] B. Biswas, A.A. Kumar, Y. Bisht, et al., Bioresource Technol. 242 (2017) 344–350.
[90] C. Chen, J. Zhu, S. Jia, et al., Energy 162 (2018) 460–475.
[91] S. Wang, S. Zhao, X. Cheng, et al., Bioresource Technol. 319 (2021) 124176.
[92] B.B. Uzoejinwa, X.H. He, S. Wang, et al., J. Therm. Anal. Calorim. 136 (2019) 2001–2016.
[93] Y. Zhu, Y. Qin, W. Song, et al., J. Energy Inst. 120 (2025) 102018.
[94] M. Gong, W. Jiang, S. Wang, et al., J. Environ. Chem. Eng. 12 (2024) 114010.
[95] S. Wang, Y. Mukhambet, S. Esakkimuthu, et al., J. Clean. Prod. 348 (2022) 131245.
[96] S. Masoumi, A. Dalai, Biomass Bioenergy 151 (2021) 106168.
[97] R. Mishra, V. Kumar, P. Kumar, et al., Fuel 316 (2022) 123377.
[98] G. Subhash, M. Rajvanshi, G. Kumar, et al., Bioresource Technol. 343 (2021) 126155.
[99] C. Jazrawi, P. Biller, Y. He, et al., Algal Res. 8 (2015) 15–22.
[100] S. Dong, X. Huang, X. Yang, Fuel 324 (2022) 124641.
[101] L.C. Bondurant, W. Obeid, P.G. Hatcher, Org. Geochem. 182 (2023) 104637.
[102] B. Zhang, B.K. Biswal, J. Zhang, et al., Chem. Rev. 123 (2023) 7193–7294.
[103] U. Shashikumar, K.R. Ranjan, A. Sharma, et al., Biomass Bioenergy 187 (2024) 107278.
[104] W.Z. Cheng, O. Zmora, R. Kopel, et al., Aquaculture 195 (2001) 35–49.
[105] C.Y. Yang, X.R. Ma, Y.H. Fan, et al., J. Energy Inst. 123 (2025) 102277.
[106] W. Zhang, J. Li, T. Liu, et al., Bioresource Technol. 342 (2021) 126011.
[107] C. Yuan, S. Zhao, J. Ni, et al., Fuel 334 (2023) 126488.
[108] R. Kumar, V. Strezov, Renew. Sust. Energy. Rev. 135 (2021) 110152.
[109] M. Auersvald, B. Shumeiko, D. Vrtiška, et al., Fuel 248 (2019) 98–110.
[110] C. Yang, S. Wang, Z. Jiang, et al., Fuel 317 (2022) 123528.
[111] I.N. Bravo, S.B. Velásquez-Orta, R. Cuevas-García, et al., Fuel 241 (2019) 255–263.
[112] G. Haarlemmer, L. Matricon, A. Roubaud, Biofuel. Bioprod. Bior. 18 (2024) 1782–1798.
[113] A. Cosgun, M. Günay, R. Yildirim, Green Chem 25 (2023) 3354–3373.
[114] O. Djandja, Y. Shan, L. Fan, et al., Fuel 353 (2023) 129284.
[115] H. Ullah, Z. Ul Haq, S. Naqvi, et al., J. Anal. Appl. Pyrol. 170 (2023) 105879.
[116] X. Liu, X. Zhang, K. Charoenkal, et al., J. Energy Inst. 117 (2024) 101859.
[117] L. Leng, W. Zhang, Q. Chen, et al., Bioresource Technol. 362 (2022) 127791.
[118] T. Liu, W. Zhang, D. Xu, et al., Sci. Total. Environ. 920 (2024) 170779.
[119] W. Wu, C. Huang, Y. Tsai, Algal Res. 74 (2023) 103230.
[120] B. Maddi, E. Panisko, T. Wietsma, et al., Biomass Bioenergy 93 (2016) 122–130.
[121] P. Duan, Z. Chang, Y. Xu, et al., Bioresource Technol. 135 (2013) 710–719.
[122] C. Yang, S. Wang, J. Yang, et al., Green Chem. 22 (2020) 8210–8232.
[123] Y. Hu, M. Gong, S. Feng, et al., Renew. Sust. Energy Rev. 101 (2019) 476–492.
[124] S. Dong, Z. Liu, X. Yang, Chin. Chem. Lett. 35 (2024) 109142.

[125] D. Xu, G. Lin, S. Guo, et al., Renew. Sust. Energy Rev. 97 (2018) 103–118.
[126] J. Lu, J. Watson, Z. Liu, et al., J. Hazard. Mater. 423 (2022) 126961.
[127] L. Matricon, A. Roubaud, G. Haarlemmer, et al., J. Supercrit. Fluid. 196 (2023) 105867.
[128] B. Zhao, Z. Shi, X. Yang, Ind. Eng. Chem. Res. 56 (2017) 6378–6390.
[129] P. Singh, K. Mohanty, Energy Fuels 39 (2025) 10465–10478.
[130] T. Wang, Y. Liu, Q. Liu, et al., Life Sci. 215 (2018) 182–189.
[131] B. Si, J. Li, Z. Zhu, et al., Sci. Total. Environ. 630 (2018) 1124–1132.
[132] J. Watson, J. Lu, R. de Souza, et al., Energy 167 (2019) 189–197.
[133] H. Li, Z. Liu, Y. Zhang, et al., Bioresource Technol. 154 (2014) 322–329.
[134] D. Yu, G. Xie, Q. Chen, et al., Biomass Bioenergy 165 (2022) 106571.
[135] W. Costanzo, U. Jena, R. Hilten, et al., Algal Res. 12 (2015) 377–387.
[136] J. Lu, Z. Liu, Y. Zhang, et al., ACS Sustain. Chem. Eng. 6 (2018) 14501–14509.
[137] J. Yang, H. Niu, K. Corscadden, et al., Appl. Energ. 228 (2018) 1618–1628.
[138] R.B. Madsen, H. Zhang, P. Biller, et al., Energy Fuels 31 (2017) 4122–4134.
[139] L. Garcia Alba, C. Torri, C. Samorì, et al., Energy Fuels 26 (2011) 642–657.
[140] C. Jazrawi, P. Biller, A.B. Ross, et al., Algal Res. 2 (2013) 268–277.