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## CRITICAL REVIEW

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# Hydrothermal liquefaction *vs.* fast/flash pyrolysis for biomass-to-biofuel conversion: new insights and comparative review of liquid biofuel yield, composition, and properties†

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Hydrothermal liquefaction (HTL) and fast/flash pyrolysis are thermochemical processes (TPs) with proven potential to convert biomass into liquid biofuel, which can be comparable to crude oil. HTL is generally preferred for wet biomass, while fast/flash pyrolysis is more suitable for dried biomass, as moisture content plays a crucial role in determining the appropriate conversion method. Beyond moisture content, the biochemical and elemental composition of biomass significantly impacts the physical and chemical characteristics of the resulting liquid biofuels, often increasing the need for upgrading. This review provides a comprehensive comparison of HTL and fast/flash pyrolysis for converting five biomass types—lignocellulosic biomass, microalgae, macroalgae, municipal sludge, and food waste—into liquid biofuels, highlighting the impact of biomass composition on biofuel yield and quality. By linking biomass type, process severity, and liquid biofuel quantity, this study offers a structured framework for selecting the optimal conversion process and severity range to maximize biofuel yield in large-scale applications. Additionally, this review identifies various organic compounds and their concentrations in liquid biofuels produced through HTL and fast/flash pyrolysis from different biomass sources, serving as a valuable resource for developing novel multistage and selective upgrading processes.

### Green foundation

1. HTL and fast/flash pyrolysis are key thermochemical processes for converting biomass into liquid biofuels. Traditionally, moisture content has guided process selection, but this review highlights how both biomass composition and process type influence biofuel yield and quality. Expanding selection criteria beyond moisture improves efficiency, reduces waste, and optimizes resource use.

2. With growing demand for sustainable energy, choosing the right biomass and conversion method is crucial. This review identifies optimal biomass types for HTL and fast/flash pyrolysis, minimizing upgrading needs. By linking biomass composition to conversion efficiency, it supports efficient biofuel production.

3. By analyzing biomass composition and its impact on biofuel quality, this review aids in developing hybrid, selective, and multistage upgrading processes. These insights will enhance biofuel efficiency, minimize environmental impact, and drive scalable renewable energy solutions, advancing sustainable fuel production.

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## 1. Introduction

The continuous rise in the global population is driving industries to operate at full capacity to meet increasing human needs. Even in the 21st century, fossil fuels remain the dominant energy source, supplying more than three-quarters of the world's energy demand.[1] Crude oil forms from organic materials over millions of years under specific temperature and pressure conditions in aquatic environments. This slow natural process, however, cannot keep up with the growing demands of industries in the near future. Instead, organics can be processed using efficient techniques for biofuel pro-

duction, providing a sustainable solution to meet global energy needs.[2] Biomass, a renewable energy source of organic origin, is one of the primary candidates for biofuel production.[3]

With the use of heat and complicated chemical reactions, thermochemical processes (TPs) can convert biomass into biofuels.[4] Among TPs, fast/flash pyrolysis and hydrothermal liquefaction (HTL) show significant potential for producing liquid biofuels from biomass. The elemental characteristics of biomass—carbon (C), hydrogen (H), nitrogen (N), oxygen (O), sulfur (S), along with its proximate features, moisture and ash contents, and biochemical composition (proteins, carbohydrates, and lipids)—are crucial in determining the operational conditions for HTL and fast/flash pyrolysis, as these factors can influence both the yield and quality of the resulting liquid biofuels.[5,6] Each biomass type has distinct characteristics; therefore, HTL and fast/flash pyrolysis should be optimized according to these features to maximize liquid biofuel yield and enhance its quality. For biomass to serve as an effective feedstock for biofuel production, it must be renewable, cost-effective, efficient, and a reduced environmental impact compared to conventional fossil fuels.[7,8] This study reviews five commonly used biomass feedstocks for biofuel production *via* fast/flash pyrolysis and HTL: lignocellulosic biomass, microalgae, macroalgae, municipal sludge, and food waste, as they are widely recognized as renewable organic resources with significant potential for biofuel production.

Lignocellulosic biomass, the most abundant source of biomass for fuel production, ranks as the fourth most significant energy source after coal, petroleum, and natural gas.[9] Composed primarily of cellulose, hemicellulose, and lignin, it offers substantial potential for biofuel production. While lignin is highly resistant to biodegradation, cellulose and hemicellulose can be hydrolyzed into various sugars, such as glucose, xylose, arabinose, and galactose.[10] The distinctive composition of lignocellulosic biomass has positioned it as a key subject in renewable energy research, especially for biofuel production through TPs.

Algal biomass, including both microalgae and macroalgae, stands out as a highly valuable renewable energy source due to its exceptional photosynthetic efficiency, high biomass productivity, and rapid growth rates compared to terrestrial plants. Algae also excel in carbon dioxide ($CO_2$) fixation and oxygen ($O_2$) production. They thrive in liquid media across diverse climates, including marginal areas like deserts and coastal regions, utilizing non-potable water or even wastewater. Unlike traditional crops, algae require minimal water, do not compete with food crops for land, and enable year-round production with the advantage of daily harvesting.[11,12] Microalgae are unicellular organisms with simple cellular structures that can rapidly reproduce, making them ideal for biofuel production due to their high lipid content. In contrast, macroalgae are multicellular, structurally complex organisms with specialized parts like blades and holdfasts, mainly accumulating carbohydrates, which makes them suitable for biogas and bioethanol production. Additionally, microalgae's metabolic

pathways can be easily engineered for higher biomass yield, while macroalgae grow slower and rely on more complex nutrient absorption systems.[13] As a result of its unique properties, algal biomass is a prominent feedstock for producing liquid biofuels through fast/flash pyrolysis and HTL.

Municipal sludge is increasingly recognized as a renewable energy source rather than waste due to its biochemical composition, offering significant potential for profitable biofuel production.[14,15] Wastewater treatment plants typically produce two types of sludge: primary and secondary. Primary sludge, generated in the primary clarifier, contains solid materials such as feces, biodegradable organic matter, and grease, making it rich in lipids. Secondary sludge, or activated sludge, is produced in the biological processes and consists mainly of microbial cells and suspended solids, making it protein-rich. These sludge types are often mixed and treated by anaerobic digestion (AD) to produce biogas and digested sludge.[16] However, municipal sludge can also be processed directly *via* TPs to be converted to value-added products or used as digested sludge for biofuel production through TPs after AD.

Food waste, which accounts for nearly one-third of all food produced for human consumption, contributes approximately 1.3 billion tonnes of waste annually, generating around 3.3 billion tonnes of $CO_2$-equivalent greenhouse gas emissions. Rich in organic materials, food waste is seen as an ideal resource for bioenergy conversion and effective waste management.[17] It contains a wide range of organic components, including starches, proteins, oils, fats, phosphates, nutrients, amino acids, and natural acids.[18] Given its rich content of proteins, carbohydrates, and lipids, food waste is considered as one of the suitable feedstocks for TPs to be converted to biofuels.

From an economic perspective, liquid biofuel production from biomass involves various cost components, including biomass supply, dewatering or drying, pumping, catalysts, phase separation, and by-product management. Among these, biomass supply represents the largest share of the total production cost for the resulting liquid biofuel.[19] The production costs range from US$ 20 to US$ 100 per dry tonne for lignocellulosic biomass,[20] between US$ 1253 and US$ 2016 per dry ash-free tonne for microalgae cultivation,[21] and from US$ 200 to US$ 300 per dry tonne for macroalgae production.[22] In this regard, municipal sludge and food waste are cost-free feedstocks since they are produced as waste and their production has a direct correlation with population. As a result, the conversion of municipal sludge and food waste into liquid biofuels through fast/flash pyrolysis and HTL offers a more economical pathway compared to the use of lignocellulosic or algal biomass. The characteristics of liquid biofuels derived from different biomass types can vary significantly, necessitating varying degrees of upgrading with high costs. Therefore, decisions should factor in feedstock supply, pretreatment, and the costs associated with upgrading the liquid biofuels. This study does not focus on the economic aspects of feedstock and upgrading process costs, as large-scale applications of HTL and fast/flash pyrolysis are still in their early stages. For an

accurate cost analysis, further research is needed to evaluate the quality of liquid biofuels derived from different biomass types through HTL and fast/flash pyrolysis, and to develop the corresponding upgrading processes before scaling up these processes.

To the best of our knowledge, no comprehensive review currently provides biomass-specific optimal process temperature and reaction time ranges for both HTL and fast/flash pyrolysis to maximize liquid biofuel yield. Furthermore, no study systematically identifies and compares the biomass-specific physical and chemical quality of liquid biofuels obtained from these processes. Moreover, a significant gap exists in the literature regarding the levels and types of organic compounds present in liquid biofuels derived from various biomass types through fast/flash pyrolysis and HTL. Therefore, the first objective of this review is to compare temperature, reaction time, and efficiency in fast/flash pyrolysis and HTL across various biomass types, focusing on liquid biofuel yield while considering the biomass's elemental and proximate characteristics. The second objective is to assess the physical and chemical quality of liquid biofuels in relation to biomass biochemical composition, identifying key organic compounds and their concentrations in biofuels. Addressing these gaps will enhance the understanding of biofuel production *via* TPs. Additionally, analyzing the composition of organic compounds in liquid biofuels derived from different biomass types through HTL and fast/flash pyrolysis will pave the way for the development of novel, more efficient, selective, scalable, and multistage biofuel upgrading strategies. Ultimately, this comparative review determines the most suitable biomass types for each thermochemical pathway based on liquid biofuel characteristics, rather than solely relying on biomass moisture as the key factor for processing *via* HTL or fast/flash pyrolysis.

The structure of this review is as follows: Section 2 introduces the liquid biofuels produced from fast/flash pyrolysis (pyrolysis oil) and HTL (bio-crude oil). It also discusses the chemical reactions occurring in fast/flash pyrolysis and HTL as the temperature increases. Section 3 presents the expected liquid biofuel yield ranges for HTL and fast/flash pyrolysis, along with the corresponding temperature and reaction time ranges for each biomass type. Subsequently, Section 4 compares the physical and chemical characteristics of biofuels derived from different biomass types. By identifying the typical biochemical composition of each biomass type, Section 4 also examines the organic compounds present in biofuels produced through HTL and fast/flash pyrolysis, along with their respective levels. Section 5 discusses the biomass-specific advantages and disadvantages of HTL and fast/flash pyrolysis, along with the existing research gaps.

## 2. Thermochemical processes for liquid biofuel production

Thermochemical processes are typically conducted under harsh operational conditions, with temperatures ranging from 180 to 1000 °C (ref. 23 and 24) and pressure varying between 1.013 bar (in pyrolysis) and 20–400 bar (in HTL).[25,26] The choice between HTL and fast/flash pyrolysis is currently based on the moisture content of the biomass,[27] without considering the impact of biomass biochemical composition on the chemical characteristics of the liquid biofuels. The specific temperature, reaction time, and pressure levels in these processes are applied based on the feedstock's composition to maximize the liquid biofuel yield.

### 2.1 Pyrolysis

With pyrolysis, biomass is thermally decomposed without oxygen into liquid (pyrolysis oil), solid (biochar), and gases. The pyrolysis processes yield different proportions of these products based on the chemical reactions within feedstocks at varying temperatures.[28,29] Pyrolysis commonly occurs at temperatures surpassing 300 °C, initiating intricate reactions within biomass. The initial phase, cracking, ranging from ambient temperature to 200 °C, is associated with the evaporation of moisture and light volatiles. During this phase, the breakage of bonds and the formation of hydroperoxide, –COOH, and –CO groups occur due to moisture evaporation.[30] The subsequent stage, spanning from 200 to 500 °C, involves the rapid devolatilization and decomposition of specific kinds of carbohydrates, proteins, and lipids. At this stage, the generation of oxygen-rich functional groups and repolymerization of decomposed compounds also occur.[31,32] The final stage, occurring above 500 °C, is characterized by the degradation of lignin and other organic matter with stronger chemical bonds and gasification.[30] Lignin degradation does not occur exclusively at temperatures exceeding 500 °C; however, its degradation is significantly accelerated at higher temperatures compared to that of carbohydrates, proteins, and lipids. At all pyrolysis temperatures, the degradation of all organic compounds occurs to varying extents. During the degradation processes, all pyrolysis products are formed; however, the yields of pyrolysis oil, biochar, and gases are influenced by biomass characteristics, temperature, reaction time, and heating rate.[33] Since pyrolysis oil is the primary product of fast/flash pyrolysis, this study focuses on its yield and characteristics derived from five different biomass types.

**2.1.1. Pyrolysis oil.** Pyrolysis oil serves as a renewable biofuel capable of substituting for conventional fossil fuels after several upgrading processes. Pyrolysis oil is characterized as dark brown, freely flowing organic liquid consisting predominantly of highly oxygenated compounds.[34] Pyrolysis oil can be highly acidic based on the feedstock used for the pyrolysis process, making it unstable and corrosive. Acidity of pyrolysis oil can lead to challenges in transportation, piping, and storage, as it tends to corrode most metals.[35] Chemically, pyrolysis oil is an intricate blend comprising water, and various organic compounds, such as ketones, phenols, aldehydes, aliphatics, aromatics and acids, as well as lignin compounds. Certain components of pyrolysis oil lead to undesirable traits, such as high corrosivity, poor stability, low viscosity, and a low heating value, which hinder its long-term

storage and use.[36] Mainly, organic compounds like aldehydes, ketones, and carboxylic acids have been identified as major contributors to these undesirable features.[37] However, biomass characteristics can alter the pyrolysis oil's characteristics. Based on biomass composition used in fast/flash pyrolysis and applied operational conditions, pyrolysis oil can contain different levels of organics,[38] which is discussed in Section 4.

**2.1.2 Fast/flash pyrolysis.** In fast pyrolysis, biomass is quickly heated to temperatures between 400 and 900 °C in an oxygen-free environment. This process is marked by efficient heat transfer, rapid heating, short vapor residence time, specific reactor types, and careful temperature control.[39] Flash pyrolysis of biomass is characterized by rapid devolatilization in an oxygen-free setting, fast particle heating, high reaction temperatures between 450 and 1000 °C, and extremely short gas residence times.[23] During the fast/flash pyrolysis, organics of the biomass are mainly converted to pyrolysis oil. Different types of reactors can be used in fast/flash pyrolysis for conversion of volatile matter (VM) of biomass to pyrolysis oil. In this regard, Huang et al.[40] analyzed the application of fast pyrolysis to sewage sludge with 3.10 wt% fixed carbon (FC), 40.10 wt% VM, 5.60 wt% moisture, and 56.80 wt% ash. The process was carried out within a temperature range of 400 to 700 °C, with a flowing gas rate varying from 50 to 300 mL min$^{-1}$ in a drop tube quartz reactor. The production of pyrolysis oil was approximately 45.30 wt% when the temperature was set at 500 °C and the sweeping gas flow rate was 300 mL min$^{-1}$. While the sewage sludge had high ash, the specific reactor design led to high yield of pyrolysis oil in their study. Utilizing microalgae with 14.59 wt% FC, 72.68 wt% VM, 4.39 wt% moisture, and 8.34 wt% ash, Wang et al.[41] conducted fast pyrolysis within a fluidized bed reactor at a temperature of 500 °C. They reported 53.00 wt% yield of pyrolysis oil. For flash pyrolysis, Makibar et al.[42] applied flash pyrolysis on Populus nigra, which had 14.80 wt% FC, 75.40 wt% VM, 9.30 wt% moisture, and 0.50 wt% ash. Using a pilot-scale conical spouted bed reactor, they operated within a temperature range of 425–525 °C and a gas flow rate of 350–360 Nl min$^{-1}$. Their study demonstrated the reactor's suitability, consistently achieving significant pyrolysis oil yields, with the maximum reaching 69 wt% at 455 °C. Alvarez et al.[43] examined flash pyrolysis of sewage sludge, which contained 8.60 wt% FC, 54.20 wt% VM, and 37.20 wt% ash. The process was carried out using a conical spouted bed reactor, with continuous biomass feeding and removal of char, at temperatures spanning from 450 to 600 °C. The highest pyrolysis oil yield of ≈50 wt% (dry basis) was achieved at 500 °C. This suggests that reactor type is a key factor influencing pyrolysis oil yield in the fast pyrolysis of biomass.

Biomass particle size is another crucial parameter in fast/flash pyrolysis, as it influences both the yield of liquid biofuel and the selection of appropriate reactor types.[44] In a study conducted by Shen et al.,[45] the effect of particle size on pyrolysis oil yield was investigated using oil mallee biomass with a composition of 48.40 wt% C, 6.30 wt% H, 0.10 wt% N, 45.20 wt% O, and 0.50 wt% ash. Fast pyrolysis in a fluidized-bed reactor

at 500 °C revealed that increasing the particle size from 0.30 mm to approximately 1.50 mm led to a reduction in pyrolysis oil yield. Similarly, Guizani et al.[46] conducted fast pyrolysis of beech wood with 15.20 wt% FC, 84.30 wt% VM, 8.70 wt% moisture, and 0.50 wt% ash in a drop-tube reactor at temperatures ranging from 450 to 600 °C. Using biomass particle sizes of 370, 490, and 640 μm, they found that gas residence time had minimal influence on oil yield, while the highest yield was achieved with 370 μm particles at 500 °C. These studies highlight the importance of optimizing both particle size and reactor configuration. Reactor type plays a pivotal role in fast/flash pyrolysis, as it governs heat transfer efficiency and reaction rates, directly impacting the extent of cracking, devolatilization, and decomposition reactions. Consequently, reactor type significantly influences pyrolysis oil yield and product distribution yield.[47,48] As pyrolysis technology has advanced, various reactor designs have been explored to improve pyrolysis oil production from biomass. Each reactor type has its own properties, potential for oil yield, and distinct advantages and disadvantages. Various reactors have specific requirements for biomass particle size, which are essential for efficient heat transfer and smooth operation. For instance, fluidized bed pyrolysis reactors typically require biomass particles ranging from 2 to 6 mm, which necessitate preprocessing steps such as cutting and grinding. Raza et al.[49] and Campuzano et al.[50] provide a comprehensive review of the reactors used in pyrolysis processes for biomass processing. Therefore, this study does not delve further into the effects of reactor types on pyrolysis oil production via fast/flash pyrolysis.

In fast/flash pyrolysis, biomass must be dried to a moisture content below 15 wt% to prevent negative effects on pyrolysis product properties. While grinding and drying improve pyrolysis oil yields, they also increase costs. After proper preparation, the biomass is introduced into the reactor for pyrolysis. The resulting char serves as a catalyst for vapor cracking, and specialized cyclones are employed to separate the char, effectively removing it from the reactor immediately after pyrolysis. However, some small char particles may still mix with the liquid product. To prevent further decomposition, vapors and gases are quickly cooled using pyrolysis liquid condensers, which cool the vapors rapidly by direct contact with pyrolysis oil or hydrocarbon liquid.[51–53] While VM is crucial for pyrolysis oil production, a high ash content in biomass can limit pyrolysis oil yield in fast/flash pyrolysis processes by promoting char formation.[54] Therefore, before applying fast/flash pyrolysis, it is essential to analyze the biomass's VM, ash content and composition, and moisture level to ensure it meets the necessary prerequisites for efficient processing and optimal liquid biofuel production. To improve the feasibility of this process for biofuel production, further research is needed to address energy efficiency and economic aspects of reducing particle size. Given the high costs of milling, grinding, and sieving biomass on an industrial scale, additional studies are crucial to design pyrolysis reactors that effectively minimize the impact of particle size during the conversion process.

Biomass characteristics, including elemental composition, ash content, and particle size, along with pyrolysis parameters such as reactor type, temperature, and reaction time, can significantly affect pyrolysis oil yield. Since different biomass types vary in elemental composition and ash content, these differences influence the overall pyrolysis process and pyrolysis oil yield. Table 1 presents the key characteristics of biomass and operational conditions used in fast/flash pyrolysis for maximizing the pyrolysis oil yield derived from lignocellulosic biomass, microalgae, macroalgae, municipal sludge, and food waste. Table 1 clearly indicates that temperature is a critical factor in pyrolysis oil yield. Contrary to common assumptions, higher temperatures in fast/flash pyrolysis do not always reduce pyrolysis oil yield. Instead, increasing the temperature can enhance oil yield up to the point where gasification becomes the dominant reaction. The optimal temperature varies depending on biomass characteristics, heating rate, and reactor type. Table 1 highlights that each type of biomass needs specific temperature and residence time conditions to maximize pyrolysis oil yield. For scaling up fast/flash pyrolysis processes, in addition to biomass characteristics, reaction temperature, and residence time, special attention must be given to biomass particle size and reactor type. With numerous variables at play, optimizing fast/flash pyrolysis at large scales can be challenging. However, when the process is carefully fine-tuned to match biomass characteristics, it becomes a promising method for efficiently producing pyrolysis oil from a diverse range of feedstocks.

## 2.2 Hydrothermal processes

Hydrothermal processes (HTPs) employ water as a pivotal solvent and reactant to convert biomass into value-added products. This process may occur in subcritical water ($T$ < 374.15 °C and $P$ < 220.64 bar) and/or supercritical water ($T$ > 374.15 °C and $P$ > 220.64 bar), sometimes with organic co-solvents, in an oxygen-free environment. In HTPs, four main products are aqueous phase, hydrochar, bio-crude, and gases. It should be noted that in HTPs, four main products are generated; however, similar to pyrolysis, the yield for each product varies in each process.[66] A key advantage of HTPs over pyrolysis is their ability to directly use water as a reaction medium, which removes the need to remove moisture from biomass. As a result, the energy consumption of HTPs compared to pyrolysis can be significantly lower. In HTPs, it is typically practical to manage feedstock with solids making up to 30 wt% of the total weight. The maximum solid loading is determined by the ease of preparing and pumping the feed material. Consequently, feedstock with high moisture content still requires dewatering but does not necessitate the extensive drying typically needed for pyrolysis.[67]

There are three main reactions in HTPs: (1) hydrolysis or depolymerization: the temperature needed for depolymerization in HTPs generally falls within the range of 150–250 °C, and the temperature choice is related to the particular characteristics of the feedstock being processed;[68] (2) decomposition: within HTPs, the smaller molecules produced through hydro-

lysis undergo a sequence of thermal decomposition reactions. These reactions include dehydration, decarboxylation, decarbonylation, deamination, dehydrogenation, and the selective bond cleavage caused by high temperatures. The decomposition of different groups of compounds in HTPs typically takes place within a temperature span of 180–374 °C. Beyond 374 °C, in supercritical conditions, gasification can become the predominant process;[69] (3) repolymerization: at elevated temperatures within HTPs, the assorted reactive fragments generated during decomposition reactions begin to recombine, giving rise to the formation of compounds present in bio-crude oil. These reactions happen simultaneously, making it impossible to pinpoint the exact start and end times of each reaction. Large molecules produced through these recombination reactions are particularly instrumental in the formation of bio-crude. In contrast, smaller molecules tend to remain in the aqueous phase. Numerous organic molecule groups found in bio-crude oil are the outcomes of recombination reactions involving long-chain fatty acids.[70] The products of HTP reactions are affected by factors like temperature, residence time, and the characteristics of the feedstock. As a result, the mechanisms governing various aspects of HTPs are not yet fully understood. As bio-crude oil is the primary product of HTL, this study examines the impact of temperature and residence time on the yield and quality of bio-crude oil produced from various biomass types using the HTL process.

**2.2.1. Biocrude-oil.** Bio-crude oil is a liquid with a dark brown color characterized by a substantial hydrocarbon content.[71] When obtained from biomass sources, bio-crude is considered a viable and environmentally sustainable alternative fuel source that can function as a substitute for fossil fuels.[72] Similar to pyrolysis oil, bio-crude oil comprises a diverse range of organic compound groups, including acids, alkanes, alkenes, aromatic hydrocarbons, aliphatics, N-heterocyclic compounds, ketones, alcohols, esters, and amides. Fig. 1 displays examples of organic compounds that can be present in pyrolysis oil and bio-crude oil. The proportions of these organic compounds in liquid biofuels are significantly affected by the biochemical composition of the biomass undergoing HTL, the precise operating conditions utilized in the HTL, and the approach used for liquid biofuel separation from other products. Bio-crude oil offers versatility, meaning that it can be further refined into a variety of end products, including gasoline, jet fuel, diesel, naphtha, fuel oil, and a heavier fraction suitable for the production of engine lubricants.[73,74] Among HTL's products, bio-crude oil is the most feasible bio-fuel type as an alternative to fossil fuels in industries.[75,76] Therefore, with various upgrading processes that take into account its organic acids, bio-crude oil has the potential to become a viable alternative to conventional crude oil.

**2.2.2 Hydrothermal liquefaction.** Achieving a higher yield of bio-crude oil in the HTL process requires a delicate equilibrium in all depolymerization, decomposition, and repolymerization reactions. The operating conditions of HTL must be intense enough to facilitate the breakdown of organic com-

**Table 1** Biomass elemental composition, ash content, and operational conditions for fast/flash pyrolysis of various biomass for maximizing pyrolysis oil production

| Biomass Name | C (wt%) | H (wt%) | N (wt%) | O (wt%) | Ash (wt%) | $T$ (°C) | Residence time (sec) | Particle size (mm) | Reactor type | Max. pyrolysis oil yield (wt%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Lignocellulosic biomass** | | | | | | | | | | | |
| Kraft lignin | — | — | — | — | — | 399.85 | — | — | Fixed bed | 24.30 | 55 |
| | | | | | | 499.85 | | | | 30.20 | |
| | | | | | | 599.85 | | | | 26.00 | |
| Wood chips | — | — | — | — | — | 399.85 | — | — | | 57.40 | |
| | | | | | | 499.85 | | | | 65.40 | |
| | | | | | | 599.85 | | | | 71.10 | |
| Oat straw | 44.11 | 5.98 | 0.62 | 43.65 | 5.64 | 500 | 0.75–2.50 | 0.25–0.75 | Drop tube | 51.16 | 56 |
| | | | | | | 600 | | | | 28.51 | |
| | | | | | | 700 | | | | 8.47 | |
| Corn straw | 43.12 | 6.19 | 1.44 | 35.68 | 13.57 | 500 | 0.75–2.75 | | | 52.09 | |
| | | | | | | 600 | | | | 26.30 | |
| | | | | | | 700 | | | | 9.41 | |
| Palm kernel shell | 48.82 | 5.68 | 0.42 | 45.08 | 3.87 | 600 | 5.00–6.00 | 0.075–0.125 | Entrained flow | 73.74 | 6 |
| | | | | | | 700 | | | | 68.21 | |
| | | | | | | 800 | | | | 65.88 | |
| | | | | | | 900 | | | | 53.33 | |
| **Microalgae** | | | | | | | | | | | |
| *Chlorella vulgaris* | 43.75 | 6.07 | 7.86 | 41.61 | 5.54 | 600 | 5.00–6.00 | <0.105 | Entrained flow | 45.51 | 6 |
| | | | | | | 700 | | | | 58.35 | |
| | | | | | | 800 | | | | 60.22 | |
| | | | | | | 900 | | | | 52.60 | |
| *Scenedesmus* sp. | 32.10 | 4.80 | 5.30 | 22.10 | 35.20 | 480 | 2.00 | 2.00 | Fluidized bed | 55.00 | 57 |
| *Chlorella vulgaris* remnant | 45.04 | 6.88 | 6.64 | 29.42 | 8.34 | 500 | — | 0.42–0.70 | Fluidized bed | 53.00 | 41 |
| **Macroalgae** | | | | | | | | | | | |
| *Saccharina japonica* | 32.89 | 6.17 | 0.93 | 60.01 | 20.21 | 350 | <3.00 | 0.30–0.50 | Bubbling fluidized-bed | 44.99 | 58 |
| | | | | | | 375 | | | | 40.21 | |
| | | | | | | 400 | | | | 37.41 | |
| | | | | | | 425 | | | | 30.75 | |
| | | | | | | 450 | | | | 28.40 | |
| | | | | | | 500 | | | | 26.67 | |
| *Ulva lactuca* | 33.60 | 5.10 | 3.30 | 28.20 | 29.10 | 550 | 0.50–2.00 | <1.00 | Centrifugal | 65.00 | 59 |
| Seaweed powder | 36.44 | 5.14 | 3.72 | 39.36 | 14.71 | 400 | 60.00 | — | Thermogravimetric analyzer | 23.57 | 60 |
| | | | | | | 500 | | | | 31.87 | |
| | | | | | | 600 | | | | 36.87 | |
| | | | | | | 700 | | | | 37.99 | |
| **Municipal sludge** | | | | | | | | | | | |
| Mixed activated and primary sludge | 38.30 | 5.00 | 3.40 | 37.30 | 16.00 | 400 | 1.70 | 1 | Fluidized bubbling bed | 48.00 | 61 |
| | | | | | | 500 | | | | 53.00 | |
| Digested sewage sludge | 25.50 | 4.50 | 4.90 | 25.80 | 37.20 | 450 | <1.00 | 0.50–3.00 | Conical spouted bed | 45.00 | 43 |
| | | | | | | 500 | | | | 48.00 | |
| | | | | | | 600 | | | | 47.00 | |
| Sewage sludge | 40.60 | 7.10 | 7.70 | 41.20 | 37.20 | 450 | <100.00 ms | 0.50–3.00 | Conical spouted bed reactor | 44.80 | 62 |
| | | | | | | 500 | | | | 48.50 | |
| | | | | | | 600 | | | | 45.40 | |
| **Food waste** | | | | | | | | | | | |
| Waste fish oil | — | — | — | — | — | 525 | 17.00 | — | Continuous pilot plant tubular | 72.83 | 63 |
| Potato peel waste | 43.80 | 6.00 | 4.10 | 46.20 | 9.30 | 450 | 8.00 | 1 | Laboratory auger | 22.70 | 64 |
| Potato peel waste residue | 47.80 | 6.40 | 4.00 | 41.80 | 6.50 | | | | | 25.60 | |
| Grape seeds powder | 50.90 | 5.40 | 2.50 | 36.90 | 4.10 | 750 | 600.00 | — | Oven | 28.92 | 65 |
| | | | | | | 850 | | | | 32.56 | |
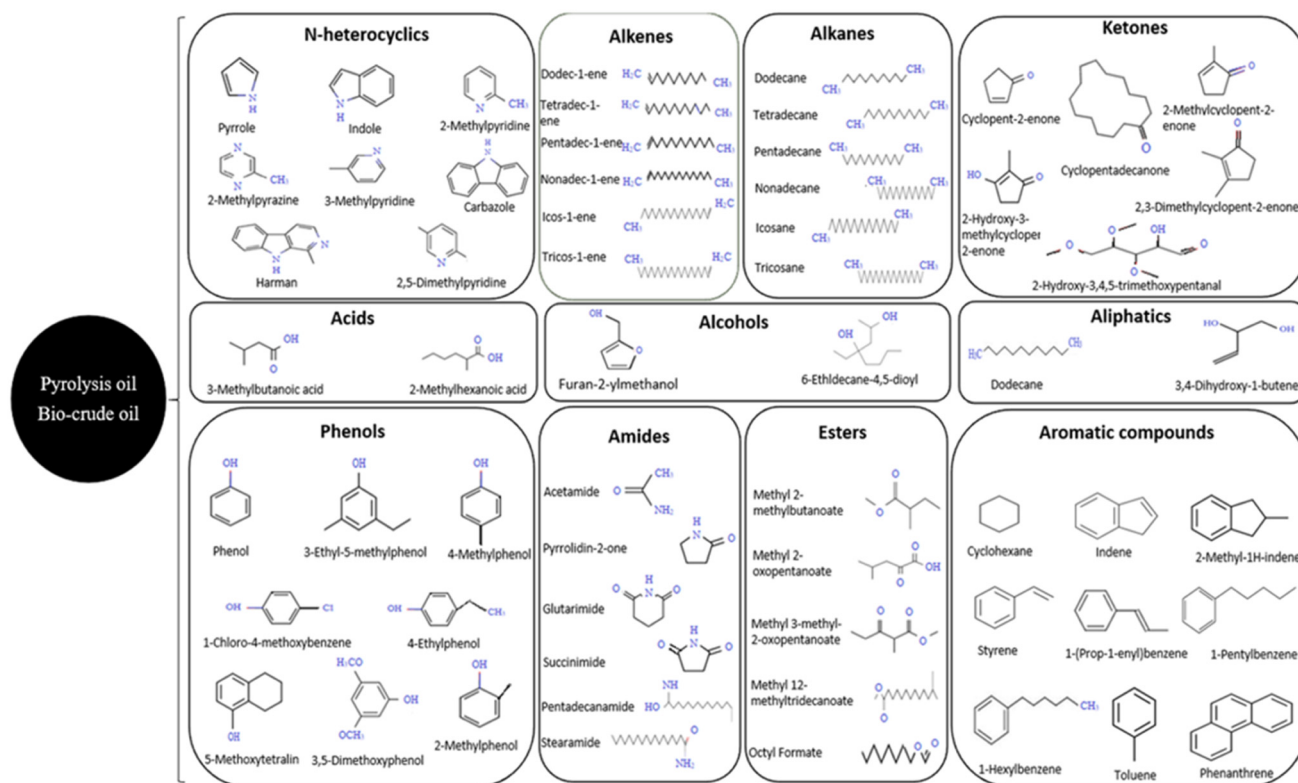
**Fig. 1** Organic compounds that may exist in pyrolysis oil and biocrude oil derived from different biomass.[4,38,40,77]

pounds into the constituents that contribute to bio-crude oil formation. However, it is equally important to avoid excessively severe conditions, as heightened temperatures may result in the decomposition of bio-crude oil into gaseous products. Striking the right balance is essential for the effective optimization of the HTL process.[4] Thus, optimizing operational parameters, including temperature, reaction time, solvent type, and pressure are crucial steps for the HTL process efficiency.

Instead of utilizing the moisture of biomass as the solvent, organic solvents are also investigated in HTL as they play a key role in bio-crude oil yield. The selection of solvent affects both the temperature needed to achieve the maximum bio-crude yield in the HTL process and the overall yield of bio-crude oil. Numerous studies have demonstrated that using biomass moisture or water as the sole solvent typically results in lower yields of water-insoluble oily products compared to organic solvents such as methanol, ethanol, isopropanol, and acetone.[78–81] By using alcohol or acetone as solvent, it is possible to reach supercritical conditions at lower temperatures. This is primarily attributed to the high critical temperature and dielectric constant of water, which limits its ability to effectively dissolve hydrophobic, high-molecular-weight decomposition products from biomass components like cellulose, hemicellulose, and lignin.[82] Organic solvents—particularly alcohols—exhibit several advantageous properties for the HTL process. Alcoholic solvents possess lower critical temperatures and pressures compared to water, enabling liquefaction

under milder reaction conditions. Moreover, their lower dielectric constants enhance the solubility of non-polar, fragmented biomass products, thereby improving the efficiency of the liquefaction process and increasing biocrude oil yields.[82–84] In this context, Li et al.[85] assessed the effect of using acetone, ethanol, and methanol as solvents on the bio-crude oil yield from HTL of sewage sludge at temperatures ranging from 280 to 360 °C. The highest yields were 42.3 wt% at 360 °C with ethanol, 43.1 wt% at 360 °C with acetone, and 26.3 wt% at 280 °C with methanol. Singh et al.[86] evaluated the impact of water, ethanol, and methanol as solvents for HTL of Ulva fasciata at 300 °C for 15 minutes. Methanol produced the highest bio-crude yield.

Additionally, organic solvents can act as hydrogen donors during HTL, stabilizing reactive intermediates and suppressing repolymerization reactions, which would otherwise reduce the biocrude yield and increase the formation of char and gaseous byproducts.[87,88] It should be noted that while organic solvents enhance liquefaction conditions, they do not provide the catalytic $H^+$ and $OH^-$ ions that water generates at high temperatures, which play a crucial role in hydrolysis reactions during HTL. To address this, several studies have explored the use of mixed solvent systems, combining water with organic solvents to simultaneously leverage the catalytic benefits of water and the solubilizing, stabilizing effects of alcohols and other organics. This co-solvent strategy has shown promise in optimizing biocrude yield and quality by balancing hydrolysis and

stabilization pathways during HTL.[89] In this regard, Li et al.[90] applied HTL to secondary sludge with a moisture content of 83.05 wt% using three different solvents: pure water, a 1:1 mixture of water and n-hexane, and a 1:1 mixture of water and methanol. The experiments were conducted at temperatures ranging from 300 °C to 380 °C and reaction times of 0–60 minutes. They found that the maximum bio-crude yields were 37.1 wt% at 340 °C for 20 minutes with pure water, 46.5 wt% at 340 °C for 40 minutes with the water/methanol mixture, and 39.3 wt% at 340 °C for 0 minutes using the water/n-hexane mixture. Han et al.[91] used HTL to convert microalgae with 90 wt% moisture in the reactor into bio-crude oil. The reaction was carried out in a reactor at temperatures of 275 °C, 300 °C, and 350 °C for 30 minutes, using pure water, 10% isopropyl alcohol, and 10% ethylene glycol as co-solvents. The highest bio-crude yields reported were 29.9 wt% at 325 °C with water, 35.4 wt% at 350 °C with isopropyl alcohol, and 30.4 wt% at 350 °C with ethylene glycol. Yan et al.[92] used kitchen food waste as the feedstock for the HTL process, conducted at temperatures ranging from 240 to 280 °C for 30 minutes with varying percentages of ethanol as the co-solvent. They found that up to 50% (v/v) of ethanol had no significant effect on the bio-crude yield. However, when 62.5% (v/v) ethanol was used, the bio-crude oil yield increased by about 115% compared to using pure water as the solvent.

It can be argued that the reaction environment plays a key role in optimizing bio-crude yield during the HTL process. For lignocellulosic biomass, food waste, and macroalgae, an alkaline solvent may be more advantageous compared to microalgae and municipal sludge when producing bio-crude oil. For instance, Biller and Ross[93] conducted HTL on microalgae and cyanobacteria with varying compositions: two rich in protein and lipids and two rich in protein and carbohydrates. The process was performed at 350 °C using water, 1 M sodium carbonate, and 1 M formic acid as solvents. They found that lipids and proteins were efficiently converted into bio-crude with water, while carbohydrates showed improved conversion with $Na_2CO_3$. Indeed, different types of biomass exhibit varying behaviors during HTL with different solvents. Solvents not only influence the bio-crude yield but can also alter the characteristics of the liquid products. Therefore, solvent selection is highly dependent on the biochemical composition of the biomass as well as the temperature and pressure conditions of the HTL process. While the use of appropriate solvents can positively influence bio-crude oil yield, selecting an unsuitable solvent may merely increase the overall cost of the HTL conversion without providing any significant improvement in bio-crude oil yield. Further research into developing biomass-specific solvent selection strategies could help identify the most appropriate solvents for each biomass type in the HTL process, while also considering the potential additional costs to overall liquid biofuel production.

The conversion of lignocellulosic biomass, microalgae, macroalgae, municipal sludge, and food waste along with their elemental and proximate composition at different HTL conditions is presented in Table 2. Each biomass type requires specific HTL operational conditions to be converted to the maximum amount of bio-crude oil. Further, the maximum bio-crude oil yield varies based on biomass composition. The HTL process is generally less complex than fast/flash pyrolysis in terms of biomass particle size and reactor type for liquid biofuel production. However, similar to fast/flash pyrolysis, the presence of ash in biomass may limit bio-crude yield, as ash tends to promote the formation of more hydrochar during the HTL process.[94] It is worth mentioning that a higher ash content in biomass does not necessarily result in a lower bio-crude oil yield, as the ash composition and specific operational conditions can have a significant impact on maximizing bio-crude oil yield in the HTL process, which is discussed in Section 3. Table 2 indicates that the solvent, along with temperature and reaction time, can be key parameters for bio-crude oil yield in HTL. For large-scale applications, optimizing temperature and reaction time based on biomass characteristics is crucial. In the context of solvents, it is important to note that they are biomass-specific in the HTL process. While using co-solvents or alternative solvents instead of biomass moisture may improve the bio-crude oil yield, it is essential to evaluate their long-term costs and impact on HTL product characteristics. The HTL process produces a substantial amount of aqueous phase (HTL-AP) alongside bio-crude oil, and managing HTL-AP remains a significant bottleneck in the process.[95] While there is a comprehensive review on valorization techniques for HTL-AP,[96] much remains unknown about the effects of solvents on HTL-AP characteristics for valorization. Therefore, further studies are essential to investigate the impact of solvents on the characteristics of HTL-AP and to explore potential valorization techniques, all while maximizing bio-crude oil yield and analyzing its quality.

As biomass contains carbohydrates and proteins, the Maillard reaction occurs in HTL and it has significant effects on products' yields and quality.[112] The Maillard reaction between hydrolyzed carbohydrates and hydrolyzed proteins occurs during HTL and/or pyrolysis processing of biomass, generating N-containing compounds.[113] In a study conducted by Fan et al.,[114] the impact of the Maillard reaction on bio-crude yield at 250 °C, 300 °C, and 350 °C was examined. At 350 °C, bio-crude yields were 15.20 wt% for lactose, 13.00 wt% for maltose, and 19.70 wt% for lysine. However, combining lysine with sugars significantly increased yields to 58.00 wt% for lactose and lysine, and 59.90 wt% for maltose and lysine. These findings highlight the role of the Maillard reaction in enhancing bio-crude yield. Additionally, Tang et al.[115] found that the highest bio-crude yield was achieved at 280 °C with a 60-minute retention time using a 3:1 protein-to-glucose ratio, suggesting that optimizing this ratio enhances bio-crude production. Studies on model compounds in HTL consistently reveal that a combination of lipids, proteins, and carbohydrates can improve bio-crude oil yield. In this regard, Lu et al.[116] explored the effect of substrate composition on HTL products by analyzing individual and mixed model compounds, including soybean oil (lipids), soy protein (proteins), cellulose, xylose, and lignin, at 350 °C for 30 minutes. For individual model compounds, the bio-crude yields were 82.00 wt% for lipids, 21.10 wt% for proteins,

**Table 2** Biomass elemental analysis, ash content, and operational conditions for HTL of various feedstocks for bio-crude oil production

| Biomass Name | C (wt%) | H (wt%) | N (wt%) | O (wt%) | Ash (wt%) | Solvent | T (°C) | Residence time (min) | Pressure (bar) | Max. bio-crude yield (wt%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Lignocellulosic biomass** | | | | | | | | | | | |
| Corn stover | 43.57 | 5.84 | 0.56 | 49.98 | 6.96 | Water | 250 300 350 375 | 0.00–60.00 | 75.84–234.42 | 22.20 at 15 min and 110.31 bar 29.25 at 0 min and pressure of 151.68 17.70 at 15 min and 179.26 and 217.18 bar 14.25 at 15 min and pressure of 196.5 and 241.31 bar | 97 |
| Wheat straw | 42.15 | 6.21 | 0.82 | 50.82 | 6.92 | $K_2CO_3$ | 400 | 15.00 | 320.00 | 22.00 | 98 |
| Eucalyptus | 47.85 | 5.81 | 0.10 | 46.23 | 1.15 | | | | | 28.00 | |
| Pinewood | 49.90 | 6.30 | 0.30 | 42.80 | 0.59 | | | | | 27.00 | |
| Rice straw | 36.20 | 5.20 | 0.70 | 40.30 | — | Milli-Q water, tap water, seawater, recycled wastewater, industrial wastewater | 350 | 30.00 | 180.00 | 36.40 in industrial wastewater | 99 |
| **Microalgae** | | | | | | | | | | | |
| Chlorella vulgaris | 52.60 | 7.10 | 8.20 | 32.20 | 7.00 | Water, $Na_2CO_3$, HCOOH | 350 | 60.00 | — | 38.00 in water | 100 |
| Nannochloropsis occulta | 57.80 | 8.00 | 8.60 | 25.70 | 26.40 | | | | | 37.50 in water | |
| Spirulina | 55.70 | 6.80 | 11.20 | 26.40 | 7.60 | | | | | 31.00 in water | |
| Porphyridium creuntum | 51.30 | 7.60 | 8.00 | 33.10 | 24.40 | | | | | 22.00 in water | |
| Scenedesmus obliquus | 33.40 | 4.70 | 4.40 | 16.50 | 40.80 | Water | 250 300 350 | 7.00–30.00 | 175–225 225–270 260–280 | 21.50 31.00 35.05 | 101 |
| Chlorella sp. | 56.20 | 6.90 | 7.70 | 28.70 | 11.70 | Water | 350 | 1.40 5.80 | 180.00 | 39.70 36.80 | 102 |
| **Macroalgae** | | | | | | | | | | | |
| Sargassum tenerrimum | 32.10 | 4.70 | 0.93 | 60.72 | 26.50 | Water, $C_2H_5OH$ | 260 280 300 | 15.00 | 45.00–120.00 | 18.50 in $C_2H_5OH$ 25.20 in $C_2H_5OH$ 20.00 in $C_2H_5OH$ | 103 |
| Ulva fasciata | — | — | — | — | 25.40 | Water | 280 | 15.00 | — | 12.00 | 104 |
| Enteromorpha sp | — | — | — | — | 23.20 | | 280 | | | 7.00 | |
| Sargassum tenerrimum | — | — | — | — | 32.00 | | 280 | | | 9.00 | |
| Enteromorpha prolifera | 28.75 | 5.22 | 3.65 | 32.28 | 30.10 | Water, 5% $Na_2CO_3$ | 220 240 260 280 300 320 | 5.00–60.00 | — | 9.60 at 30 min in water 12.50 at 30 min in water 18.24 in 5% $Na_2CO_3$ at 30 min 19.80 in 5% $Na_2CO_3$ at 30 min 23 in 5% $Na_2CO_3$ at 30 min 17.65 at 30 min in water | 105 |
| **Municipal sludge** | | | | | | | | | | | |
| Swine manure | 46.02 | 6.10 | 2.57 | 45.31 | 11.45 | Water | 350 | 15.00 | — | 33 | 106 |
| Sewage sludge | 51.94 | 7.28 | 8.33 | 32.44 | 25.10 | | | | | 37 | |
| Mixed primary and secondary sludge | 47.90 | 5.70 | 3.70 | 32.30 | 9.80 | Water | 350 | 15.00 | 170.00 | 38.5 | 107 |
| Primary sludge | 47.80 | 6.50 | 3.60 | 34.10 | 7.50 | | | | | 34.7 | |
| Secondary sludge | 43.60 | 6.60 | 7.90 | 25.00 | 16.20 | | | | | 20 | |

**Table 2** (Contd.)

| Biomass | | | | | | | | | | | |
| Name | C (wt%) | H (wt%) | N (wt%) | O (wt%) | Ash (wt%) | Solvent | $T$ (°C) | Residence time (min) | Pressure (bar) | Max. bio-crude yield (wt%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Dehydrated sewage sludge | 15.60 | 2.30 | 1.00 | 13.70 | 67.40 | Water, 2.28 aqueous phase: 1 water | 330 | 30.00 | 250.00 | 30.50 in second run with 17.90 aqueous phase in water | 108 |
| Food waste | | | | | | | | | | | |
| Food waste | 48.18 | 7.3 | 4.52 | 39.73 | 5.40 | Water | 280 310 340 | 30.00 | — | 29 30 38 | 109 |
| Food waste | 47.80 | 5.11 | 4.78 | 42.10 | 3.30 | Water | 200 300 350 400 500 600 | 30.00 30.00 30.00 30.00 1.00 and 30.00 1.00 and 30.00 | 353 353 138–357 353 353 353 | 12 28 36 at 169 bar 30 23 at 1 min 30.5 at 1 min | 110 |
| Mixed synthetic food waste | 56.16 | 8.05 | 2.61 | 33.19 | 4.68 | Water | 280–360 | 10.00–60.00 | 12–110 | 46.9 at 360 °C and 40 min | 111 |

4.60 wt% for cellulose, 6.60 wt% for xylose, and 1.40 wt% for lignin. In dual mixtures, combining proteins with carbohydrates or proteins with lignin resulted in higher bio-crude yields, while cellulose and xylose did not show significant effects. A counter-productive interaction was found when lipids were mixed with lignin, suggesting mutual hindrance in conversion. This under-scores the significance of maintaining a well-balanced elemental composition influence in the HTL process to leverage synergistic effects and optimize the conversion of biomass into bio-crude oil. Therefore, it becomes apparent that the biomass composition significantly influences the production of bio-crude oil. Optimizing the conversion of carbohydrates and proteins into bio-crude relies on specific ratios to leverage the Maillard reaction. The literature is limited in providing insights into the optimal carbohydrate-to-protein ratio in HTL studies. Further research is needed to determine the ideal carbohydrate-to-protein-to-lipid ratio in the HTL process. This will facilitate the development of cost-effective pretreatment methods to adjust the biochemical composition of biomass, especially waste biomass, leading to optimized bio-crude oil production. The effects of the biochemical composition of biomass on liquid biofuel characteristics are discussed further in Section 4.

## 3. Comparison of thermochemical process severity for maximizing biofuel yield

Tables 1 and 2 show that lignocellulosic and algal biomass, municipal sludge, and food waste have been extensively explored for liquid biofuel production using both HTL and fast/flash pyrolysis, regardless of biomass moisture levels. The varying levels of C, H, N, O, S, and ash in biomass influence pyrolysis oil and bio-crude oil yields. Fig. 2 illustrates the average distribution of these elements and ash in different biomass types. Table 3 summarizes the yields of liquid bio-fuels obtained from fast/flash pyrolysis and HTL of ligno-cellulosic biomass, microalgae, macroalgae, municipal sludge, and food waste, without the use of catalysts or co-solvents in either process. Based on Fig. 2 and Table 3, C and H levels are directly linked to liquid biofuel yields, meaning that higher C and H content in biomass results in greater biofuel pro-duction. However, the unavoidable presence of O and N sig-nificantly affects biofuel quality, as discussed in Section 4.

In the context of TPs that predominantly generate liquid biofuels, as summarized in Table 3, microalgae exhibit higher yields compared to other biomass types in both fast/flash pyrolysis and HTL. This high yield from microalgae is likely due to its relatively higher C content compared to other biomass sources as demonstrated in Fig. 2. While ligno-cellulosic biomass and macroalgae yield more liquid biofuel in fast/flash pyrolysis than in HTL, municipal sludge and food waste generate similar liquid biofuel yields in both processes.

Table 3 and Fig. 2 suggest that although a high carbon content in biomass can lead to increased liquid biofuel pro-
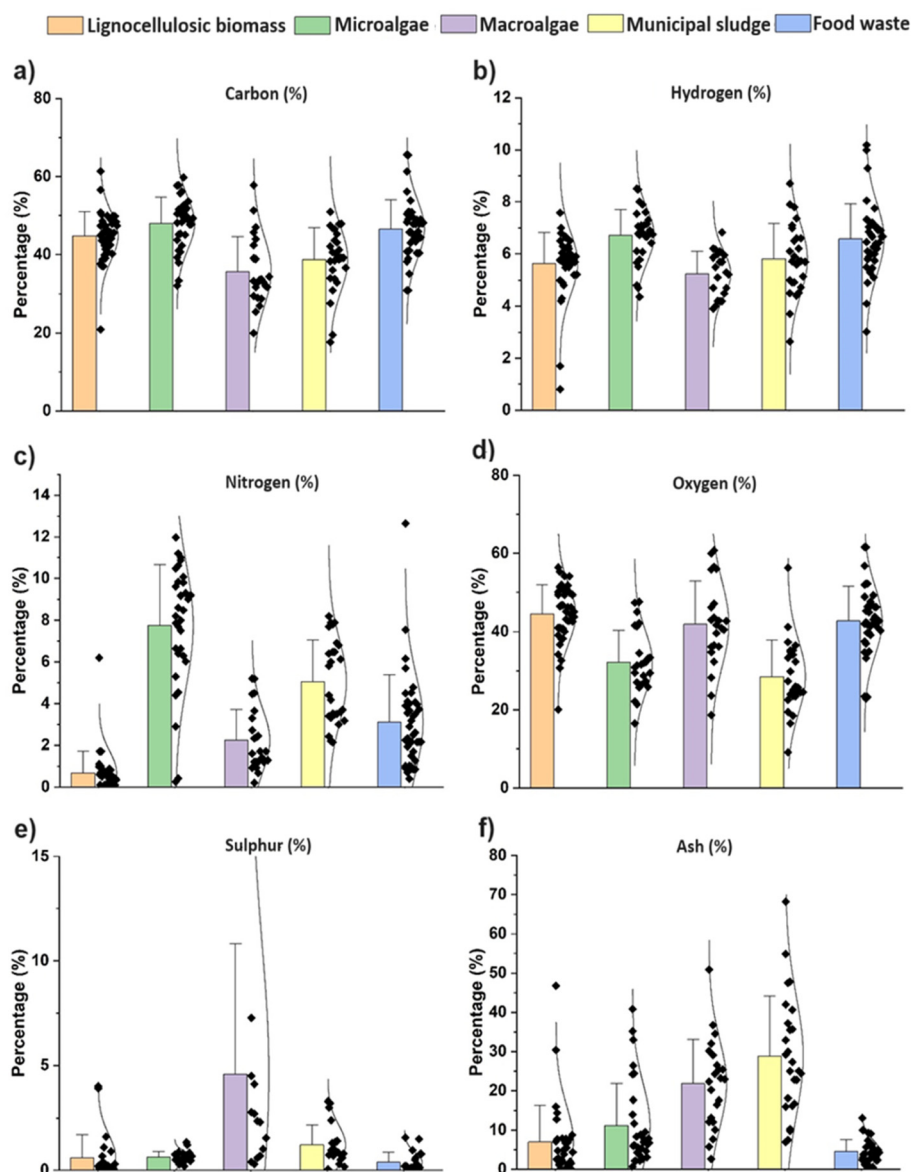
**Fig. 2** Distribution of (a) C, (b) H, (c) N, (d) O, (e) S, and (f) ash in different biomass used for biofuel production through pyrolysis and HTPs.[40,41,57,61–65,93,111,116–169]

**Table 3** The dry basis yield range of liquid biofuels from the fast/flash pyrolysis and HTL processes of different biomass without using catalysts

| Biomass | Thermochemical process | Yield of pyrolysis oil (wt%) | Yield of bio-crude (wt%) |
|---|---|---|---|
| Lignocellulosic biomass | | | |
| | Fast/flash pyrolysis | 14.5–54.7 | — |
| | HTL | — | 15.6–31.1 |
| Microalgae | | | |
| | Fast/flash pyrolysis | 39.6–65.4 | — |
| | HTL | — | 24.4–44.6 |
| Macroalga | | | |
| | Fast/flash pyrolysis | 25.3–52.9 | - |
| | HTL | — | 9.4–28.1 |
| Municipal sludge | | | |
| | Fast/flash pyrolysis | 21.5–43.5 | — |
| | HTL | — | 18.1–40.5 |
| Food waste | | | |
| | Fast/flash pyrolysis | 13.0–49.2 | — |
| | HTL | — | 15.2–52.1 |

duction, a high ash content does not necessarily have a negative effect on liquid biofuel yields in fast/flash pyrolysis and HTL. This is evidenced by municipal sludge, which has a high ash content, and food waste, which has a low ash content, producing comparable amounts of liquid biofuels. The ash in biomass is predominantly composed of inorganic matter, with its composition being strongly influenced by both the source of the biomass and the environmental conditions under which it is produced.[170] While these inorganics are largely retained in the solid products of HTL and fast/flash pyrolysis, they can also influence the yield of liquid biofuels.[4]

To gain deeper insights into the role of inorganics in liquid biofuel production, the optimal strategy involves supplementing the feedstock with additional inorganic materials and conducting HTL and/or fast/flash pyrolysis to evaluate their synergistic or antagonistic effects on biofuel yield.[171–174] In this context, iron (Fe) serves as an effective transition metal catalyst, substantially enhancing the yield of liquid biofuels. Kandasamy et al.[175] reported that adding 0.45 g of $Fe_3O_4$ to 33 mL of slurry containing 10–11 wt% dried microalgae increased the bio-crude oil yield in the HTL process by approximately 9% compared to a run without $Fe_3O_4$. In another study, Malins et al.[176] investigated the effects of three metal catalysts—RANEY® nickel, $FeSO_4$, and $MoS_2$—on bio-crude oil production from municipal sludge via HTL at temperatures ranging from 200 to 350 °C and reaction times between 10 and 100 minutes. All catalysts were applied at a loading of 5 wt% relative to the dried sludge mass. The findings indicated that $FeSO_4$ produced the greatest improvement in bio-crude oil yield. Xu et al.[177] similarly observed a notable enhancement in bio-crude oil yield from lignocellulosic biomass when employing an Fe-based catalyst during the HTL process conducted at 349.85 °C for 40 minutes. Huang et al.[178] reported that the addition of an Fe-based catalyst at 5 wt% of the dried sludge mass during fast pyrolysis of municipal sludge enhanced the pyrolysis oil yield by about 6% relative to the catalyst-free process. Chen et al.[179] confirmed that incorporating a cobalt (Co)-based catalyst, a transition metal, at 10 wt% of the microalgae mass markedly enhanced the bio-crude oil yield in HTL conducted at 320 °C for 30 minutes. The study further revealed that the Co-based catalyst promoted the conversion of carbohydrates. Furthermore, Qian et al.[180] reported that $Zn^{2+}$ facilitated the hydrolysis of carbohydrates and lignin while also promoting deoxygenation reactions. Likewise, a range of transition metals—including $Cr^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Ni^{2+}$, and $Zn^{2+}$—have exhibited similar catalytic activities. These effects involve accelerating carbohydrate hydrolysis, facilitating the dehydration of monosaccharides (e.g., glucose and xylose) into furfural derivatives, promoting the formation of organic acids such as lactic, levulinic, and formic acids, and breaking down heavy compounds into low-molecular-weight products within liquid biofuels produced through HTL and fast/flash pyrolysis.[181–186] It should be emphasized that the catalytic efficiency of transition metals is strongly influenced by both their specific type and concentration. From the literature, it can be concluded that when

biomass contains up to 10 wt% of transition metals based on its total dried weight, the ash content is more likely to have a beneficial effect on liquid biofuel yield in both HTL and fast/flash pyrolysis.

Post-transition metals such as aluminum (Al) and lead (Pb) have demonstrated catalytic effects comparable to transition metals, promoting the depolymerization, decomposition, and repolymerization of carbohydrates and lignin, which contributes to enhanced liquid biofuel yields during HTL and fast/flash pyrolysis of biomass.[187,188] Conversely, alkali and alkaline earth metals—including $Na^+$, $K^+$, $Li^+$, $Ca^{2+}$, $Ba^{2+}$, and $Mg^{2+}$—have been shown to either enhance or reduce liquid biofuel yield by affecting repolymerization reactions in the HTL and fast/flash pyrolysis of biomass.[189,190] The alkali and alkaline earth metals found in biomass ash predominantly promote the hydrolysis of lipids, carbohydrates, and lignin, enhance fatty acid decarboxylation, facilitate dehydration and hydrogenation reactions, and contribute to Maillard reactions. Nevertheless, their effectiveness in cleaving peptide bonds within proteins is relatively limited.[90,123,191] As a result, the presence of alkali metals can have both beneficial and adverse impacts on liquid biofuel yield during HTL and/or fast/flash pyrolysis, depending on their concentration and interaction with biomass components. In summary, the ash composition of biomass is highly influential in either promoting or hindering key reactions—such as depolymerization, decomposition, and repolymerization—that affect liquid biofuel yield in fast/flash pyrolysis and HTL processes. Nonetheless, it is important to recognize that the organic fraction of biomass, along with its specific composition, remains the primary factor governing liquid biofuel production.

Among effective operating parameters in liquid biofuel yield, temperature and residence time are the most practical parameters to be optimized in the HTL and fast/flash pyrolysis processes.[192–198] Temperature and reaction time can affect pressure, reactor design, and the amount of energy required for TPs. The correlation between temperature and reaction time can be defined as the severity of TPs. Severity can be calculated by eqn (1).[4,199]

$$\text{Severity} = \log\left[\sum_{i=1}^{n} t_i \times \exp\left(\frac{T_i - 100}{14.75}\right)\right] \quad (1)$$

In eqn (1), $n$ represents the number of treatment stages applied in TPs, $t_i$ is the reaction time in minutes, excluding ramping and cooling time, and $T_i$ is the reaction temperature in degrees Celsius (°C). For example, conducting an HTL run at 350 °C for 15 minutes would result in a severity factor of $\log\left[15 \times \exp\left(\frac{350 - 100}{14.75}\right)\right] = 8.54$.

Fig. 3 illustrates the temperature range and reaction time for fast/flash pyrolysis and HTL for maximizing liquid biofuel yield for each type of biomass. It is generally accepted that fast/flash pyrolysis requires harsher process conditions than HTL for liquid biofuel production from biomass.[27,200,201] Presence of water in HTL may facilitate organics conversion at
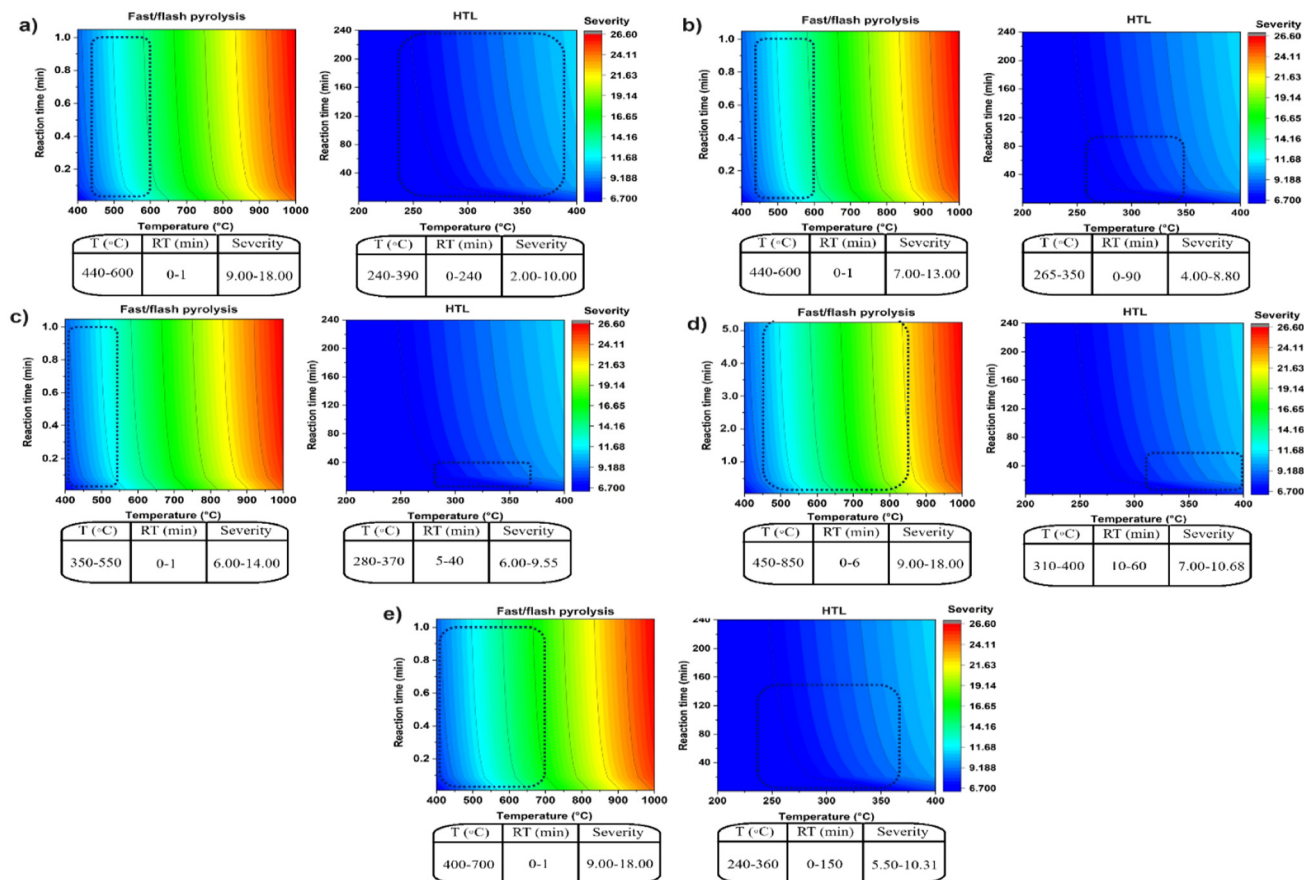
**Fig. 3** Temperature (*T*), reaction time (RT), and severity range for achieving maximum liquid biofuel yield *via* fast/flash pyrolysis and HTL from (a) lignocellulosic biomass;[75,97,128,157,159,202–214] (b) microalgae;[6,57,160,215–229] (c) macroalgae;[58–60,103,104,230–241] (d) municipal sludge;[62,76,107,130,161,242–257] (e) food waste.[109,111,164,258–270]

lower process severity. However, as shown in Fig. 3, the severity of the process is biomass-specific. To maximize liquid biofuel yield from lignocellulosic biomass, microalgae, municipal sludge, and food waste, more severe conditions are required in fast/flash pyrolysis compared to HTL. However, macroalgae can be converted to pyrolysis oil under conditions similar to those required for HTL to produce bio-crude oil. Interestingly, municipal sludge requires harsher conditions in both fast/flash pyrolysis and HTL compared to lignocellulosic biomass, algal biomass, and food waste to achieve optimal liquid biofuel yields. Therefore, to optimize the HTL and/or fast/flash pyrolysis processes for maximizing liquid biofuel production from biomass, a specific range of severity given in Fig. 3, can be tested based on the biomass type. As discussed in Section 4.4, proteins, carbohydrates, and lipids are decomposed at different temperatures, and the biomass' biochemical composition, particularly the ratio of carbohydrates, proteins, and lipids may have a significant impact on the optimum process severity for maximizing liquid biofuels yield in TPs.

In conclusion, in this section, the analysis of literature results suggests that the optimal process severity in fast/flash pyrolysis and HTL depends largely on the biomass types. Therefore, recommendations have been made for the tempera-

ture, reaction time, and severity ranges suitable for each biomass in fast/flash pyrolysis and HTL for maximizing liquid biofuel yield for each biomass type (lignocellulosic biomass, microalgae, macroalgae, municipal sludge, and food waste). Another important consideration is that achieving the highest biofuel yield does not always equate to the best biofuel quality. Therefore, the following sections evaluate the biofuel physical and chemical quality produced from the five biomass types *via* fast/flash pyrolysis and HTL.

## 4. Physical and chemical characteristics comparison of bio-crude oil and pyrolysis oil

Higher heating value (HHV) is one of the most significant parameters for the quality analysis of biofuels. HHV is the quantity of heat released by a unit mass or volume of fuel (mainly at 25 °C) upon combustion, with the resulting products subsequently cooling back to a temperature of 25 °C. This value includes the latent heat of the vaporization of water. HHV can be measured using a bomb calorimeter

according to the American society for testing and materials (ASTM) standard D-2015 (which was withdrawn by ASTM in 2000 and not replaced) or calculated using the Dulong formula or the Milne formula.[271,272] While the presence of H and C is critical for liquid biofuels, the presence of O and N can adversely affect the liquid biofuel quality by causing corrosion, $NO_x$ emission, and catalyst fouling during upgrading processes.[273] Therefore, hydrogen-to-carbon ratio (H/C), oxygen-to-carbon ratio (O/C), carbon-to-nitrogen ratio (C/N), HHV, density, pH, levels of organic compounds, and viscosity of liquid biofuels are among the main parameters that should be evaluated regarding the quality of the liquid biofuel.

Temperature and the reaction time are highly effective on the deoxygenation and denitrogenation efficiency. By increasing the process temperature, the H content changes slightly, but the O percentage decreases due to enhanced deoxygenation. Consequently, the C percentage increases at higher temperatures. This results in a reduction of the H/C and O/C ratios in the bio-crude with increasing temperature.[274] However, liquid biofuel production decreases at high temperatures, resulting in less liquid biofuel, as indicated in Table 1 for fast/flash pyrolysis and Table 2 for HTL. Feedstock type also plays a key role in deoxygenation and denitrogenation during HTL and fast/flash pyrolysis. Since the feedstock for the HTL and pyrolysis processes is biomass, the presence of N-containing and oxygenated compounds is unavoidable in the liquid biofuel, affecting the density, thermal stability, acidity, HHV, and viscosity of the liquid biofuels.[275,276] Based on the van Krevelen diagram depicted in Fig. 4, both fast/flash pyrolysis

and HTL can decrease the H/C and O/C ratios of the feedstocks if appropriate operational conditions are applied. Therefore, it can be said that it is worth applying fast/flash pyrolysis or HTL to biomass as they can produce liquid biofuels with much higher energy potential compared to biomass itself.

In Table 4, HHV, density, and moisture of pyrolysis oil obtained from the fast/flash pyrolysis and bio-crude oil generated by the HTL process of lignocellulosic biomass, microalgae, macroalgae, municipal sludge, and food waste are compared. As can be seen, pyrolysis oil has lower HVV compared to bio-crude oil in all types of feedstocks. High ash content may limit the liquid biofuel yield—as shown in Tables 1 and 2 for HTL and fast/flash pyrolysis, respectively—by promoting char formation. However, the presence of ash in biomass does not significantly affect the energy potential of the resulting biofuels, as indicated in Table 4. Therefore, biomass with high ash content, such as municipal sludge and macroalgae, can still be utilized for biofuel production *via* fast/flash pyrolysis and HTL without negatively impacting the energy quality of the biofuels.

### 4.1 Hydrogen-to-carbon and oxygen-to-carbon ratios of liquid biofuels

According to the van Krevelen diagram depicted in Fig. 4, while dehydrogenation is limited in both fast/flash pyrolysis and HTL, deoxygenation is much more intense in HTL compared to fast/flash pyrolysis. In this regard, Mullen *et al.*[158] applied fast pyrolysis at 500 °C to corn stover with H/C, O/C, and HHV of 1.27, 0.64, and 18.3 MJ kg⁻¹, respectively, and
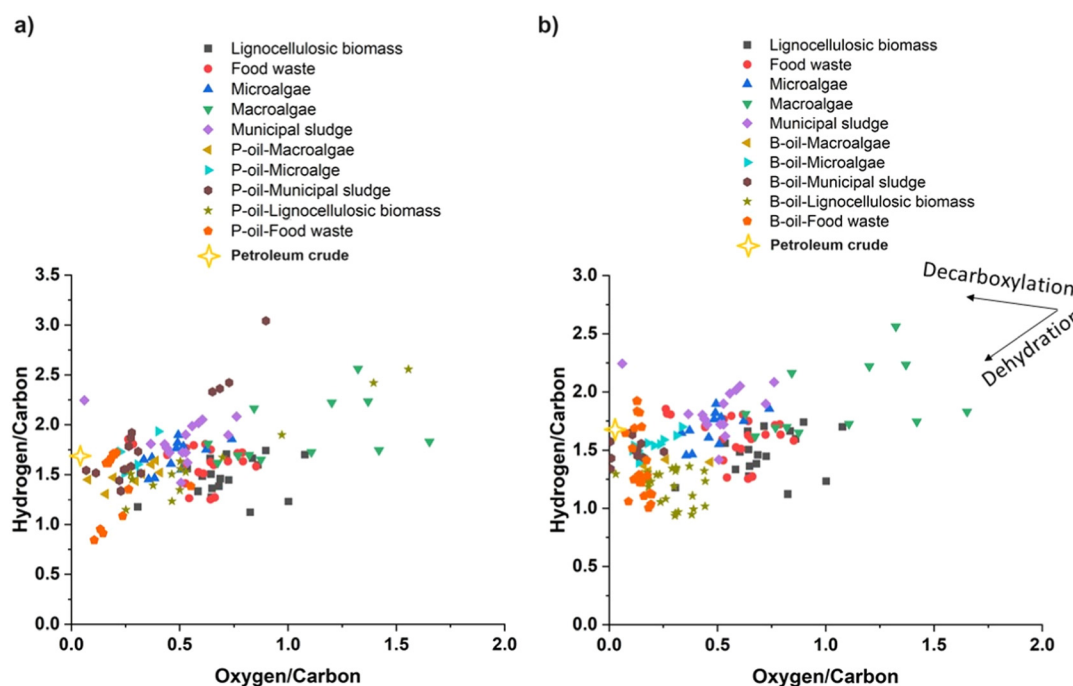


**Fig. 4** van Krevelen diagram of various biomass and their (a) pyrolysis oil[40,41,55,57,59,62,64,65,93,158–163,213,218,233,263,264,277,278] and (b) bio-crude oil.[97,98,101–103,105,107,109–111,128,130,169,190,237,254,279–283] P-oil–Biomass name: pyrolysis oil derived from that biomass; B-oil–Biomass name: Bio-crude oil derived from that biomass.

**Table 4** Pyrolysis oil and bio-crude oil characteristics of different biomass through fast/flash pyrolysis and HTL

| Biomass | Name | HHV (MJ kg$^{-1}$) | Ash (wt%) | Operational conditions | Pyrolysis oil or Bio-crude oil | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | H/C[a] | O/C[a] | C/N[a] | HHV (MJ kg$^{-1}$) | Moisture (wt%) | Density (g ml$^{-1}$) | |
| **Lignocellulosic biomass** | | | | | | | | | | | |
| Pyrolysis oil | Corn cobs | 17.80 | 1.98 | T[b] = 500 °C | 1.63 | 0.50 | 115 | 26.20 | 25.30 | — | 158 |
| | Corn stover | 18.30 | 4.88 | — | 1.53 | 0.52 | 53.30 | 24.30 | 9.20 | 1.18 at 25 °C | 159 |
| | Maize-cob | 18.06 | 3.90 | T: 600 °C; RT[b]: 3–30 min | 1.52 | 0.27 | 279 | 30.59 | — | — | 284 |
| | Wood | 21.50 | 2.70 | T: 550 °C; RT: 0.8 s | 1.51 | 0.46 | 133 | 24.00 | 25.30 | 1.12 at 40 °C | |
| | Straw | 21.30 | 5.80 | | 1.24 | 0.46 | 39 | 23.70 | 25.70 | 1.15 at 40 °C | |
| | Lignin | 27.40 | 12.10 | | 1.45 | 0.28 | 45 | 29.70 | 27.50 | 1.09 at 40 °C | |
| | Craft lignin | — | — | T: 399.85–599.85 °C | 1.15 | 0.25 | — | 20.00–31.00 | 5.30–7.20 | — | 55 |
| | Wood chips | — | — | | 1.35 | 0.50 | — | 14.00–23.00 | 26.50–32.5 | — | |
| | Rice husk | 16.02 | 17.03 | T: 500 °C; RT: 45 s | 2.28 | 3.06 | 24.40 | 16.30 | — | 1.06 at 20 °C | 263 |
| | Beech wood | — | 0.80 | T: 450–600 °C; RT: 16.6 s | 2.28 | 1.21 | — | 21.70–25.10 | 7.80–21.00 | 1.10 at 22 °C | 213 |
| Bio-crude oil Bio-crude oil | Corn stover | 14.14 | 6.96 | T: 250–375 °C; RT: 0–60 min | 1.29 | 0.33 | 47.10 | 27.47–35.13 | — | — | 97 |
| | Wheat straw | 16.53 | 6.92 | T: 400 °C; RT: 15 min | 1.32 | 0.17 | 52.00 | 35.50 | — | — | 98 |
| | Eucalyptus | 18.14 | 1.15 | | 1.24 | 0.16 | 93.70 | 35.79 | — | — | |
| | Pinewood | 19.50 | 0.59 | | 1.30 | 0.16 | 67.50 | 33.66 | — | — | |
| | Natural hay | 13.20 | 7.80 | T: 240–320 °C; RT: 30 min | 1.22 | 0.20 | — | 25.30–31.50 | — | — | 128 |
| | Oak wood | 21.40 | 2.00 | | 1.08 | 0.40 | — | 22.70–27.50 | — | — | |
| | Walnut shell | 14.70 | 1.50 | | 1.05 | 0.30 | — | 23.60–28.50 | — | — | |
| | Cellulose | 17.00 | 0.00 | | 0.94 | 0.40 | — | 21.10–24.60 | — | — | |
| | Beech wood | — | 0.80 | T: 300 °C; RT: 60 min | 1.19 | 0.30 | — | 27.00–30.10 | <1 | 1.14 at 22 °C | 213 |
| | Rice husk | 14.93 | 14.77 | T: 260–340 °C; RT: 20 min | 1.36 | 0.37 | 30.96 | 25.03 | — | — | 285 |
| **Microalgae** | | | | | | | | | | | |
| Pyrolysis oil | Chlorella vulgaris remnant | 19.44 | 8.34 | T: 500 °C | 1.93 | 0.40 | 4.68 | 24.57 | 15.89 | — | 41 |
| | Chlorella vulgaris | 23.00 | 4.30 | T: 450–550 °C | — | — | — | 27.00–32.00 | 55.00–64.0 | — | 160 |
| | Synthetic microalgae | 16.40 | 24.20 | T: 550 °C | — | — | — | 24.00 | 61.00 | — | 218 |
| | Chlorella vulgaris | 17.72 | 4.70 | T: 400 °C; RT: 2 s | 1.51 | 0.24 | 8.64 | 27.90 | 2.00 | — | |
| | N starved Chlorella vulgaris | 20.23 | 2.50 | | 1.67 | 0.18 | 16.30 | 28.90 | 2.10 | — | |
| | Chlorella vulgaris | — | 5.54 | T: 600–900 °C; RT: 5–6 s | — | — | — | — | 7.23–47.21 | — | 6 |
| Bio-crude oil | Chlorella vulgaris | 23.20 | 7.00 | T: 350 °C; RT: 60 min | 1.73 | 0.11 | 17.50 | 35.10 | — | — | 93 |
| | Nannochloropsis occulta | 17.90 | 26.4 | | 1.69 | 0.105 | 20.30 | 34.50 | — | — | |
| | Spirulina | 21.20 | 7.60 | | 1.50 | 0.11 | 12.20 | 36.80 | — | — | |
| | Porphyridium creuntum | 14.70 | 24.40 | | 1.50 | 0.14 | 14.80 | 35.70 | — | — | |
| | Chlorella sp. | 19.90 | 11.70 | T: 350 °C; RT: 1.40 and 5.80 min | 1.68 | 0.009 | 36.50 | 32.90 and 36.10 | — | — | 102 |
| | Spirulina | 19.95 | 9.54 | T: 260 °C; RT: 60 min | 1.97 | 0.42 | 8.30 | 27.49–29.76 | — | — | 281 |
| | Scenedesmus sp. | 15.70 | 40.80 | T: 250–350 °C; RT: 7–30 min | 1.50 | 0.13 | 15.40 | 31.20–35.00 | — | — | 101 |
| **Macroalgae** | | | | | | | | | | | |
| Pyrolysis oil | Saccharina japonica | — | 20.21 | T: 350–550 °C; RT: 60 min | 1.45 | 0.07 | 22.40 | 32.97–33.36 | — | — | 233 |
| | Kappaphycus alvarezii | 15.70 | 12.10 | T: 500 °C; RT: 15 min | — | — | — | 24.50 | — | — | 278 |
| | Sargassum wightii | 11.20 | 13.20 | | — | — | — | 30.90 | — | — | |
| | Turbinaria ornata | 13.80 | 22.37 | | — | — | — | 30.20 | — | — | |

**Table 4** *(Contd.)*

| Biomass Name | HHV (MJ kg⁻¹) | Ash (wt%) | Operational conditions | H/C$^a$ | O/C$^a$ | C/N$^a$ | HHV (MJ kg⁻¹) | Moisture (wt%) | Density (g ml⁻¹) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| *Saccharina japonica* | 12.11 | 20.21 | T: 350–550 °C; RT: < 3 s | 1.43 | 0.30 | 27.80 | 24.80–28.27 | — | — | 58 |
| *Ulva lactuca* | 12.90 | 29.10 | T: 550 °C; RT: 0.8 s | 1.44 | 0.36 | 17.3 | 25.70 | 26.60 | 1.14 at 40 °C | 59 |
| **Bio-crude oil** | | | | | | | | | | |
| *Sargassum tenerrimum* | — | 26.50 | T: 260–300 °C; RT: 15 min | 1.61 | 0.43 | 15.40 | 22.40 | — | — | 103 |
| *Enteromorpha prolifera* | — | 30.10 | T: 300 °C; RT: 30 min | 1.42 | 0.26 | 13.90 | 28.74 | — | — | 105 |
| *Sargassum angustifolium* | 13.25 | 22.90 | T: 250–350 °C; RT: 20–60 min | 1.37 | 0.16 | 34.40 | 33.91 | — | — | 282 |
| *Laminaria digitata* | 13.10 | 23.90 | T: 350 °C; RT: 15 min | 1.32 | 0.18 | 20.60 | 32.00 | — | — | 237 |
| *Laminaria saccharina* | 12.20 | 21.80 | | 1.26 | 0.14 | 29.00 | 33.00 | — | — | |
| *Laminaria hyperborea* | 14.20 | 16.60 | | 1.26 | 0.15 | 22.90 | 33.90 | — | — | |
| *Alaria Esculenta* | 13.90 | 25.20 | | 1.29 | 0.14 | 22.60 | 33.80 | — | — | |
| *Derbesia tenuissima* | 12.40 | 34.70 | T: 330–341 °C; RT: 8 min | 1.22 | 0.11 | 13.10 | 33.20 | — | — | 286 |
| *Ulva ohnoi* | 11.70 | 30.70 | | 1.35 | 0.11 | 14.60 | 33.80 | — | — | |
| *Chaetomorpha linum* | 10.30 | 36.60 | | 1.29 | 0.12 | 12.20 | 32.50 | — | — | |
| *Cladophora coelothrix* | 12.70 | 25.50 | | 1.33 | 0.11 | 11.80 | 33.30 | — | — | |
| *Oedogonium* sp. | 15.80 | 20.60 | | 1.34 | 1.08 | 13.30 | 33.70 | — | — | |
| *Cladophora vagabunda* | 16.40 | 17.80 | | 1.39 | 0.11 | 12.20 | 33.50 | — | — | |
| **Municipal sludge** | | | | | | | | | | |
| **Pyrolysis oil** | | | | | | | | | | |
| Mixed sludge | 17.35 | 29.23 | T: 300–500 °C | 3.04 | 0.90 | 8.59 | | — | — | 161 |
| Anaerobically digested sludge | 14.40 | 32.87 | | 1.87 | 0.27 | 10.40 | | — | — | |
| Aerobically digested sludge | 12.31 | 29.94 | | 1.92 | 0.27 | 11.40 | | — | — | |
| Dehydrated aerobically digested sludge | — | 56.8 | T: 400–700 °C | 1.55 | 0.24 | — | | — | — | 40 |
| Anaerobically digested and dried sludge | 11.10 | 37.20 | T: 400–600 °C | 2.33 | 0.65 | 7.95 | | 23.00 | 1.05 | 62 |
| **Bio-crude oil** | | | | | | | | | | |
| Thickened excess activated sludge | 16.50 | 25.00 | T: 500 °C | 1.52 | 0.11 | 8.14 | 24.70 | 10.30 | — | 162 |
| Dewatered digested sludge | 8.60 | 47.50 | | 1.54 | 0.06 | 10.70 | 27.90 | 78.70 | — | |
| Dried excessive activated sludge | 15.00 | 27.30 | | 1.78 | 0.26 | 8.26 | 23.90 | 17.00 | — | |
| Secondary sludge | 16.10 | 35.50 | T: 260–350 °C; RT: 10 min | 1.50 | 0.12 | 19.20 | 34.84–35.94 | — | — | 130 |
| Primary sludge cake | 21.10 | 7.00 | T: 300–350 °C | 1.45 | 0.13 | 27.20 | 30.20–34.60 | — | — | 254 |
| Secondary sludge | 22.15 | 40.63 | T: 350 and 400 °C; RT: 15 min | 1.67 | 0.09 | 18.80 | 35.30 and 35.95 | — | — | 190 |
| Mixed sludge | 19.90 | 9.80 | T: 350 °C; RT: 15 min | 1.34 | 0.006 | 20.50 | 33.10 | — | — | 107 |
| Primary sludge | 20.70 | 7.50 | | 1.57 | 0.006 | 20.70 | 37.80 | — | — | |
| Secondary sludge | 20.00 | 16.20 | | 1.43 | 0.009 | 16.60 | 34.80 | — | — | |
| Bio-degassed sewage sludge | 21.27 | 34.02 | T: 350 and 400 °C; RT: 15 min | 1.62 and 1.63 | 0.12 and 0.11 | 18.40 and 19.60 | 35.22 and 35.42 | — | — | 76 |
| **Food waste** | | | | | | | | | | |
| **Pyrolysis oil** | | | | | | | | | | |
| Waste cereals | 19.86 | 1.90 | T: 800 °C; RT: 10 min | 1.63 | — | 21.40 | 27.40 | 79.90 | — | 163 |
| Waste peanuts crisps | 24.75 | 2.20 | | 3.17 | — | 41.70 | 14.10 | 73.90 | — | |
| Potato peel waste | 17.40 | 9.30 | T: 450 °C; RT: 8 s | — | — | — | — | 86.80 | — | 64 |
| Potato peel waste residue | 19.20 | 6.50 | | — | — | — | — | 77.20 | — | |
| **Bio-crude oil** | | | | | | | | | | |
| Grape seeds powder | 20.50 | 4.10 | T: 750 and 850 °C; RT: 10 min | 0.84 | 0.10 | 19.20 | 27.54–32.06 | — | — | 65 |
| Chestnut shel | 19.00 | 0.80 | | 0.91 | 0.15 | 42.60 | 20.80–31.41 | — | — | |
| Mixed food waste | 18.43 | 11.07 | T: 475 °C; RT: 60 min | 1.71 | 0.19 | 12.90 | 29.69 | — | — | 264 |
| Food waste | 20.64 | 0.51 | T: 280–340 °C RT: 30 min | 1.52 | 0.10 | 21.90 | 37.33 | — | — | 109 |
| Simulated food waste | 22.30 | 5.40 | T: 200–600 °C RT: 1–30 min | 1.07 | 0.09 | 14.40 | 35.00 | — | — | 110 |
| Food waste | 20.90 | 3.30 | T: 240–295 °C RT: 0–30 min | 1.65 | 0.07 | 69.40 | 35.50–40.20 | — | — | 169 |

**Table 4** (Contd.)

| Biomass | | | | Pyrolysis oil or Bio-crude oil | | | | | | |
| Name | HHV (MJ kg$^{-1}$) | Ash (wt%) | Operational conditions | H/C$^a$ | O/C$^a$ | C/N$^a$ | HHV (MJ kg$^{-1}$) | Moisture (wt%) | Density (g ml$^{-1}$) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| Food waste mixture | 24.51 | 4.68 | T: 280–360 °C RT: 10–60 min | 1.68 | 0.11 | 24.63 | 38.15 | — | — | 111 |
| Salad dressing | 30.76 | 4.89 | | 1.83 | 0.12 | 282.96 | 39.68 | — | — | |
| Cream cheese | 31.16 | 3.10 | | 1.92 | 0.12 | 380.21 | 40.38 | — | — | |
| Beef | 29.31 | 2.30 | | 1.92 | 0.13 | 51.09 | 39.56 | — | — | |
| Chicken | 22.61 | 4.68 | | 1.69 | 0.15 | 9.13 | 34.41 | — | — | |
| Hamburger bun | 18.79 | 2.37 | | 1.82 | 0.14 | 77.43 | 38.55 | — | — | |
| Vegetable | 17.16 | 13.11 | | 1.41 | 0.17 | 13.37 | 32.48 | — | — | |
| Fruit peels | 17.82 | 5.00 | | 1.27 | 0.17 | 37.22 | 32.71 | — | — | |

$^a$ H/C, O/C, and C/N are calculated using the formula of $\frac{H\%/1.008}{C\%/12.011}$, $\frac{O\%/15.999}{C\%/12.011}$, and $\frac{C\%/12.011}{N\%/14.0067}$, respectively. $^b$ T: temperature; RT: residence time.

obtained pyrolysis oil with H/C, O/C and HHV of 1.52, 0.52, and 24.3 MJ kg$^{-1}$, respectively. On the other hand, Mathanker et al.[97] applied HTL at 375 °C to corn stover with H/C, O/C ratios, and HHV of 1.59, 0.86, and 14.14 MJ kg$^{-1}$, respectively, and produced bio-crude oil with H/C, O/C, and HHV of 1.29, 0.13, and 35.13 MJ kg$^{-1}$. Similarly, Merdun et al.[161] tested fast pyrolysis on mixed primary and secondary sludge with H/C, O/C, and HHV of 0.15, 1.34, and 17.35 MJ kg$^{-1}$, respectively, and generated pyrolysis oil with H/C and O/C of 3.04 and 0.89, respectively. On the contrary, Liu et al.[107] examined the effect of HTL on mixed sludge with H/C, O/C, and HHV of 1.41, 0.51, and 19.9 MJ kg$^{-1}$, respectively, and produced bio-crude oil with H/C, O/C, and HHV of 1.33, 0.006, and 33.1 MJ kg$^{-1}$, respectively. These studies have supported the fact that liquid oil produced by the HTL process has higher HHV and lower H/C and O/C ratios compared to fast/flash pyrolysis, requiring less intense post-upgrading processes. Higher deoxygenation of biomass during the HTL process can be beneficial for the upgrading processes.

According to Fig. 4, municipal sludge and food waste have a lower O/C ratio than lignocellulosic biomass, microalgae, and macroalgae in the pyrolysis and HTL processes. The HTL process can produce bio-crude oil from municipal sludge that is comparable to crude oil regarding H/C and O/C values,[107] from food waste[111] and microalgae[281] regarding H/C value. Notably, pyrolysis of macroalgae generally produces higher-quality liquid biofuel compared to HTL in terms of H/C and O/C values. Fast/flash pyrolysis of municipal sludge and ligno-cellulosic biomass can produce liquid biofuels with lower H/C and higher O/C ratios than feedstock, highlighting the influence of process severity on these biomass types. In contrast, HTL consistently improves H/C and O/C ratios across various biomass types and operational conditions. Thus, the choice between fast/flash pyrolysis and HTL significantly affects the H/C and O/C ratios of the resulting biofuel. Trying to optimize many variables in fast/flash pyrolysis, including biomass particle size, reactor type, and process severity, can make it challenging to improve the H/C and O/C ratios of liquid biofuels. In contrast, HTL offers more consistent improvements in these ratios across various biomass sources as it has limited variables.

As shown in Table 5, bio-crude oil derived from municipal sludge and food waste has an O/C value closest to that of crude oil among the different feedstocks. This suggests that these biomass types can be processed via HTL with minimal need for upgrading. In contrast, liquid biofuels derived from lignocellulosic biomass, microalgae, and macroalgae through both fast/flash pyrolysis and HTL require significant upgrading to remove oxygenated compounds, as their O/C ratios are considerably higher than that of crude oil.

## 4.2 Carbon-to-nitrogen ratio of liquid biofuels

The N content of the produced liquid biofuels is another critical parameter affecting their quality. When biomass contains a high amount of protein, the resulting liquid biofuel will have a high N content.[301] A greater C/N ratio of the liquid fuel is

**Table 5** Comparison of pyrolysis oil and bio-crude oil properties from various biomass sources

| Properties | Crude oil[287,288] |
|---|---|
| O/C | 0.001 |
| H/C | 1.68 |
| C/N | 507–967 |
| HHV (MJ kg$^{-1}$) | 41.7–47 |
| pH | N/A |
| Moisture (wt%) | <1 |
| Density (g ml$^{-1}$) | 0.85–0.90 |

| | Pyrolysis oil$^a$ | Bio-crude oil$^b$ |
|---|---|---|
| | **Lignocellulosic biomass** | |
| O/C | 0.20–1.10 | 0.15–0.45 |
| H/C | 1.20–2.00 | 1.00–1.36 |
| C/N | 20–205 | 50–300 |
| HHV (MJ kg$^{-1}$) | 13–32 | 19–36 |
| pH | 2.5–4.9 | N/A |
| Moisture (wt%) | 9–29 | 1–5 |
| Density (g ml$^{-1}$) | 1.05–1.18 | 1.01–1.15 |
| | **Microalgae** | |
| O/C | 0.20–0.35 | 0.10–0.30 |
| H/C | 1.50–1.80 | 1.35–1.70 |
| C/N | 6.10–16.40 | 11.00–17.15 |
| HHV (MJ kg$^{-1}$) | 23–33 | 24–37 |
| pH | 9.3–10.2 | N/A |
| Moisture (wt%) | 15–60 | 1–5 |
| Density (g ml$^{-1}$) | N/A | N/A |
| | **Macroalgae** | |
| O/C | 0.15–0.40 | 0.10–0.35 |
| H/C | 1.35–1.63 | 1.20–1.40 |
| C/N | 18.20–40.20 | 14.60–45.00 |
| HHV (MJ kg$^{-1}$) | 24–34 | 21–34 |
| pH | 3.3–6 | N/A |
| Moisture (wt%) | 25–35 | 2–10 |
| Density (g ml$^{-1}$) | ~1 | ~1 |
| | **Municipal sludge** | |
| O/C | 0.15–0.70 | 0.005–0.15 |
| H/C | 1.35–2.60 | 1.40–1.65 |
| C/N | 6.50–11.50 | 15.00–30.05 |
| HHV (MJ kg$^{-1}$) | 16–28 | 30–38 |
| pH | 3.5–8.5 | N/A |
| Moisture (wt%) | 15–79 | N/A |
| Density (g ml$^{-1}$) | ~1 | ~1 |
| | **Food waste** | |
| O/C | 0.10–0.35 | 0.09–0.20 |
| H/C | 0.90–1.70 | 1.01–1.90 |
| C/N | 12.35–45.30 | 15–380 |
| HHV (MJ kg$^{-1}$) | 15–32 | 32–42 |
| pH | 3–9 | N/A |
| Moisture (wt%) | 50–80 | 0.3–4 |
| Density (g ml$^{-1}$) | 1–1.50 | <1 |

$^a$ Data are gathered and analyzed from ref. 40, 41, 55, 57–59, 62, 64, 65, 158–163, 213, 218, 233, 263, 264, 278, 284, 289–295. $^b$ See ref. 89, 93, 97, 98, 101–103, 105, 107, 109–111, 128, 130, 169, 190, 213, 234, 237, 254, 281, 282, 296–300.

favorable as the C/N ratio of crude oil varies between 507–967.[302] Lower C/N ratios can result in NO$_x$ emissions when the liquid biofuel is burned,[303] as well as several other issues, such as increased viscosity, instability leading to cross-linking or oligomerization, and catalyst poisoning in standard refining processes.[304] Therefore, appropriate post-upgrading processes should be applied when the N content of the liquid biofuel is high. As can be seen from Table 5, among five

reviewed feedstocks, pyrolysis oil and bio-crude oil derived from microalgae and municipal sludge contains high N content compared to lignocellulosic, macroalgae, and food waste derived liquid biofuels. Compared to fast/flash pyrolysis, the C/N ratio of bio-crude oil produced from the same feed-stocks in the HTL process is significantly higher, indicating that HTL is more effective at mitigating the impact of high N content in biomass on the resulting liquid biofuel.

In conclusion, in this section, the analysis of the literature confirms that microalgae and municipal sludge consistently produce liquid biofuels with higher N content compared to other feedstocks. Some lignocellulosic biomass and food waste can have a high C/N ratio, depending on their source, but still not comparable to crude oil. The HTL process is notably more effective at reducing N content than fast/flash pyrolysis, leading to higher C/N ratios for bio-crude oils from all biomass. This is likely due to the fact that more than 55% of the N is recovered in the aqueous by-product (HTL-AP), rather than remaining in the bio-crude oil during the HTL process.[252] The high C/N ratio of liquid biofuels in Table 5 suggests that denitrogenation upgrading processes are essential for liquid biofuels. While fast/flash pyrolysis and HTL can produce biofuels with H/C ratio close to crude oil under certain operational conditions, their C/N ratio remains significantly lower. This highlights the need for additional strategies during or after TPs to achieve more favorable O/C and C/N ratios. Identifying oxygenated and N-containing compounds will be crucial in developing hybrid upgrading processes. The levels of organic compounds in bio-crude and pyrolysis oil are discussed in detail in Section 4.4.

### 4.3 Physical characteristics of liquid biofuels derived from different biomass

The amount of biofuel entering the fuel injector of a combustion engine is determined by its density, which is influenced by various factors, including the type of feedstock used for its production. Biofuel density is crucial in nozzle design and can impact the engine's operational feasibility.[305,306] It directly affects fuel atomization, which in turn influences the engine's thermal efficiency.[307] The viscosity of the biofuel is of great importance as it influences the biofuel's pumpability, atomization, and penetration.[308] The acidity of biofuel is another key factor regarding the quality of the produced biofuel, and it is a measure that indicates the amount of free fatty acids and acids produced from the degradation reactions of biomass. According to the ASTM D6751-07b standard, the total acid number (TAN) for crude oil should not exceed 0.5 mg KOH per g of oil.[309] Moisture in biofuel is another concern, as it can lead to water accumulation, microbial growth, and corrosion in storage and transportation equipment.[310] The following subsections summarize biomass-type specific information.

**4.3.1 Lignocellulosic biomass.** For lignocellulosic biomass, Haarlemmer et al.[213] tested fast pyrolysis and HTL on beech wood and found that the density and viscosity of pyrolysis oil were approximately 1.1 g cm$^{-3}$ at 22 °C and 13–70 mPa s at 40 °C, respectively. In comparison, while the density of bio-

crude oil is similar, its viscosity is significantly higher, around 67 000 mPa s at 40 °C, which can be problematic and requires further upgrading to enhance pumpability. Bio-crude oil contains less than 1 wt% moisture, whereas the moisture content of pyrolysis oil ranges from 7.8 to 21 wt%. TAN of pyrolysis oil and bio-crude oil derived from beech wood is 45–109 and 32–67 mg KOH per g, respectively. Pittman et al.[311] applied fast pyrolysis to corn stalks and found that increasing the pyrolysis temperature and the water content slightly in the biomass decreased the moisture content of the produced pyrolysis oil from 54.7 to 27 wt%. However, this also increased the viscosity of the oil from 1.60 to 41.4 cSt and its HHV from 17.40 to 25.84 MJ kg$^{-1}$. TAN and pH of the pyrolysis oil varied between 81.7–85.8 mg KOH per g and 2.66–3.29, respectively. Nizamuddin et al.[312] analyzed the bio-crude oil derived from the HTL process of corn stalk using ethanol as the solvent. They found that the bio-crude oil had only 4.76 wt% moisture, and its HHV was 30.52 MJ kg$^{-1}$. From the literature, it can be concluded that the acidity of pyrolysis oil is generally higher compared to bio-crude oil derived from lignocellulosic biomass. The pH of pyrolysis oil obtained from lignocellulosic biomass ranges from 2.5 to 4.9.[313–317] In addition, pyrolysis oil derived from lignocellulosic biomass contains a significant amount of water (more than 20 wt%), whereas the water content of bio-crude oil from lignocellulosic biomass is less than 5 wt%. Despite these differences, both pyrolysis oil and bio-crude oil have densities within the same range for lignocellulosic biomass.

**4.3.2 Microalgae.** For microalgae, Hognon et al.[318] used *Chlamydomonas reinhardtii* as the feedstock for both fast pyrolysis and HTL. For fast pyrolysis, the feedstock was dried to a moisture content of less than 10 wt%, whereas for HTL, it was used without drying, with a moisture content of 80–90 wt%. They indicated that the moisture content of pyrolysis oil is much higher than that of bio-crude oil. In their study, they optimized HTL and fast pyrolysis temperatures to maximize liquid biofuel yield and HHV. They found that the bio-crude oil yield could reach up to 71.4 wt% with an HHV of 23.5–36.1 MJ kg$^{-1}$, while the pyrolysis oil yield could vary from 53.3 to 60.2 wt% with an HHV of 32.6–33.5 MJ kg$^{-1}$. It is important to note that increasing the temperature up to a certain point can enhance both yield and HHV. However, beyond a specific threshold, increasing the temperature may reduce the liquid biofuel yield due to gasification, although it continues to improve the HHV value. Sotoudehniakarani et al.[160] characterized the pyrolysis oil obtained from *Chlorella vulgaris* and confirmed that at higher pyrolysis temperatures, the water content of the pyrolysis oil decreased, varying between 55–64%. They found that the pH of the pyrolysis oil from microalgae ranged between 9.60 and 10.10. They explained that these results suggested that N-containing proteins were primarily converted into pyrolysis oil, which could explain the increase in the pH of the pyrolysis oil generated at higher temperatures. The pH of pyrolysis oil obtained from microalgae varied between 9.30 and 10.20.[319–322] The high N content of microalgae may be a cause for the high pH of pyrolysis oil derived from this

biomass. Jena and Das[322] processed *Spirulina platensis* using both HTL and pyrolysis to produce liquid biofuel. They found that for pyrolysis oil, the pH was about 9.43 ± 0.09, density was 1.12 ± 0.08 g ml$^{-1}$, viscosity was 90.50 ± 11 cP at 40 °C, and HHV was 31.50 ± 2 MJ kg$^{-1}$. For bio-crude oil, the corresponding values were approximately pH 9.60, density 0.97 g ml$^{-1}$, viscosity 189.80 cP at 40 °C, and HHV 34.21 MJ kg$^{-1}$. Thus, similar to lignocellulosic biomass, bio-crude oil derived from microalgae contains lower moisture and density compared to pyrolysis oil, and its viscosity is higher than that of pyrolysis oil. The acidity of the liquid biofuel may not be a concern when using microalgae since it produces alkaline biofuel.

**4.3.3 Macroalgae.** Regarding macroalgae, Zhao et al.[323] analyzed the pyrolysis oil generated from the fast pyrolysis process of *Enteromorpha prolifera*. They observed that the pyrolysis oil had a pH of 2.56 ± 0.11, a density of 1.03 ± 0.02 g ml$^{-1}$, a moisture content of 32.45 ± 2.55 wt%, and an HHV of 25.33 ± 3.01 MJ kg$^{-1}$. Ly et al.[58] pyrolyzed *Saccharina japonica* at different temperatures. At 350 °C, the yield was 44.99 wt%, the pH was 4.68, and the HHV was 24.80 MJ kg$^{-1}$. At 500 °C, the yield decreased to 26.67 wt%, the pH increased to 6.08, and the HHV increased to 28.27 MJ kg$^{-1}$. Pyrolysis oil obtained from the fast pyrolysis process of *Ulva lactuca* is characterized and compared to lignocellulosic-derived pyrolysis oil by Trinh et al.[59] They determined that the pH, density, moisture, and HHV of macroalgae-derived pyrolysis oil were around 4.3, 0.98 g ml$^{-1}$ at 40 °C, 26.6 wt%, and 25.7 MJ kg$^{-1}$, respectively, while lignocellulosic-derived pyrolysis oil had a pH of 3.2–3.9, a density of 1.09–1.15 g ml$^{-1}$ at 40 °C, moisture content of 25.7–27.4 wt%, and an HHV of 23.7–29.7 MJ kg$^{-1}$. Xu et al.[236] applied HTL to *Enteromorpha prolifera* and reported that the bio-crude oil had a moisture content of 7 wt% with an HHV of 39.4 MJ kg$^{-1}$. Since the drying of biomass can be significantly costly and macroalgae contains a high moisture content, the pyrolysis of macroalgae is not very common. Additionally, pyrolysis oil derived from macroalgae has a slightly acidic pH and contains a significant amount of moisture (>25 wt%). However, bio-crude oil generated *via* HTL of macroalgae has a much lower moisture content.

**4.3.4 Municipal sludge.** Municipal sludge is commonly used for both pyrolysis and HTL. Alvarez et al.[62] conducted fast pyrolysis on anaerobically digested sewage sludge and observed that the produced pyrolysis oil contained a pH of 8.5, density of 1.050 g ml$^{-1}$, viscosity of 28 cSt at 40 °C, and moisture of 23 wt%. In another study, sewage sludge was processed by Trinh et al.[244] *via* fast pyrolysis at different temperatures. They discovered that the water content of pyrolysis oil derived from sewage sludge did not decrease with increasing temperature; instead, it increased from 27.8 wt% at 457 °C to 28.5 wt% at 625 °C. They also noted that the density, viscosity, and HHV changed from 1.08 g ml$^{-1}$, 81.1 mPa s at 40 °C, and 15.5 ± 1.1 MJ kg$^{-1}$ at 457 °C to 1.07 g ml$^{-1}$, 137.7 mPa s at 40 °C, and 23.1 ± 0.5 MJ kg$^{-1}$ at 625 °C. Zuo et al.[324] reported that sewage sludge-derived pyrolysis oil's pH, viscosity, and HHV were 4.3, 41 cSt at 40 °C, and 25.4 MJ kg$^{-1}$, respectively. On the other

hand, Liu et al.[107] analyzed the bio-crude oil produced by HTL of mixed sludge, primary sludge, and secondary sludge and reported that mixed sludge had a TAN of 74.5 mg KOH per g with an HHV of 33.1 MJ kg$^{-1}$ and viscosity of 1570 mPa s at 22 °C, primary sludge had a TAN of 65 mg KOH per g with an HHV of 37.8 MJ kg$^{-1}$, and secondary sludge had a TAN of 44.8 mg KOH per g with an HHV of 34.8 MJ kg$^{-1}$. Jarvis et al.[325] processed primary sludge via the HTL process and determined that bio-crude oil generated from primary sludge had a density of 1 g ml$^{-1}$, viscosity of 571 cSt at 40 °C, moisture content of 13 wt%, and TAN of 65 mg KOH per g.

The wide range of results reported for municipal sludge has the problem of lack of specific feedstock information. Municipal sludge characteristics can vary depending on the source of unit processes (primary, secondary, mixed, or digested sludges), process operation (separate versus combined sewer, hydraulic and sludge retention times, conventional versus advanced treatment processes, chemical dosing for dewatering), location of the plant as well as sampling season, especially for secondary sludge from biological treatment processes. Often, literature reports results for different types of municipal sludge without any specifics leading to varied results in the characteristics of liquid biofuel derived from municipal sludge across studies. Generally, due to municipal sludge's high moisture content even after digestion, HTL is considered more suitable than pyrolysis for treating municipal sludge. However, it is important to note that the ash content of municipal sludge can negatively impact bio-crude yield, making hydrothermal carbonization (HTC) a preferable treatment option in such cases.

**4.3.5   Food waste.** For food waste, Liang et al.[64] used potato peel waste and potato peel waste residue as the feedstock for fast pyrolysis. They observed that pyrolysis oil derived from these food wastes had a pH of 8.3 ± 0.3 with a moisture content of around 80%. In another study, Ly et al.[264] pyrolyzed mixed food waste and characterized the produced pyrolysis oil, reporting an HHV of 29.69 MJ kg$^{-1}$ and a pH of 3.27. Kadlimatti et al.[326] processed food waste via microwave-assisted pyrolysis and found that the pyrolysis oil's pH, density, viscosity, moisture content, and HHV were 4.5, 1.04 g ml$^{-1}$, 1.16 cSt, 50.12 wt%, and 19.95 MJ kg$^{-1}$, respectively. Regarding the use of food waste as feedstock for HTL, Chen et al.[269] characterized the bio-crude oil obtained from the HTL process of food waste with 74 wt% moisture and indicated that the bio-crude oil had 0.3 wt% moisture with an HHV of 34.79 MJ kg$^{-1}$. Anouti et al.[327] applied HTL to blackcurrant pomace with a moisture content of 59.6 wt% and reported that the produced bio-crude oil's moisture, density, viscosity, TAN, pH, and HHV were <1 wt%, 0.975 ± 0.15 g ml$^{-1}$, 495 mPa s at 40 °C, 133 ± 25 mg KOH per g, 3.3, and 35.5 ± 2.5 MJ kg$^{-1}$, respectively. Saengsuriwong et al.[109] also tested HTL on food waste and reported that the HHV of the bio-crude oil was 37.33 MJ kg$^{-1}$. Therefore, food waste is a type of biomass with high water content, limiting its application for pyrolysis without treatment. Pyrolysis oil derived from food waste contains a lot of moisture, requiring a post-upgrading process for moisture

removal as well as for balancing H/C, O/C, and N/C ratios. HTL, on the other hand, is highly advantageous for processing food waste as it generates bio-crude oil with a comparable HHV to crude oil, and the bio-crude has negligible moisture. Regarding energy potential, food waste has the highest potential among all feedstocks reviewed in this paper for liquid biofuel production from biomass, as its HHV is comparable to that of crude oil. This means that, due to its high HHV and lower O/C ratio, food waste can be combined with lignocellulosic biomass, municipal sludge, and algal biomass to enhance liquid biofuel production and improve the energy potential of biofuels obtained through co-fast/flash pyrolysis and/or co-HTL.

### 4.4.   Chemical characteristics of bio-crude oil and pyrolysis oil derived from different biomass

The organic components of biomass, including carbohydrates, proteins, lipids, and lignin, are primarily converted into liquid biofuels during fast/flash pyrolysis and HTL processes. In contrast, the inorganic fraction of biomass predominantly accumulates in the solid by-products.[256,328] The relative composition of these components significantly influences both the yield of liquid biofuels and the concentrations of organic compounds present in bio-crude and pyrolysis oil. Fig. 5 illustrates the distribution of carbohydrates, proteins, lipids, and lignin in lignocellulosic biomass, microalgae, macroalgae, municipal sludge, and food waste.

The breakdown of carbohydrates in biomass leads to the formation of alcohols, ketones, and carboxylic acids. Aromatic hydrocarbons and phenols primarily originate from the protein fraction in biomass, and their production increases as the temperature increases. The primary decomposition of phenylalanine and tyrosine involves decarboxylation, deamination, and the simultaneous breaking of C–C bonds through concerted rupturing (resulting in radical formation) pathways.[335] The Maillard reaction affects the presence of N-containing compounds in liquid biofuels.[336] The increased temperature in pyrolysis promoted the Maillard reaction, which involves the incorporation of N by transforming quaternary-N into a more stable N formation. Consequently, the Maillard reaction leads to the formation of heterocyclic N-containing compounds.[337] Long-chain fatty acids are obtained through the pyrolysis of lipids in biomass. Despite the thermal cracking of triglycerides leading to the production of short-chain hydrocarbons, long-chain fatty acids can persist if the residence time is short.[338] Additionally, aromatic hydrocarbons can be formed from lipids at elevated temperatures, during which cyclization and aromatization reactions take place.[339] Phenols can be generated from proteins, carbohydrates, and lignin.[138,339] Fig. 6 indicates the detailed pathways of alcohols, acids, phenols, ketones, aliphatic and aromatic hydrocarbons, N-containing compounds, and oxygenated compounds formation from carbohydrates, proteins, lipids, and lignin through fast/flash pyrolysis.

The presence of water in HTL introduces a higher level of complexity to the reactions compared to fast/flash pyrolysis. As
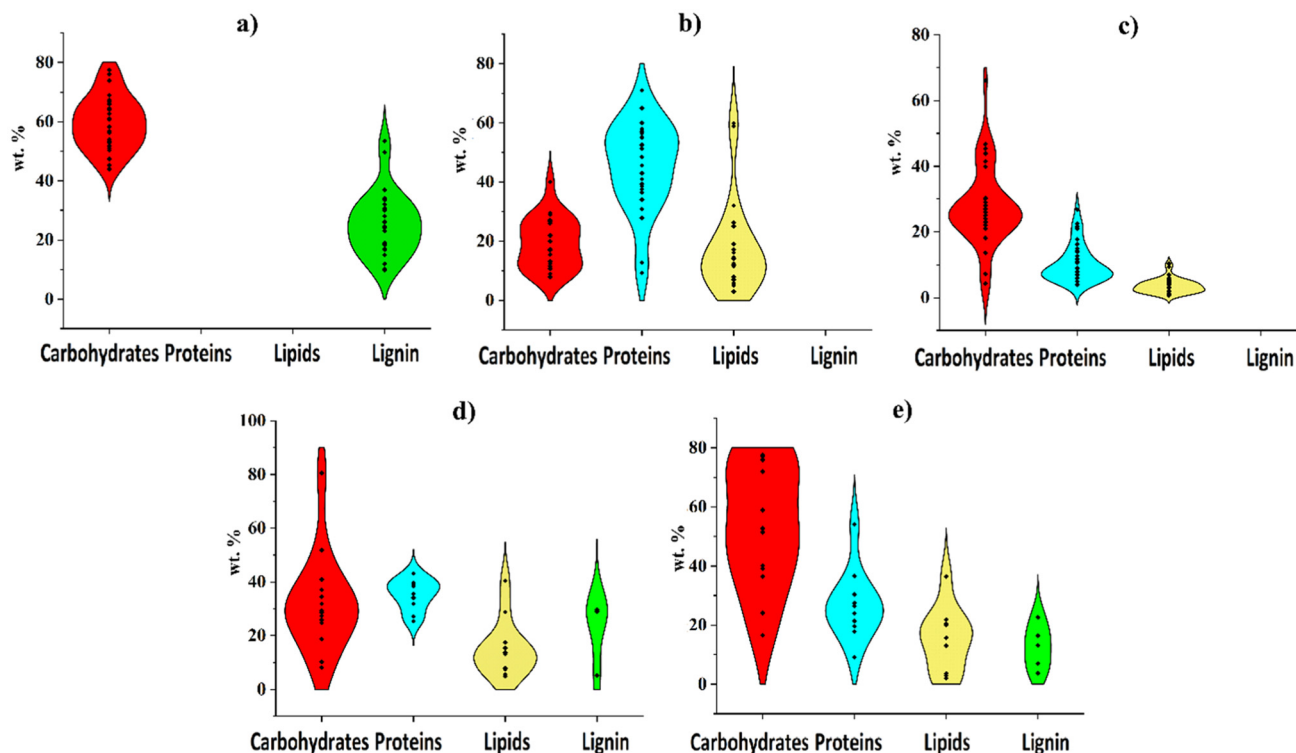
**Fig. 5** Distribution of carbohydrates, proteins, lipids, and lignin in (a) lignocellulosic biomass;[6,75,97,202,204,207,209,210,212,329] (b) microalgae;[6,57,93,160,215,217–220,222,224–227,330,331] (c) macroalgae;[59,60,104,232,234,235,240] (d) municipal sludge;[76,161,249–251,332,333] (e) food waste.[109–111,169,261,262,267,268,270,283,334] Note: protein and lipid distribution in lignocellulosic biomass and lignin distribution in microalgae and macroalgae are not reported due to the lack of references that reported these compounds.

shown in Fig. 7, HTL involves a variety of reactions, including hydrolysis, dehydration, hydration, deoxygenation, deamination, and hydrogenation, affecting carbohydrates, proteins, lipids, and lignin. Unlike pyrolysis, the water in HTL facilitates the formation of more complex compounds, which are ultimately incorporated into bio-crude oil. Fig. 8 illustrates the pathways leading to the formation of various alcohols, acids, phenols, ketones, aliphatic and aromatic hydrocarbons, as well as N and oxygenated compounds, all derived from the biomass components during HTL. The concentration of organic compounds in liquid biofuels plays a crucial role in determining the quality of the resulting bio-oils. While some information is available regarding the effects of specific chemicals in biofuels, there remains a significant gap in understanding how each chemical affects the fuel properties of bio-crude oil and pyrolysis oil. Certain compounds may lead to storage and transportation challenges, while others can contribute to pollutant emissions during combustion or lower the heating value of the biofuels. N-heterocyclic compounds, in particular, are a critical concern. Due to the N content in biomass, originating from its cellular structure and protein composition, the presence of N-containing compounds in liquid biofuels is inevitable.[345] The presence of N-heterocyclic compounds in biofuels can lead to increased $NO_x$ emissions during combustion. Additionally, these compounds can affect the odor of biofuels and pose challenges during the upgrading process. They

tend to adhere to acidic catalysts, potentially deactivating them and reducing their effectiveness.[346]

Aromatics reduce the fuel quality of liquid biofuels due to their lower H/C ratio, which decreases energy density. Their presence also raises environmental concerns by promoting the formation of polycyclic aromatic hydrocarbons (PAHs) during combustion.[353] Wang et al.[354] reported that the presence of $C_8$–$C_{15}$ cyclic alkanes instead of high-carbon aromatics can improve the HHV, H/C, and O content of pyrolysis oil obtained from lignocellulosic biomass via fast pyrolysis.

Alcohols can influence liquid biofuels positively or negatively, depending on the position of the hydroxyl (–OH) group. Long-chain alcohols offer higher energy density than short-chain ones due to their lower O/C ratio. However, both alcohols and acids can cause storage problems, such as corrosion.[355] Esters are key components of liquid biofuels and can enhance fuel quality. However, their presence may increase the O/C ratio, reducing the heating value of biofuels.[356] Aldehydes and ketones are present in liquid biofuels. While certain aldehydes enhance fuel properties, most contribute to instability, unpleasant odors during combustion, and storage issues due to their corrosiveness. Similarly, ketones can improve some fuel properties but may also alter the O/C ratio, leading to biofuel instability and corrosion.[357]

Phenols, primarily derived from lignin in biomass, are commonly found in liquid biofuels. They pose challenges during
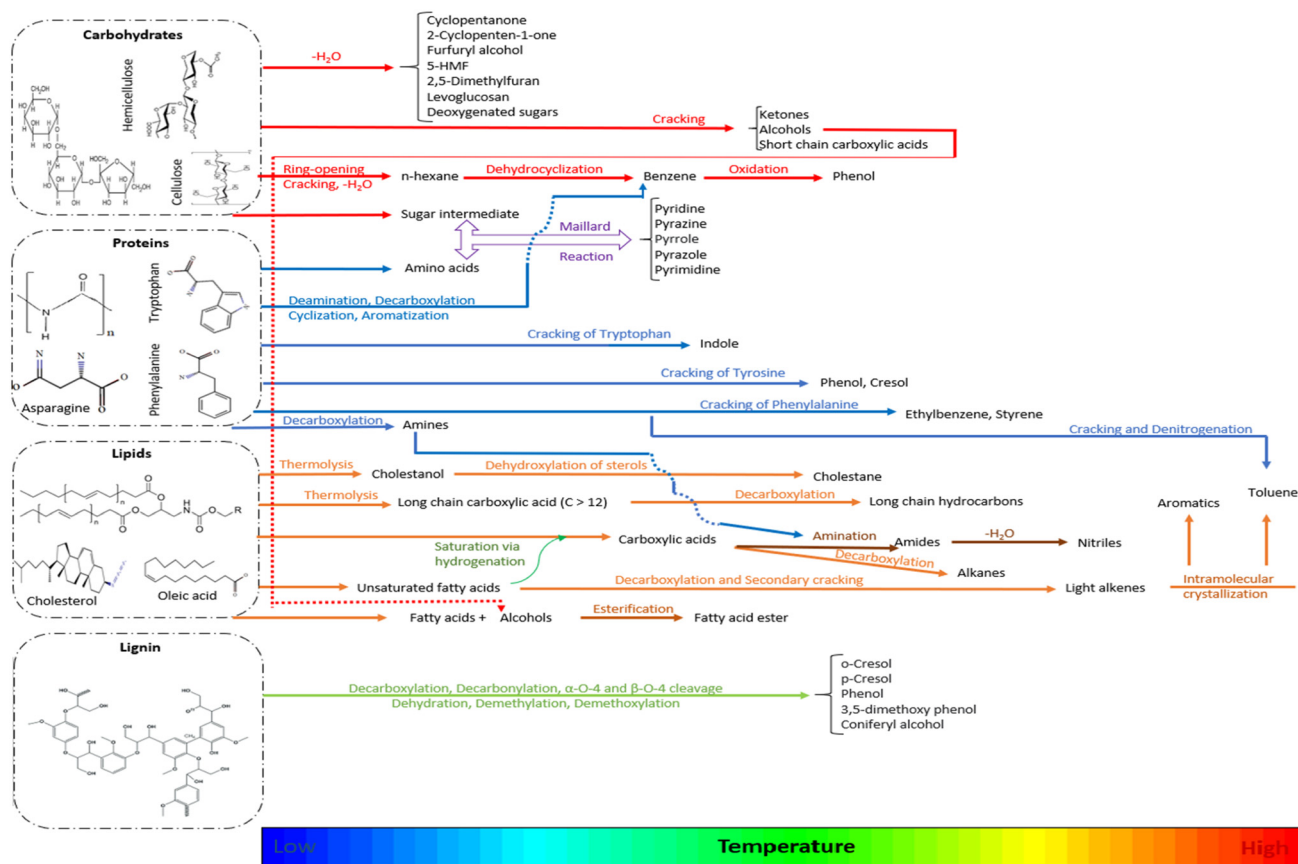
**Fig. 6** Plausible reaction pathways of pyrolysis of carbohydrates, proteins, lipids, and lignin.[138,340–344]

upgrading processes due to coke formation and their corrosive nature, which can also affect the storage of liquid biofuels.[358] Additionally, phenols can originate from cellulose and hemicellulose during TPs.[359]

Fig. 8 presents the comparative relative areas (%) of alcohols, acids, phenols, ketones, aliphatics, aromatics, N-containing compounds, and oxygenated compounds in bio-crude oil and pyrolysis oil derived from five different types of biomass, as analyzed by gas chromatography-mass spectrometry (GC-MS). The list of organic compounds used to generate Fig. 8 is provided in Table S1.† As shown, oxygenated compounds make up a smaller relative area (%) in bio-crude oil compared to pyrolysis oil in lignocellulosic biomass, algal biomass, municipal sludge, and food waste. It means that the HTL process is more effective in deoxygenation than fast/flash pyrolysis regardless of the biomass characteristics. Biomass's biochemical composition plays a crucial role in the distribution of organic compounds. Lignin in lignocellulosic biomass results in bio-crude oil with phenols (12–38%) and pyrolysis oil with phenols (2–25%). Microalgae, with high protein content, produce bio-crude oil (14–66%) and pyrolysis oil (16–27%) with higher levels of N-containing compounds. Aromatics in microalgae-derived bio-crude oil and pyrolysis oil are present in similar relative amounts to N-containing compounds. Macroalgae, with higher carbohydrates and lower pro-

teins and lipids, yields bio-crude oil (9–23%) and pyrolysis oil (9–42%) with significant ketones. Municipal sludge, containing high levels of proteins, carbohydrates, and lignin, produces bio-crude oil and pyrolysis oil with high N-containing compounds (bio-crude oil: 18–48%, pyrolysis oil: 13–30%) and phenols (bio-crude oil: 2–9%, pyrolysis oil: 8–16%). Biomass with higher carbohydrates and lipids, like food waste, leads to liquid biofuels with high acidity. Food waste-derived bio-crude oil and pyrolysis oil contain 35–70% and 5–30% acids, respectively. Therefore, the common belief about the acidity of pyrolysis oil is inaccurate. The acidity of both bio-crude oil and pyrolysis oil is primarily influenced by the carbohydrate content in the biomass used as feedstock for fast/flash pyrolysis or HTL. The HTL and pyrolysis processes have minimal impact on the acidity of the produced liquid biofuels.

Although adjusting the severity of fast/flash pyrolysis and HTL can affect the concentration of organic compounds in liquid biofuels,[58,252] it is insufficient to achieve the optimal acidity, HHV, and desired levels of O and N-containing compounds necessary for proper storage, transport, and combustion. Therefore, post-treatment upgrading processes are essential to enhancing liquid biofuels for use as viable fossil fuel substitutes.

Physical methods, chemical processes, steam reforming, and supercritical fluids can all be used to upgrade bio-crude
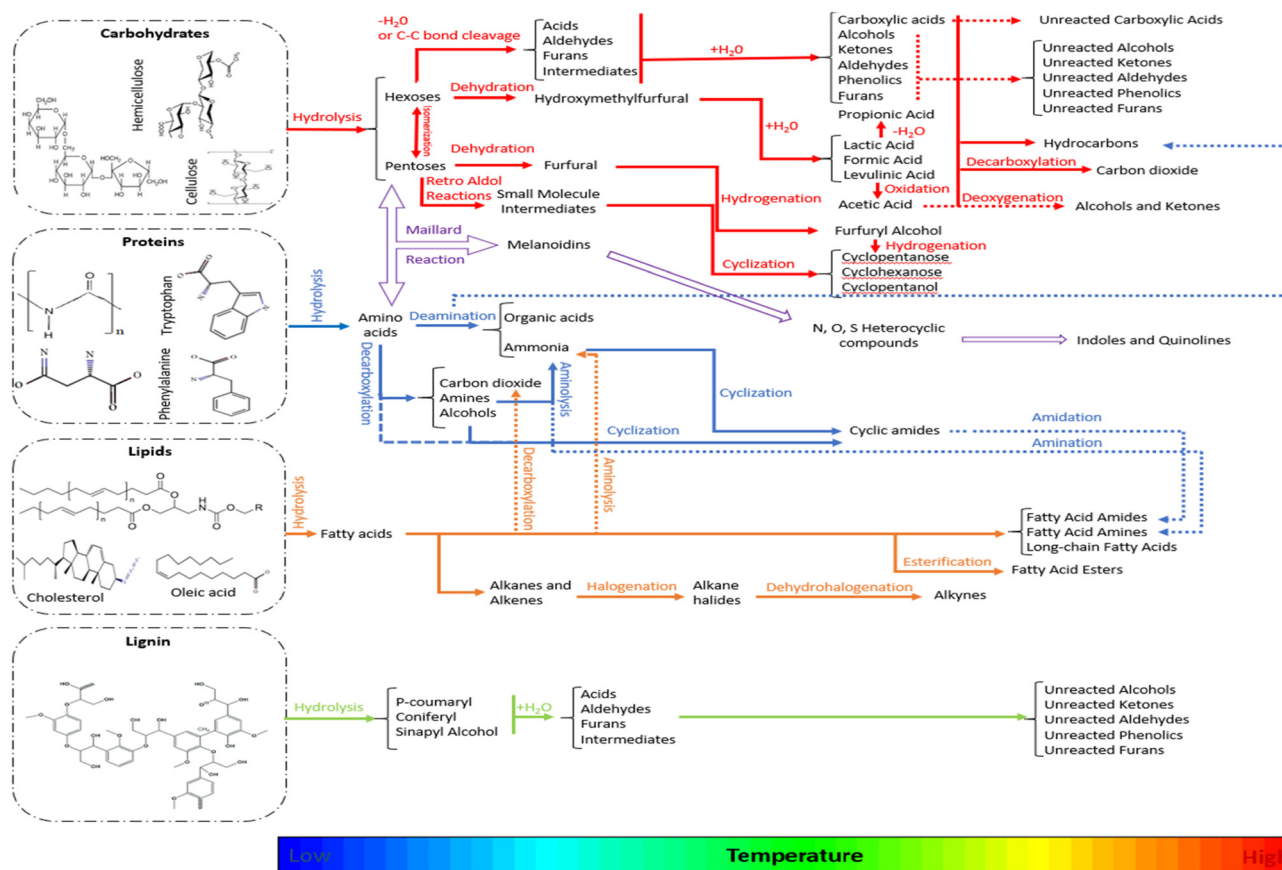
**Fig. 7** Plausible pathways of hydrothermal reactions of carbohydrates, proteins, lipids, and lignin.[4,120,347–352]

oil and pyrolysis oil. Physical methods like filtration, solvent addition, and emulsification can enhance properties such as reducing impurities, improving viscosity, density, and HHV. However, these methods alone are not enough to make liquid biofuels a viable alternative to fossil fuels.[361] Supercritical fluids are effective in removing O-containing compounds, such as carboxylic acids, aldehydes, and levoglucosan, while improving the HHV of liquid biofuels. However, their application typically requires significant energy input and may lead to equipment corrosion during the process.[362] Steam reforming operates at high temperatures (700–1000 °C) with the help of a catalyst. By combining catalytic steam reforming with the water–gas shift reaction, it efficiently produces hydrogen ($H_2$) as a clean energy resource. This method also has its own limitations and cannot remove many of the organic compounds in liquid biofuels to make them comparable to crude oil.[363]

Chemical methods also offer the potential for removing certain organic compounds in liquid biofuels. Esterification, which involves adding alcohol under mild conditions, can improve the HHV and viscosity of liquid biofuels by removing some O-containing compounds. However, this method is ineffective in removing N-containing compounds.[364] Hydrodeoxygenation (HDO) is a widely used method for eliminating O-containing compounds in bio-crude oil and pyrolysis oil, with the goal of increasing the H/C ratio and reducing the

O/C ratio. Recent studies have concentrated on developing catalysts to improve the HDO upgrading process.[365,366] Since several studies have already reviewed liquid biofuel upgrading processes,[363,367,368] this article does not provide a detailed description of each upgrading method. However, it should be noted that while these upgrading processes can improve the characteristics of bio-crude oil and pyrolysis oil to some extent, none has emerged as a definitive solution. Liquid biofuels derived from different biomass types contain varying levels of organic compounds and impurities. Therefore, selecting the appropriate upgrading process is crucial to enhancing liquid biofuels quality while minimizing costs.

The choice of upgrading processes should be guided by the specific chemical and physical properties of liquid biofuels, with the levels of organic compounds playing a key role in determining suitable upgrading methods. As shown in Fig. 8, the composition of organic compounds can guide the identification of appropriate processes for bio-crude oil and pyrolysis oil derived from various biomass types, including lignocellulosic biomass, microalgae, macroalgae, municipal sludge, and food waste. For example, the removal of N-containing compounds is less critical for bio-crude oil from lignocellulosic biomass than for that derived from microalgae. This comparative review highlights a significant research gap in the field of liquid biofuels: understanding how different organic
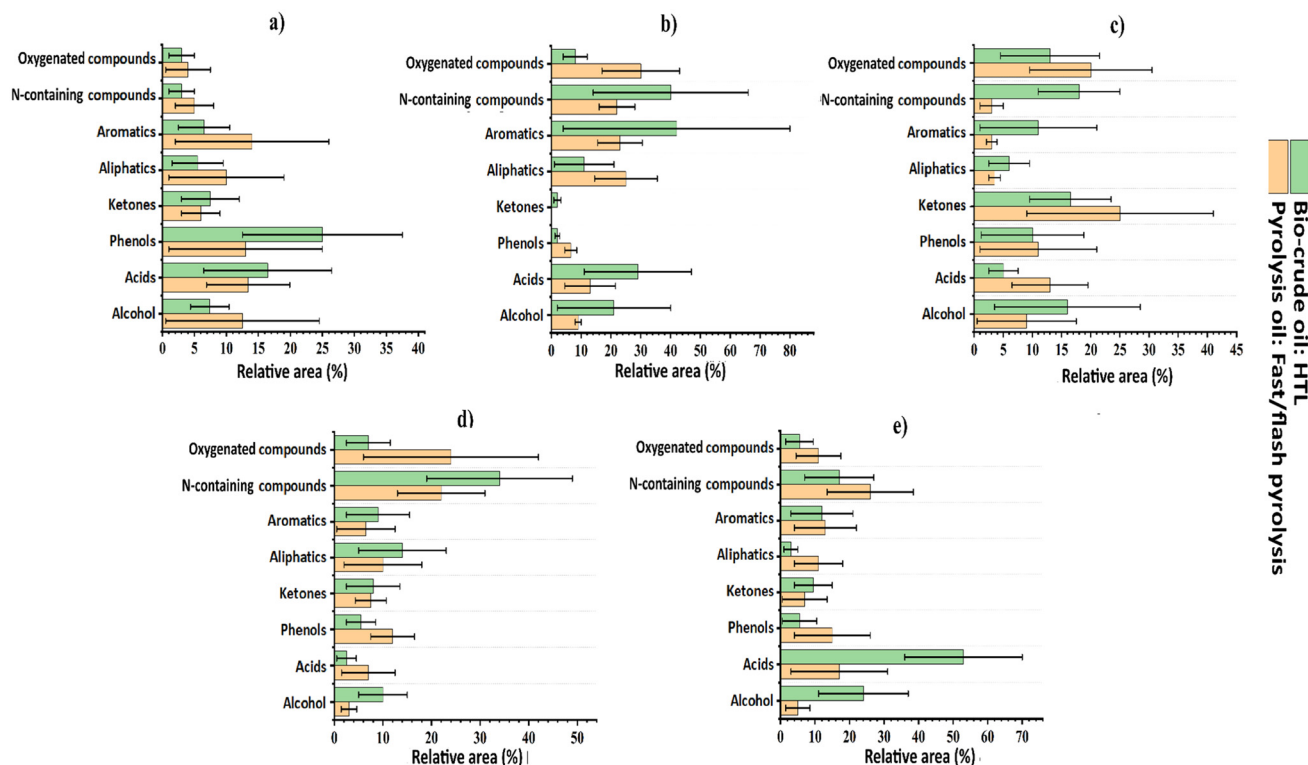
**Fig. 8** Comparing relative area (%) of organic compounds in bio-crude oil and pyrolysis oil after the fast/flash pyrolysis and HTL processes of (a) lignocellulosic biomass;[6,75,97,128,159,203,206,210,211,360] (b) microalgae;[6,57,215,216,218,222,224,225,229] (c) macroalgae;[58,60,103,231–233,236,238,239] (d) municipal sludge;[62,76,130,161,243,246,250,252,256] (e) food waste.[109–111,164,260–262,264,265,267,269]

compounds impact biofuel quality and the need for selective or multistage upgrading processes. Liquid biofuels derived from HTL and pyrolysis exhibit varying levels of N- and O-containing compounds, aromatics, and aliphatics, depending on the biochemical composition of the biomass. A single upgrading process may indiscriminately remove O from all organic compounds, but certain compounds like aldehydes and alcohols, despite both being oxygenated, may have distinct effects on biofuel quality and require different removal strategies. A deeper understanding of the specific impacts of various organic compound categories is essential for developing effective multistage upgrading processes that produce high-quality liquid biofuels from HTL and fast/flash pyrolysis.

## 5. Advantages and disadvantages of HTL and fast/flash pyrolysis and prospects toward application of thermochemical processes

Fast/flash pyrolysis processes are compared to the HTL process thoroughly in this review article for their potential to recover liquid biofuels from different biomass. The results reveal that biomass type plays a key role in the efficiency of the TPs as well as operational conditions for biofuel production. Therefore, neither fast/flash pyrolysis nor HTL can produce

high-quality liquid biofuel solely by optimizing operational conditions without considering the biomass type. However, each process has its own advantages and drawbacks. Several of these points are tabulated in Table 6. By comparing the advantages and disadvantages of HTL and fast/flash pyrolysis, it can be concluded that the choice of process for converting biomass into liquid biofuel should not rely solely on biomass moisture. Instead, the composition and properties of the resulting liquid biofuels, particularly the concentration of organic compounds, should be considered, as they will determine the extent of upgrading required. Both biomass pretreatment and liquid biofuel post-treatment processes can influence the economic feasibility of the overall process. In general, for industrial-scale applications, the moisture content of biomass, biofuel yield, and biofuel's characteristics can be the key factors in choosing between HTL and fast/flash pyrolysis. In terms of yield and quality of liquid biofuels, HTL can produce bio-crude oil with higher HHV compared to fast/flash pyrolysis processes for all five types of biomass reviewed in this study. However, the yield of liquid biofuels from fast/flash pyrolysis can be higher than that from HTL for specific biomass types. The level of organic compounds in liquid biofuels is highly affected by biomass's biochemical characteristics. Therefore, it is not possible to definitively determine which process is superior in all aspects. In Fig. 9, the recommended TPs for five types of feedstocks reviewed in this study are summarized based on biofuel yield and quality.

**Table 6** Biomass-specific advantages and disadvantages of HTL and fast/flash pyrolysis, along with research gaps, for liquid biofuel production

| Process | Hydrothermal processes (HTL) | Pyrolysis (fast/flash pyrolysis) |
|---|---|---|
| Advantages and (consequences) | - Comparable liquid biofuel yields for municipal sludge and food waste to fast/flash pyrolysis. (Lower capital costs.)<br>- Better quality of liquid biofuel in terms of HHV, O/C, and moisture. (Decreasing required upgrading processes.)<br>- Excessive size reduction of biomass is unnecessary, and wet biomass can be processed. (Reducing pre-treatment costs.) | - Greater liquid biofuel yield for lignocellulosic biomass and macroalgae than HTL. (Lower capital costs.)<br><br>- There is a limited production of aqueous by-product. (No further management is necessary for by-products.)<br>- Commercialized process. (Minimum unknown parameters.) |
| Disadvantages and (consequences) | - Production of significant amount of aqueous phase. (Needs further management of by-products.)<br>- Literally a novel process with a lot of unknown effective parameters. (Scaling up is risky.)<br>- Needs water to operate. (Significant amount of water consumption if biomass does not have enough moisture.)<br>- Inefficient in producing bio-crude oil with acceptable levels of organic compounds (Novel multistage upgrading processes are necessary to address storage, shipment, and combustion.) | - Drying biomass is necessary. (High pre-treatment cost if biomass has a lot of moisture.)<br>- Poor liquid biofuel quality in terms of HHV, O/C, C/N, and moisture. (Increasing required upgrading processes.)<br>- Reactor design and particle size can affect the efficiency of the process. (Making the process complicated.)<br>- Inefficient in producing pyrolysis oil with acceptable levels of organic compounds. (Novel multistage upgrading processes are necessary to address storage, shipment, and combustion.) |
| Research gaps | - Investigating the effects of various organic compounds present in bio-crude oil and pyrolysis oil on their storage stability and fuel properties<br>- Developing biomass-specific pretreatment strategies to minimize feedstock heterogeneity and achieve uniform composition for each biomass type<br>- Designing cost-effective, multistep, and selective upgrading processes targeting key organic compounds that negatively impact the quality and stability of liquid biofuels<br>- Exploring integrated process configurations and reactor designs to reduce the sensitivity of pyrolysis oil yield and quality to biomass particle size variations<br>- Developing biomass-specific resource recovery approaches from HTL-AP to enable the industrial implementation of HTL technology | |
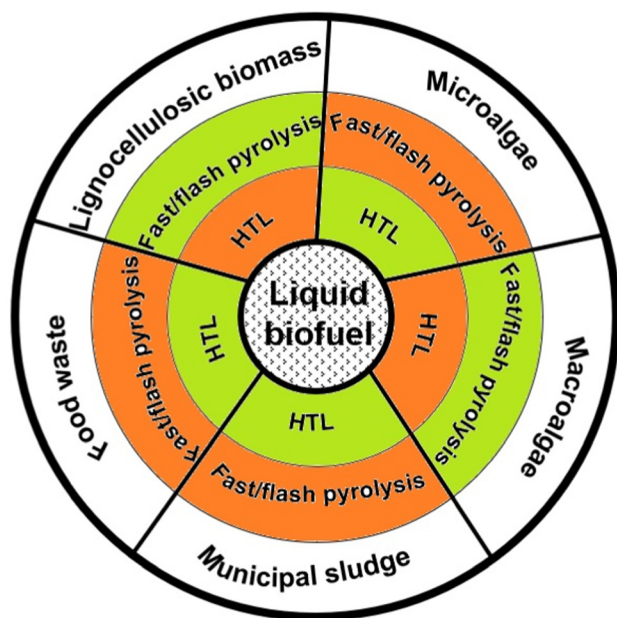


**Fig. 9** Priority of different biomass types for pyrolysis and hydrothermal processes to be converted into liquid biofuel considering biofuel yield and quality. Green color: first priority; orange color: second priority.

## 6. Conclusions

Fast/flash pyrolysis and HTL are two efficient methods for producing liquid biofuels from biomass, comparable to crude oil. The purpose of this review is to equip researchers with new insights into the anticipated liquid biofuel yield from various biomass types through HTL and fast/flash pyrolysis. Additionally, it seeks to assist scholars and industry professionals in selecting between HTL and fast/flash pyrolysis based on the physical and chemical characteristics of liquid biofuels derived from different biomass types, rather than relying solely on biomass moisture. The key findings of this review are summarized below:

• Although high C and H content in biomass can enhance liquid biofuel yield, the presence of N and O can negatively impact the quality of the resulting biofuels.

• The high ash content of biomass limits the liquid biofuel yield, but it does not affect the quality of the resulting biofuels.

• Microalgae show higher yields of liquid biofuels compared to other biomass types in both fast/flash pyrolysis and HTL.

• Lignocellulosic biomass and macroalgae generally exhibit higher conversion yields of liquid biofuel in fast/flash pyrolysis compared to HTL. In contrast, municipal sludge and food waste produce similar ranges of liquid biofuel yields with both fast/flash pyrolysis and HTL.

• The solvent choice in HTL is biomass specific. Generally, an alkaline environment in HTL can enhance bio-crude oil production. For carbohydrate-rich biomass, food waste and lignocellulosic biomass, using an alkaline catalyst is advantageous.

• The severity of HTL and fast/flash pyrolysis processes for maximizing liquid biofuel yield is biomass-specific; however, HTL generally requires less severe conditions for most biomass types.

• The HTL process can produce bio-crude oil from municipal sludge and food waste with H/C and O/C values comparable to crude oil.

• Fast/flash pyrolysis of macroalgae typically produces higher-quality liquid biofuel than HTL in terms of H/C and O/C values.

• The C/N ratio of bio-crude oil is much higher than pyrolysis oil from fast/flash pyrolysis, indicating that HTL is more effective at removing N.

• The HHV of bio-crude oil is generally much higher than that of pyrolysis oil for all feedstocks except macroalgae.

• While bio-crude oil has low moisture compared to pyrolysis oil, the densities of pyrolysis oil and bio-crude oil are within the same range for all biomass types.

• Biomass biochemical composition as well as process type can significantly affect the concentration of organic compounds in liquid biofuels.

• Identifying the carbohydrate, protein, and lipid content of biomass provides limited but useful insight into predicting the concentrations of organic compounds in liquid biofuels. Process selection should be based on each method's ability to reduce undesirable organic compounds, thereby minimizing the need for extensive upgrading.

• Alcohols, acids, ketones, phenols, aliphatics, aromatics, N-containing compounds, and oxygenated compounds in liquid biofuels serve as a driving force for developing multi-stage and/or selective upgrading processes. By addressing these organic compounds, high-quality liquid biofuels can be produced with minimal issues in storage, transport, and combustion.

## Data availability

This review does not include any software, code, or primary research results. Only secondary data were analyzed.

## Conflicts of interest

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

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