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Review

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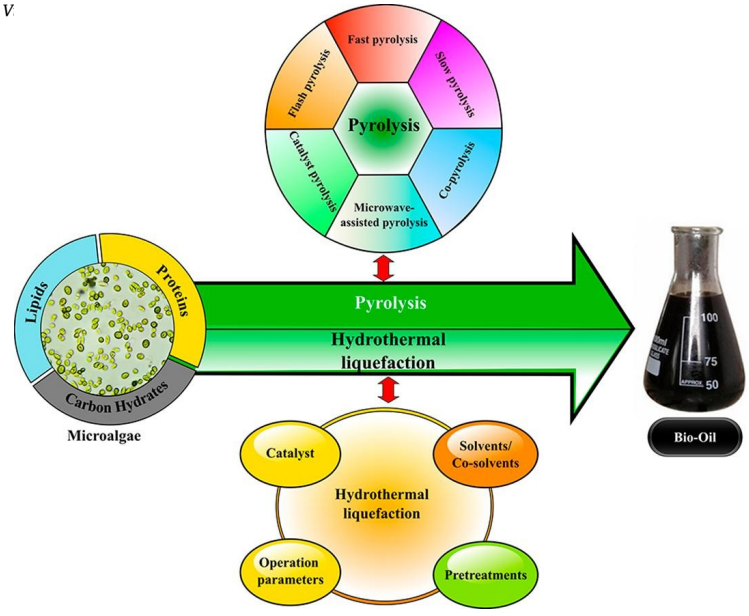
- Microalgae bio-oil (MB) is a renewable fuel for sustainability and circular economy.
- Pyrolysis and hydrothermal liquefaction process for MB production are scrutinized.
- Advanced technologies and challenges of MB production are discussed in detail.
- MB with 46 MJ/kg of heating value and 60% of yield is produced at optimal condition.



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A B S T R A C T

Microalgae have great potential in producing energy-dense and valuable products via thermochemical processes. Therefore, producing alternative bio-oil to fossil fuel from microalgae has rapidly gained popularity due to its environmentally friendly process and elevated productivity. This current work aims to review comprehensively the microalgae bio-oil production using pyrolysis and hydrothermal liquefaction. In addition, core mechanisms

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of pyrolysis and hydrothermal liquefaction process for microalgae were scrutinized, showing that the presence of lipids and proteins could contribute to forming a large amount of compounds containing O and N elements in bio-oil. However, applying proper catalysts and advanced technologies for the two aforementioned approaches could improve the quality, heating value, and yield of microalgae bio-oil. In general, microalgae bio-oil produced under optimal conditions could have 46 MJ/kg heating value and 60% yield, indicating that microalgae bio-oil could become a promising alternative fuel for transportation and power generation.

1. Introduction

Today, global activities such as industrial production and transportation are primarily dependent on fossil fuels (Chowdhury et al., 2021). However, when fossil fuels are burnt, nitrogen oxides are released into the atmosphere, causing acid rain, smog, and greenhouse gas emissions (Bakır et al., 2022; Lee et al., 2020b). Due to this reason, alternative fuel sources to fossil fuels are under investigation, creating the prospect for many renewable sources.

Admittedly, a variety of biofuel types and generations from biomass have been suggested as fossil fuel alternatives to lessen existing and possible risks in the energy industry. However, the production of first-generation biofuel from crop plants and second-generation biofuel from lignocellulosic biomass is not sustainable due to the limited supply of land for crops and plants (Thanigaivel et al., 2022; Foong et al., 2022). Resultantly, aquatic biomass garnered much interest in place of terrestrial biomass as a feedstock for third-generation biofuels. Among available aquatic biomass sources, microalgae are known as a potential source for producing biofuels because of their high yield and short growth cycle (Hoang et al., 2022). In addition, microalgae could adapt to many water sources, especially wastewater could use for cultivating microalgae.

Being one of the potential alternative fuel sources, bio-oil is considered to be sustainable, renewable, environmentally friendly, and relatively cheaper than other biofuels, making it a substitute for fossil fuels (Escalante et al., 2022). More importantly, microalgae-derived bio-oil (MB) displays a higher content of carbon and nitrogen and a lower content of oxygen than bio-oil generated from other biomass (Oasmaa et al., 2021). Besides, rich content of aromatic hydrocarbon was also found in MB (Wang et al., 2022). As reported in the literature, microalgae could be converted into numerous biofuels via two distinct processes, biochemical and thermochemical processes. Nonetheless, higher energy conversion, shorter reaction times, and inexpensive production costs are found to be the main advantages of the thermochemical process relative to the biochemical one (Choudhary et al., 2022), indicating that the thermochemical technique is considered one of the most suitable conversion paths for the production of microalgae-derived biofuels. Wang et al. (2020) recommended that the thermochemical conversion of microalgae could be considered as a promising advancement and lead to high-value products with the potential for further implementation. According to (Aysu et al., 2017), the most prospective thermochemical conversion technologies for manufacturing liquid biofuels are hydrothermal liquefaction (HTL) and pyrolysis, in which their critical characteristics were given in Table 1.

However, it could be realized that there has been a lack of comprehensive reviews of the characteristics and mechanisms of product formation in the pyrolysis and HTL process of microalgae. Therefore, the novelty of this paper is to highlight the critical characteristics of pyrolysis and HTL technologies in producing MB. More importantly, critical mechanisms of the two above-mentioned thermochemical technologies in converting the microalgae components into bio-oil are discussed in detail and scrutinized. In short, this current review could provide further understanding and fill the gaps in MB production aiming to open the promising and potential change in the application of MB to the real world, contributing to the success of commercial strategies.

2. Microalgae: Components and characteristics

Microalgae, with up to approximately 800,000 estimated species, are commonly referred to as microphytes, which are small and unicellular plant organisms (Salbitani et al., 2022). Microalgae are thought to possess many advantages as utilizing them as an energy feedstock since microalgae do not contain sulfur, have a quick rate of growth, and have a cellular structure that is not suitable for human consumption (Siddiki et al., 2022). Besides, microalgae can be a promising carbon–neutral biofuel source due to their ability to perform photosynthesis and develop by absorbing CO_2 and generating approximately half of O_2 in the atmosphere (Sathya et al., 2023). As per biochemical analysis, microalgae include lipids (0.9–77%), proteins (6.0–71%), and carbohydrates (4.0–83.6%) (Gu et al., 2020). Microalgae lipid content varies significantly according to species, as well as is greatly dependent on the stages of the growth process and cultivation conditions. In addition, microalgae have a high protein content, which has a huge impact on the nitrogen content in the products, and the nitrogen component will thus either devolatilize during the pyrolysis process and/or persist in the

Table 1
Characteristics of pyrolysis and hydrothermal liquefaction process for biofuel production from microalgae.

Thermochemical process	Pyrolysis	Hydrothermal liquefaction
Aim	Thermochemical conversion of microalgae into the aqueous phase	Thermochemical conversion of microalgae into liquid fuels
Advantages	– Low cost and easy operation for handling a broad range of feedstocks; – Reduction in the amount of waste sent to landfills and greenhouse gas; – Lowering the likelihood of water contamination;	– Not very high-energy intensive due to low operation temperature; – High energy-to-weight ratio proportion compared to the initial component; – No requirement for drying and pretreating; – All compositions including lipids, protein, and carbohydrates could be converted to bio-oil; – Obtained products having low-oxygen content, high stability, and HHV.
Disadvantages	– The product flow is more complicated than most of the other alternate procedures; – Due to the high CO levels, the product gases cannot be discharged directly into the cabin without further processing; – A large amount of energy is required for drying;	– Extreme processing constraints, sufficiently high point; – Bio-oil with increased oxygen content in comparison to heating value; – Requirement for sophisticated autoclaves; – Inability to observe the crystal as it develops;
References	(Auersvald et al., 2020; Chen et al., 2021b; Varsha et al., 2021)	(Masoumi and Dalai, 2021; Alherbawi et al., 2021; Sharma et al., 2021)

pyrolytic bio-oil (Said et al., 2022).

3. Pyrolysis technologies

Microalgae are known to contain carbohydrates, lipids, and proteins, which enable their conversion using the pyrolysis process to produce various components such as non-condensable gases, bio-oil, and biochar. Bio-oil attained from the microalgae pyrolysis could be employed in chemical industries and energy fields in various separate or combined ways (Sabariswaran et al., 2022). In this section, the characteristics and mechanisms of conventional and advanced pyrolysis technology for microalgae are completely presented and analyzed. In general, the relationship between operating conditions and pyrolysis modes with obtained product properties could be depicted in Fig. 1.

3.1. Pyrolysis mechanism

To study the mechanism and kinetics of microalgae pyrolysis, thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) would be considered as the popular methods. A particular TGA and DTG curve for the microalgae pyrolysis could be lotted in Fig. 2**a**, in which it could be seen the loss and decomposition of major components such as lipids, protein, and carbohydrates in microalgae at different temperatures (Li et al., 2021). Microalgae pyrolysis is found to include a large number of reactions in series and parallel, and could be categorized into three stages, as illustrated in Fig. 2b (Escalante et al., 2022), in which the thermal decomposition could be included three primary steps: (i) dehydration at temperatures <200 °C, (ii) devolatilization at temperatures of 200–400 °C, and (iii) decomposition of solid components at temperatures >500 °C (Escalante et al., 2022). During the microalgae pyrolysis process, the decomposition of proteins and carbohydrates is found at a temperature <400 °C (Pourkarimi et al., 2019), it could be because proteins and carbohydrates' thermal stability is much lower than that of lipids (Hong et al., 2020). For proteins, some reactions like deamination, dehydration, deoxygenation decarboxylation, cracking, and cyclization are found to be the main pyrolysis mechanism, resulting in the formation of some N-containing compounds, phenols, aromatics, and intermediates. After that, phenols and intermediates could continue converting to aromatics and aliphatics (Azizi et al., 2020). Besides, protein pyrolysis-derived NH_3 could also react/interact with fatty acids aiming to create long-chain amides/nitriles (Huang et al., 2022). In the case of carbohydrates, the pyrolysis process could generate oxygen-containing compounds and water. Indeed, a series of reactions including rearrangement, cracking, deoxygenation, decarbonylation, and dehydration could occur in the carbohydrate pyrolysis to produce ketones, alcohols, aldehydes, acids, and furans. In addition, aliphatics could be found as a portion of carbohydrate pyrolysis (Huang et al., 2022).

The main decomposition of lipids is found to occur at around 550 °C of temperature, in which the cracking and/or hydrolysis reactions play the main role in converting lipids compound of microalgae to fatty acids, followed by reactions of converting fatty acids to ketones, aldehydes, acids, alcohols, and alkenes. Furthermore, alkenes could be condensed based on the Diels–Alder principle or cyclized to produce aromatics (Yang et al., 2019). More importantly, it was found that the content of aliphatic compounds could be remarkably reduced in the case of lipid extraction from microalgae, indicating that lipids compounds play a critical part in forming aliphatic hydrocarbons through the pyrolysis process (Azizi et al., 2020). However, with higher pyrolysis temperatures (>600 °C), hydrocarbons with large molecular weight could be broken through secondary cracking reactions to create smaller molecular weight ones, leading to a reduction in the bio-oil yield (Zhong et al., 2022). Normally, microalgae have a high moisture content, indicating that they should be dried before pyrolyzing but this drying process could increase energy consumption (Liu et al., 2021). For the kinetic study, the microalgae pyrolysis has activation energy ranging from 40 kJ/mol to 250 kJ/mol (Söyler et al., 2017). The models for determining the apparent kinetic parameters were also comprehensively analyzed in

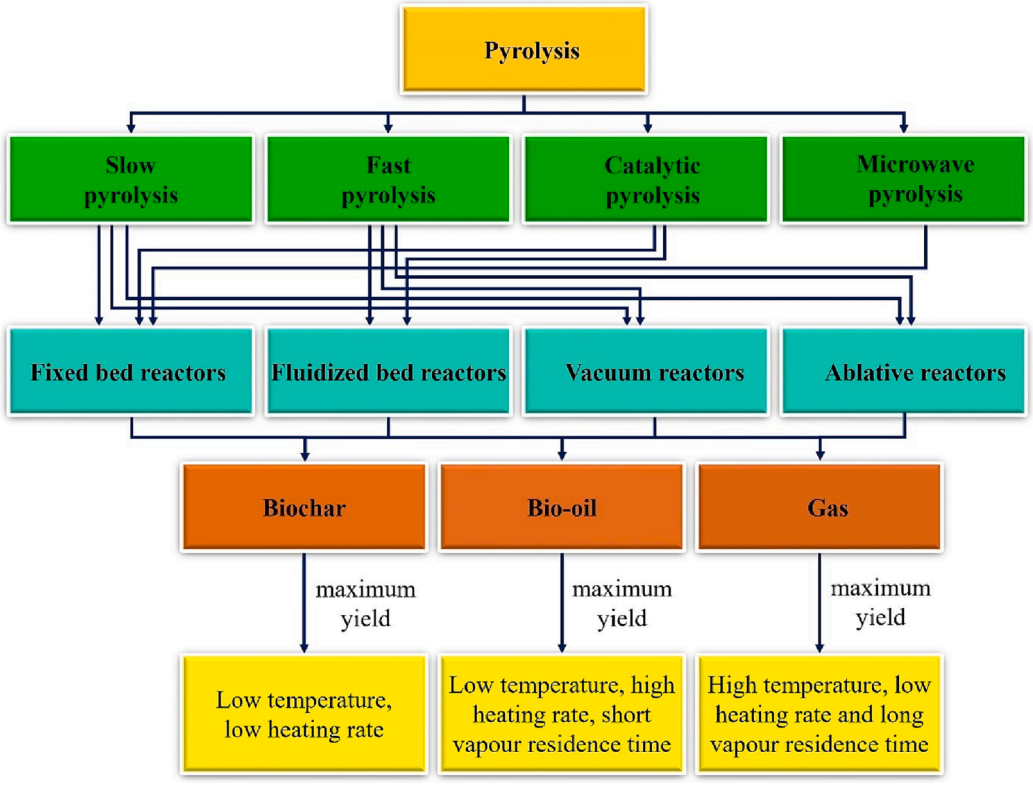

Fig. 1. Pyrolysis classification, reactors, and conditions applied to microalgae to attain the maximum yield.

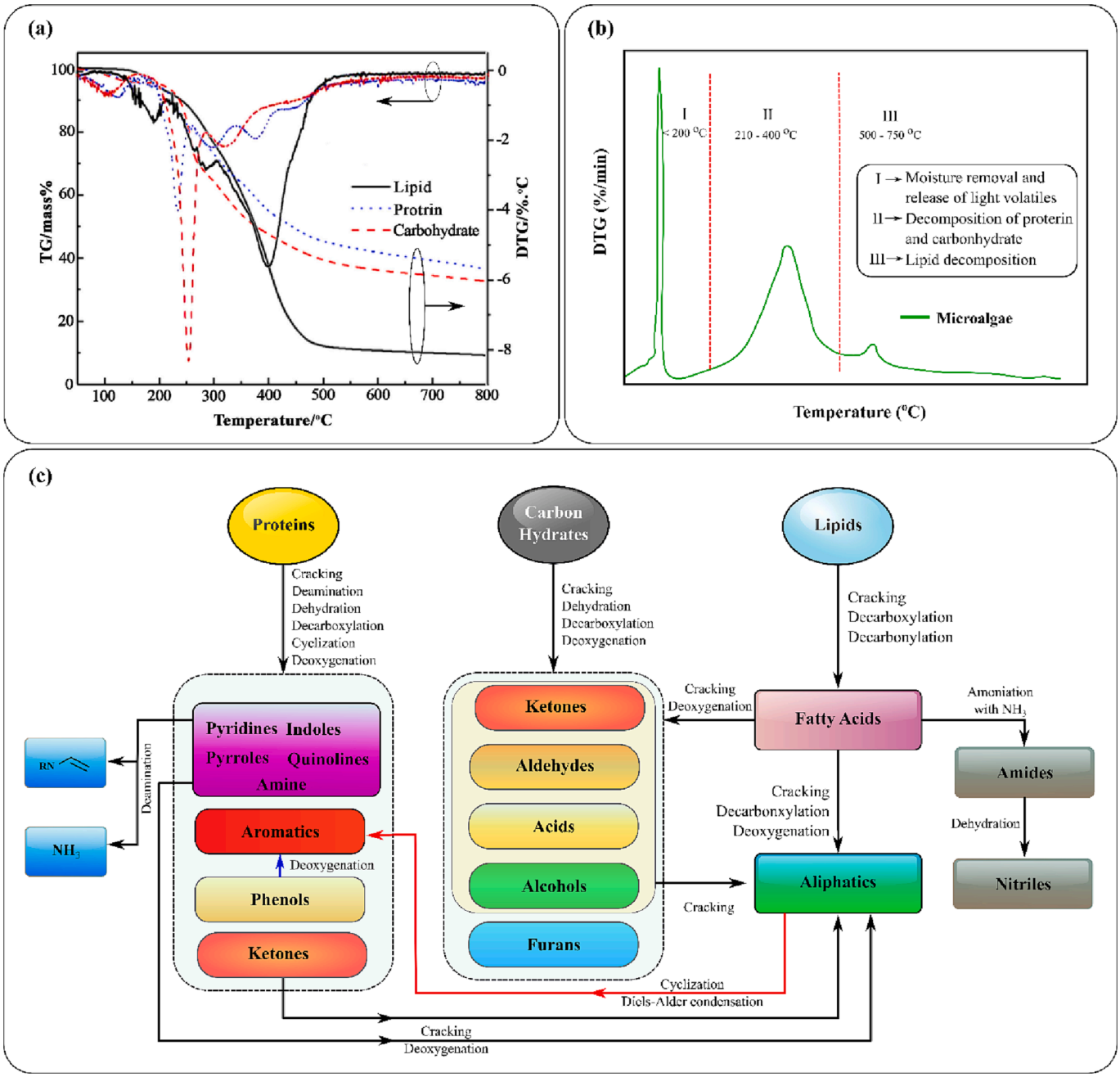

Fig. 2. (a) – Pyrolysis kinetics of major components in microalgae (Li et al., 2021); (b) – Relationship between microalgae decomposition process and temperature (Escalante et al., 2022) (LN: 5470240951684); (c) – Pyrolysis mechanism of major components in microalgae (Huang et al., 2022).

recent works (Chen et al., 2021a; Yang et al., 2019), showing that water–gas, oxidation, and water–gas shift reactions are predominant during microalgae pyrolysis. In general, the pyrolysis mechanism of microalgae could be illustrated in Fig. 2c.

3.2. Pyrolysis for bio-oil production

3.2.1. Conventional pyrolysis

Fast pyrolysis is known as a systemic process, in which biomass is heated so rapidly enough that it could reach the optimum pyrolysis temperature before it is entirely decomposed (Gao et al., 2022). The prime element affecting bio-oil production in microalgae pyrolysis is the heating pace, microalgae type, reactor types, and reaction temperature (Xiong et al., 2022). However, the pyrolysis temperature is thought to be a more important parameter than the heating rate and it affects the yield of the obtained products. Indeed, most of the studies in the literature are to look for the optimum temperature for microalgae pyrolysis to get the maximum yield of bio-oil. Indeed, the effects of temperature in fast pyrolysis of *Scenedesmus sp* on bio-oil properties were investigated by (Derakhshandeh et al., 2021). Both a dynamic pyrolysis-GC/MS device and a fixed-bed reactor were implemented during pyrolysis. At the optimal temperature pyrolysis (≈ 500 °C), crude bio-oil with a calorific content of 35–40 MJ/kg and a yield of 35.3 wt% could be produced. The produced bio-oil was found to have a 6.92 wt% of nitrogen and a 16.45 wt% of oxygen content, high-protein content of microalgae explaining the relatively high nitrogen level. Söyler et al. (2017b) conducted a study utilizing fast pyrolysis for the solid residue of *Dunaliella tertiolecta* microalgae to yield a 45.13 wt% of bio-oil at 600 °C, whereas char reached 29.34 wt%, indicating that it could be applied the fast pyrolysis process for *D. tertiolecta* to produce large quantities of renewable fuel

and chemicals. Andrade et al. (2018) evaluated the applicability of *Chlamydomonas reinhardtii* for the manufacture of chemicals and fuel through pyrolysis that was conducted at a temperature range of 450–750 °C. As per non-catalytic fast pyrolysis, the number of hydrocarbon compounds increased as the temperature rose while the number of oxygenated compounds declined. However, the pyrolysis of *Chlamydomonas reinhardtii* resulted in forming a large number of N-containing compounds due to the increasing level of protein composition. In a similar study, the outputs of *N. gaditana* pyrolysis under various conditions were analyzed by (Adamczyk and Sajdak, 2018). As a result, they indicated that the highest concentration of alkenes and alkanes was found in the liquid at 500 °C, showing that the capability to utilize the bio-oil as potential biofuel from the pyrolysis of *N. gaditana* through the presence of hydrocarbons in the liquid product.

The yield of the pyrolysis process is also significantly affected by microalgae types. Indeed, Azizi et al. (2020) evaluated the yield of bio-oil in the case of fast pyrolysis with the same conditions for *Nannochloropsis*, *Isochrysis galbana*, and *Tetraselmis*. They reported that the bio-oil yield from *Nannochloropsis*, *Tetraselmis*, and *Isochrysis galbana* is 26.79%, 24.33%, and 24.81%, respectively. A similar result of the bio-oil yield after conducting fast pyrolysis for four microalgae types was also reported by Arif et al. (2021). Relating to the effect of reactor types, Yuan et al. (2015) reported that the application of fast pyrolysis for *Chlorella vulgaris* could yield 32.69 wt% of bio-oil at a temperature of 500 °C using the fixed-bed reactor. However, the fast pyrolysis of *Chlorella vulgaris* could produce bio-oil up to 53 wt% at the same temperature as using the fluidized-bed reactor (Wang et al., 2013). Also, it was revealed that the bio-oil composition could also be noticeably affected by as-used gases for microalgae pyrolysis. Based on GC/MS analysis, the fast pyrolysis of microalgae based on CO_2 could produce bio-oil possessing a larger amount of N and O-containing compounds and oxygenates, while bio-oil attained from the fast pyrolysis supported by steam could contain greater content of hydrocarbons that could be due to deoxygenation and steam reforming reactions (Hong et al., 2020). For the N_2-based fast pyrolysis process, alcohols and nitrogenates were considered the popular compositions in bio-oil (Lee et al., 2020a). Therefore, selecting the inert gas type for the fast pyrolysis of microalgae is also very important to optimize the qualities of pyrolytic bio-oil. Furthermore, the cultivation condition of microalgae could also affect the quality, composition, and yield of bio-oil (Mustapha et al., 2023; Wang et al., 2019). In a study of Sotoudehniakarani et al. (2019), they evaluated the yield and quality of bio-oil from *Chlorella vulgaris* cultivated in complete and N-starved media after undergoing rapid pyrolysis tests with the fixed-bed reactor. Nitrogen deficiency causes the biomass to include more lipids which raise its calorific value. High bio-oil output and quality may be achieved through quick pyrolysis of nitrogen-starved microalgae. In this instance, tests have shown that the maximum production of bio-oil is around 47.7% mass on a dry basis at 500 °C. The quality of the *Chlorella vulgaris*-derived bio-oil was higher since it contains more fatty acids and fewer nitrogenous species. Additionally, the increased lipid content of the nitrogen-starved biomass causes the bio-oil to contain a significant quantity of carbon, which somewhat raises its calorific value.

Nevertheless, high oxygen content (around 30–50%) contained in microalgae was found to be the main cause of forming dominant oxygenated compounds (like acids, esters, aldehydes, furans, and ketones) in bio-oil (Zhang et al., 2019), even oxygen content could reach 54.5% for bio-oil produced from fast pyrolysis of *Enteromorpha prolifera* (Xu et al., 2019). Due to this reason, bio-oil should undergo the upgrading process to abate the oxygen content. Moreover, a protein consisting of various types of amine functional groups is considered a dominant component in microalgae, indicating that microalgae could become a potential source to generate N-containing value-added chemicals through the application of fast pyrolysis. Indeed, Escalante et al. (2022) disclosed that the concentration of N-containing compounds in fast-pyrolysis products from microalgae was much higher than those of other biomass such as agricultural by-products and wood. Therefore, some recent studies have proposed an advanced pretreatment method aiming to optimize the N and O element distribution in the obtained products after the fast pyrolysis process of microalgae. Zhang et al. (2019) reported that the oxygen contents in bio-oil from *Chlorella* sp. microalgae fast pyrolysis reduced by 17.8% when *Chlorella* sp. microalgae were pretreated by nitrogen torrefaction at 300 °C. In a recent study, Li et al. (2021) developed a novel NH_3-based torrefaction pretreatment to enhance the applicability of *Chlorella vulgaris* for N-containing heterocyclic chemical production through the fast pyrolysis process. Interestingly, the N content in bio-oil obtained for fast pyrolysis of *Chlorella vulgaris* increased by 3.21% in contrast to the abatement of oxygen content by 14.35%. Generally, the features of the pyrolysis products are dependent on temperature, greater pyrolysis temperatures were found to produce more liquid and less gaseous products. Moreover, increasing the pyrolysis temperatures of microalgae could facilitate the pyrroles formation, as well as inhibit the pyridines and indoles formation.

Flash pyrolysis could also be applied to the microalgae aiming to generate high-yield bio-oil. Maliutina et al. (2017) reported that the hydrocarbon-rich and nitrogen-containing bio-oil of *Chlorella vulgaris* microalgae through flash pyrolysis could get 60.22 wt% of yield at 800 °C of temperature. However, the obtained pyrolytic bio-oil usually possesses high acid content and viscosity, instability, and contains solids/water dissolved in bio-oil (Palumbo et al., 2019), leading to additional upgrading technologies required to improve the quality of bio-oil (Yang et al., 2019).

Fast pyrolysis was highlighted as the main path for generating hydrocarbon-rich bio-oil, while slow pyrolysis was indicated to not generate a high hydrocarbon-rich bio-oil because of the greater tendency of secondary reactions (Rocha et al., 2020). Slow-pyrolysis technique is very advantageous for bio-char yield since it produces less liquid and gaseous products. In the case of slow pyrolysis for microalgae with a temperature >600 °C, biochar containing N-rich species could be formed more favorably than bio-oil formation (Akhtar et al., 2019). Two types of conventional and carbonization slow pyrolysis techniques with slow-paced heating rates and distinct reaction temperatures could be applied to microalgae pyrolysis (Miliotti et al., 2020). For slow pyrolysis, the average production of bio-oil is 20–55% wt.%, and synthetic bio-crude oil has a high-calorie content value (Nazem and Tavakoli, 2017; Yang et al., 2019). For slow pyrolysis of *Spirulina platensis*, Rocha et al. (2020) found that there was a significant effect of the heating rate on the N-containing compounds' formation and the bio-oil yield, they indicated that the liquid product could attain the maximum yield of 64.59% at optimal conditions (556 °C of pyrolysis temperature and 10.24 °C/min of heating rate). Besides, Bordoloi et al. (2016) evaluated the effects of temperature on the compositions and yield of bio-oil generated by slow pyrolysis *of Scenedesmus dimorphus*. They revealed that the maximum yield and HHV of bio-oil were 39.6 wt% and 28.52 MJ/kg along with the fraction of N-containing compounds in the pyrolytic bio-oil was 10.6 wt% at 500 °C of optimum temperature. Additionally, the fraction of aromatic hydrocarbon was quite high, including 18% of n-hexane and 30% of toluene. However, when the pyrolysis temperature continued increasing, the bio-oil yield significantly decreased (Wang et al., 2017). From the aforementioned analysis, it could be stated that the obtained products' yield had a large dependence on pyrolysis conditions, showing that it is difficult to confirm what products (bio-oil, syngas, or biochar) would be the primary products attained from the microalgae slow-pyrolysis. Furthermore, there were a number of limitations in slow-pyrolysis technologies like long residence time (leading to the cracking and secondary reactions of the main product), and additional need for energy input, indicating that slow pyrolysis could not be a suitable method for producing bio-oil with high yield from microalgae (Pourkarimi et al., 2019b).

3.2.2. Advanced pyrolysis

Advanced pyrolysis is more advantageous than conventional pyrolysis since it requires much less energy, lower pyrolysis temperature, may eliminate contaminants from bio-oil like solid residues, and oxygen, sulfur, nitrogen, and phosphorus content, and improves the selection of products by altering the reaction pathways of pyrolysis.

3.2.2.1. Catalyst pyrolysis. For catalyst pyrolysis, the catalyst could reduce the entire pyrolysis temperature and duration, and enhance the effectiveness and performance of the whole procedure. Typically, catalytic pyrolysis of microalgae is conducted at temperatures from 300 °C to 600 °C, while HHV and yield of bio-oil using catalytic pyrolysis are between 13.4–39 MJ/kg and 20–59 wt%, respectively (Lee et al., 2020; Lee et al., 2020a). In general, MB generated from catalytic pyrolysis of microalgae has a high HHV, high aromatic content, and low acidity (Yuan et al., 2020). More important, catalysts in the pyrolysis were found to play a critical role in deoxygenating and denitrification aiming to convert O-containing compounds into aromatic compounds and N-containing compounds into ammonia, showing that catalysts could be utilized to attain high-quality MB (Sun et al., 2022). As reported, *ex-situ* and *in-situ* catalytic pyrolysis were considered as the two main pyrolysis methods aiming to get high efficiency (Shirazi et al., 2020). For *in-situ* catalytic pyrolysis of microalgae, the tar generation could be inhibited, thereby increasing the bio-oil yield. Nevertheless, the weak deoxygenation and gradually-lost catalyst activity were known as drawbacks of the *in-situ* catalytic pyrolysis (Sun et al., 2022). By contrast, avoidable interaction between as-used catalysts and feedstocks, controllable pyrolysis reactions, and recyclable catalysts are considered the strong points of the *ex-situ* catalytic pyrolysis method (Shirazi et al., 2020).

Diverse catalysts including metal, zeolite, carbon-centric, or combinations of various materials could be utilized to improve the quality and yield of product properties in microalgae pyrolysis (Liu et al., 2022). Among these, the ZSM-5 catalyst was found as the most efficient for pyrolyzing microalgae, ZSM-5 exhibited excellent shape selectivity to aromatic hydrocarbons since its pore diameter is comparable to the characteristic diameters of key petrochemicals including benzene and toluene. Furthermore, ZSM-5 could encourage the breakdown of various oxygenated substances to produce light olefins and alkanes. These alkanes could be converted into benzene or different other aromatic compounds via reaction chains such as alkylation, aromatization, and isomerization (Nishu et al., 2020). In a study of Adamakis et al. (2018), they assessed the catalytic pyrolysis of *Chlorella vulgaris* with various lipid concentrations. Before catalytic pyrolysis by ZSM-5, lipid extraction from *Chlorella vulgaris* produced a bio-crude that included more aromatic chemicals than the bio-crude formed from non-extracted *Chlorella vulgaris*. The findings imply that microalgae possessing low lipid concentrations could increase the number of aromatic compounds produced by ZSM-5 catalytic pyrolysis. Besides, Hu et al. (2021) used ZSM-5/MCM-41 for catalyzing the Enteromorpha clathrate pyrolysis under various atmospheres (H_2 and N_2 as pyrolytic agents). They revealed that ZSM-5 catalyst was effective in mitigating the formation of acids and N-containing compounds, leading to lower N-containing compounds and higher aromatic compound content. Therefore, they indicated that the synergic effect of the ZSM-5/MCM-41 catalyst and H_2 agent could enhance the bio-oil yield to 51.48%.

Also, using metal-modified ZSM-5 catalysts for fast pyrolysis could lead to less coke formation due to more selectivity to deoxygenation and the presence of strong-acid sites on the surface of catalysts (Nishu et al., 2020). Furthermore, Che et al. (2019) revealed that there was a drastic increase in aromatic hydrocarbon using 2% Zn-modified ZSM-5, while Mo et al. (2020) indicated that the catalyst pyrolysis of *Spirulina Platensis* microalgae by using ZSM-5/MgO could produce high-yield bio-oil (up to 48.6 wt%) and high HHV (36.8 MJ/kg). However, it should be noted that strong-acid sites and surface area of metal-modified ZSM-5 could be remarkably reduced when loading excessive metal in ZSM-5, resulting in limitations of diffusing reactants, thereby lowering the yield of aromatic hydrocarbon (Nishu et al., 2020). In the case of using transition metals like Ni, Co to modify the ZSM-5 catalyst, the ZSM-5 catalyst's acidity could be remarkably reduced, leading to inactive restriction of ZSM-5 catalysts and low bio-oil yield because of the coke presence. For example, Zainan et al. (2018) utilized Ni-supported ZSM-5 to pyrolyze *Chlorella vulgaris* at a range of temperatures from 300 °C to 600 °C. They observed a decrease of the total bio-oil yield by 14.54 wt% by increasing the loaded catalysts although the as-used catalyst had positive impacts on the bio-oil characteristics. The above-mentioned results could be because a micro/meso/macro-porous channel was formed in the ZSM-5 framework by adding Ni to the ZSM-5 catalyst, which facilitated reactions of aromatization and deoxygenation that were thought to control the diffusion of intermediates. A similar result was also observed for Co/Mo-supported ZSM-5, in which utilizing Co/Mo-supported ZSM-5 for catalyst pyrolysis of *Gracilaria gracilis* led to a lower bio-oil yield than the case of ZSM-5 although Co/Mo-supported ZSM-5 catalyst also reduced total concentrations of acetic/formic acid, phenol, and furfural by 1.44%, 0.77%, and 1.49% respectively (Norouzi et al., 2017). Indeed, it could be concluded that metal-modified ZSM-5 increased primarily the yield of mono-aromatic hydrocarbon, as well as reduced furan and phenols compounds in comparison with pure ZSM-5, showing that combining metal with hierarchical ZSM-5 could influence the mechanism of pyrolysis reaction through the enhancement of the production of the phenolic (Maheria et al., 2021).

In addition to ZSM-5, the metal-based catalysts were thought to be the potential ones to generate the high-yield bio-oil. For example, the use of Ni/TiO_2 for pyrolyzing *Pavlova* sp. microalgae could produce bio-oil with a maximum yield and HHV of 22.6 wt% and 37 MJ/kg respectively at 500 °C (Aysu et al., 2017). Employing Mg-Ce/Al_2O_3 catalyst could also reduce the bio-oil yield by 4.3%. Furthermore, the N element was partially removed from the liquid product via catalytic pyrolysis (Aysu et al., 2018). This result could be due to the effect of Ce in cracking the protein link of microalgae (Lee et al., 2020). Besides, the combination of Fe_3O_4-supported HZSM-5 catalysts with other metals like Zr, Mo, W, and Co could also be applied to pyrolyze *Scenedesmus obliquus* microalgae, it was revealed that ketonization and aromatization reactions could be promoted by (Zr, Mo, W, and Co)/Fe_3O_4-HZSM-5 catalysts aiming to produce more long-chain ketones, resulting in the production of pyrolytic bio-oil with highest HHV and yield of 39.12 MJ/kg and 17.73 wt% respectively along with a significant decrease of total acid amounts to 26.1% (for Co/Fe_3O_4-HZSM-5) (Mustapha et al., 2021). In a recent study, Ferreira et al. (Ferreira and Soares Dias, 2020) indicated that commercial carbonate catalysts such as Li_2CO_3, Na_2CO_3, and K_2CO_3 could increase the bio-oil yield to 38 wt% from *Chlorella vulgaris* microalgae and 50 wt% from *Scenedesmus obliquus* microalgae. In this case, carbonate catalysts could play an important role in reducing the acidity percentage relating to carbonyl species, while carbonate catalysts having higher melting points than pyrolysis result in removing nitrogenous functional groups significantly, thereby reducing N-containing compounds in the pyrolytic MB (Xu et al., 2023). In general, catalytic pyrolysis is considered the potential method to enhance bio-oil quality through the thermochemical conversion of microalgae. In comparison with fast pyrolysis, catalysts can generate more hydrocarbons, fewer compounds from the oxygenation process, and fewer acidic chemicals. However, it should highlight how fundamental it is to identify the appropriate catalyst preparation methods as they would determine the bio-oil quality in microalgae pyrolysis.

3.2.2.2. Microwave-assisted pyrolysis. Microwave-assisted pyrolysis (MAP) has become increasingly popular recently, mainly due to its use in converting several kinds of biomass into biofuels (Su et al., 2022a). MAP creates heat from the heart of the biomass and towards the plane, a distinctive method of creating thermochemical conversion heat. It is known for its short processing time, low-energy demand, efficient

transfer of heat, and selective and uniform internal heating, it also is practical for dealing with high moisture content feedstocks. In MAP, the microwave enters the feedstock particles and transforms them into thermal energy from within. This induces the formation of a temperature gradient from the inner portion of the particles to the outer and the volatile substances are released diffusely from the inner core to the outer surface through a low-temperature region, the MAP process was thus shown to be sustainable in terms of energy consumption (Chen et al., 2021b). Moreover, selective heating and easy operation are found to be the main advantages of microwave-assisted pyrolysis technology, showing that MAP technology could be commercialized and industrialized for microalgae pyrolysis (Sun et al., 2022). In comparison with conventional pyrolysis, MAP was found to be more conducive to producing aromatics, and MAP could inhibit to form S, N, and O-containing compounds in bio-oil and help to cleave chemical bonds in microalgae's s macromolecules (Ong et al., 2020), thereby producing lower S-heterocyclic compounds and lower contents of acids, alcohols, amides, amines, furans, and phenols in the pyrolytic MB. Furthermore, more aliphatic and aromatic hydrocarbon compounds and less phenol compounds could be generated using MAP compared to conventional pyrolysis approaches (Su et al., 2022a).

Previous studies indicated that MAP could be unfavorable for producing bio-oil since the chemical bonds of molecules of carbohydrates, proteins, and lipids of microalgae could be easily broken under the directly-transferred high energy of microwave, resulting in compounds degraded rapidly in the pyrolysis process and even in the obtained pyrolytic MB, causing a reduction in the MB yield (Su et al., 2022a). Furthermore, the moisture content in the input materials was thought to influence energy efficiency. Due to this reason, high-moisture microalgae should be mixed with strong-microwave additives to increase pyrolysis efficiency (Lee et al., 2020a). In the MAP process, zeolites and metal oxides are usually used as potential catalysts, while carbon-based materials could play the microwave absorbents (Chen et al., 2021a). Chen et al. (2021b) evaluated the bio-oil yield by using additives (including TiO_2 catalyst and SiC absorbent) for the MAP process of *Chlorella vulgaris* microalgae. They reported that the role of SiC is to promote both ketone production and bio-oil deoxygenation, while TiO_2 could denitrificate and deoxygenate in bio-oil. More importantly, they indicated that adding the additive to MAP of *Chlorella vulgaris* could rise the MB yield to 28.37% compared to the case without additive (14.74%). In addition, Wu et al. (2020) studied the effects of (Zn/Cu/Ni)-modified HZSM-5 on the quality of bio-oil through the MAP process of *Chlorella*. They revealed that the use of metal-modified HZSM-5 improved remarkably the quality of bio-oil, in which there was an increment of C and H contents and a drop of O content. Besides, a large amount of hydrocarbons, N-containing compounds, and alcohols were found in the liquid phase. The effects of the ratio of ZSM-5 (as the catalyst) and graphite (as microwave absorbent) in the additive used for the MAP of *Chlorella vulgaris* were also evaluated by Chen et al. (2021c). They found that the ratio of ZSM-5 catalyst in additive of 49.15% would produce bio-oil with a maximum yield of 22.7%. More interestingly, the synthesized pyrolytic bio-oil by using ZSM-5/graphite as an additive increased hydrocarbon by 69%, and reduced N-containing compounds by 24.6% compared to the case without a catalyst. In summary, the employment of additives for the MAP process of microalgae could yield high-quality and high-performance bio-oil although the microwave absorbent, catalyst, and their ratio in additive should be further investigated to get the optimum efficiency in pyrolyzing microalgae.

3.2.2.3. Co-pyrolysis. Co-pyrolysis, the process of using more than one material as feedstock, has been proven to improve widely the biofuel quantity and quality due to its simple and efficient operation, in which the thermal degradation of input feedstock occurs in a closed pyrolysis reactor without oxygen at higher operating temperatures than the thermal stability threshold of feedstock (Lee et al., 2020). As reported, chemical reactions range including de-(carboxylation/carbonylation) and de-(hydrogenation/hydration) could occur to create a large amount of radicals and functional groups. After that, functional groups and radicals could interact together to form a target product, in which the condensation of volatile components could be the base of forming liquid products (Vuppaladadiyam et al., 2021). In addition to operating parameters that are similar to those of other pyrolysis processes, the blending ratio of microalgae with other materials is also extremely important in the co-pyrolysis process. Because microalgae contain proteins with N-rich amino acids, the co-pyrolysis between microalgae and other materials are very complex. For example, the synergic mechanism of lignocellulose-based biomass and microalgae could occur via the co-pyrolysis process of lignocellulose and N-rich amino acids (Su et al., 2022b). Indeed, Chen et al. (2019) indicated that there was a significant increase in phenols/oxygenated compounds and a remarkable reduction of N-containing compounds for the bamboo waste/amino acids co-pyrolysis process. More importantly, the synergic effect of co-pyrolysis on the feedstock is one of the primary reasons for the improved biofuel quality, as demonstrated by several studies (Chakraborty et al., 2021; Kumar et al., 2023). Indeed, a prominent cooperative event between the microalgae and the additional reactants could decline oxygenated molecules, which could improve the usability of the produced MB (Fakayode et al., 2023). More importantly, the easy reaction between –C=O groups in lignocellulosic biomass with $–NH_2$ groups in amino acids of microalgae was found to be the primary reason for forming phenols, producing newly oxygenated and N-containing compounds through the ketonization and Maillard reaction, inhibiting the acetic acid formation, and providing H^+, having a significant contribution to breaking reaction of β-O-4 linkage, resulting in the lignin fragment scission.

Improved biofuel yield, activation energy, and aromatics production have also been shown via the co-pyrolysis process of microalgae with various substances. For example, the co-pyrolysis of microalgae and dying sludge from textile industries has been shown to lower the required average activation energy for the reactions (Chakraborty et al., 2021). Similarly, the co-pyrolysis of *Isochrysis* sp. microalgae and sewage sludge has been proven to improve C4 and C7 yield in biofuel (Wang et al., 2016). In another study by Chang et al. (2018) about *Nannochloropsis* sp./palm kernel shell co-pyrolysis, they reported that there was a sharp increase in aromatics to 30.39% compared to sole *Nannochloropsis* sp. pyrolysis (11.79%) and palm kernel shell pyrolysis (2.96%). More interestingly, using Cu/HZSM-5 for the above-mentioned co-pyrolysis process could increase aromatics yield to 42.65%. In a recent study, Khodaparasti et al. (2022) investigated the co-pyrolysis of *Chlorella Vulgaris* microalgae and municipal sewage sludge, indicating that the maximum MB yield was 32.354 wt% under the optimal condition with 0.82 of mixing ratio (*Chlorella vulgaris*/municipal sewage sludge), and temperature of 520 °C. Similarly, Tang et al. (2020) revealed that co-pyrolysis of *Chlorella vulgaris* and rural solid waste employing a catalyst of CaO could offer excellent efficiency in improving the bio-oil quality, in which there was a reduction of acid and N-containing compounds to 30.85% and 17.26% respectively, and an increase in light aliphatic hydrocarbons up to 11.98% and HHV. Also, Fang et al. (2018) concluded that the interaction of *Chlorella* microalgae and tire under fast pyrolysis with the support of microwave could inhibit the formation of N and O-containing compounds and promote the generation of hydrocarbon species, especially aromatic hydrocarbons in the liquid product, increasing HHV and quality of bio-oil. Also, it was reported that microalgae could enhance the production of liquid and volatile products during the coal/Scenedesmus microalgae co-pyrolysis (Nyoni et al., 2020). Interestingly, Chen et al. (2021a) concluded that the interaction of microalgae and plastic waste could promote the reactions of hydrogenation between the unsaturated products, while the molten plastic waste could create the coating effect to boost the microalgae pyrolysis. Resultantly, the co-pyrolysis of microalgae and polypropylene, polyethylene terephthalate, and polystyrene could

reduce the activation energies and solid residue amounts, except co-pyrolysis of microalgae and polyvinyl chloride due to the reaction between the alkyl groups from microalgae pyrolysis and HCl generated from PVC pyrolysis. In the case of using a catalyst for the co-pyrolysis, Majid et al. (2021) indicated that a bi-functional limestone/HZSM-5 catalyst could reduce significantly the enthalpy and activation energy of the co-pyrolysis reaction between high-density polyethylene and *Chlorella vulgaris*, facilitating the decomposition process as well as the formation of volatiles. The critical characteristics of advanced pyrolysis could be illustrated in Fig. 3.

As aforementioned analysis, in addition to the operation parameter, synergistic effects of microalgae with co-feedstock in the pyrolysis were considered as the main factor affecting positively the bio-oil generation with high quality and yield. In general, using feedstock with high content of volatiles for co-pyrolysis with microalgae could promote bio-oil generation. Therefore, it could be concluded that plastics, tires, and lignocellulosic biomass possessing high volatile content could facilitate co-pyrolyze with microalgae to raise the bio-oil yield and quality. In contrast, coal or sewage sludge has a high content of ash was found to hinder the co-pyrolysis process, showing that increasing the bio-oil yield and quality through the co-pyrolysis of microalgae and coal or sewage sludge could be very difficult. In general, the operation parameters and MB characteristics from conventional and advanced pyrolysis of microalgae were given in Table 2.

4. Hydrothermal liquefaction technologies

Hydrothermal liquefaction (HTL) is one kind of thermochemical conversion under a hot and pressurized-water environment for enough long time aiming to convert the solid biomass to drop-in fuels (Ni et al., 2022). HTL follows the principle of reacting biomass with water present in hydrothermal environments with the most effective outcomes obtained at pressures (4–35 MPa) and temperatures (200–450 °C). In this process, the microalgae biomass undergoes many reactions that depolymerize the materials, such as hydrolysis, dehydration, and decarboxylation, which form intermediate water-soluble compounds (Basar et al., 2021). This is followed by re-polymerization and condensation reactions which form water-insoluble biofuel. This section presents the key characteristics and mechanism of the HTL process for MB production.

4.1. Hydrothermal liquefaction mechanism

As stated in Section 2, microalgae containing various contents of protein, lipids, and carbohydrates could result in a remarkable difference in yield, quality, and composition of bio-oil, as well as the distribution rate of the obtained products (Gu et al., 2020). Normally, high lipid-containing microalgae are suitable for producing biodiesel through transesterification; however, not only lipids but also proteins and carbohydrates could be converted into bio-oil through the HTL process (Li et al., 2014). Due to this reason, both lipid-rich microalgae and low-lipid microalgae could be utilized to produce bio-oil using the HTL process (Mathimani and Mallick, 2019). For example, bio-oil could be produced from low-lipid *C. pyrenoidosa* microalgae with a yield of 39.4% and HHV of 35.42 MJ/kg (Li et al., 2014). However, high-protein microalgae were found to be more suitable for synthesizing bio-oil through the HTL technique compared to carbohydrate-rich ones. Moreover, high-protein microalgae could produce more short-chain hydrocarbons than low-protein microalgae, resulting in increasing bio-oil quality (Koley et al., 2018).

Relating to the HTL mechanism of microalgae, it could be seen that HTL could prevent the hydrolyzation process of monosaccharides contained in carbohydrates of microalgae because the HTL process was performed under the presence of water and at a lower temperature than the pyrolysis one, resulting in high yield of acids, alcohols, glucose, galactose, mannose, and xylose (Hu et al., 2019). However, it is quite difficult to hydrolyze proteins in microalgae due to the peptide bonds-containing protein composition that is stronger and more stable compared to carbohydrates' glycosidic bonds (Akaberi et al., 2019). In general, microalgae's proteins could be hydrolyzed to form amino acids

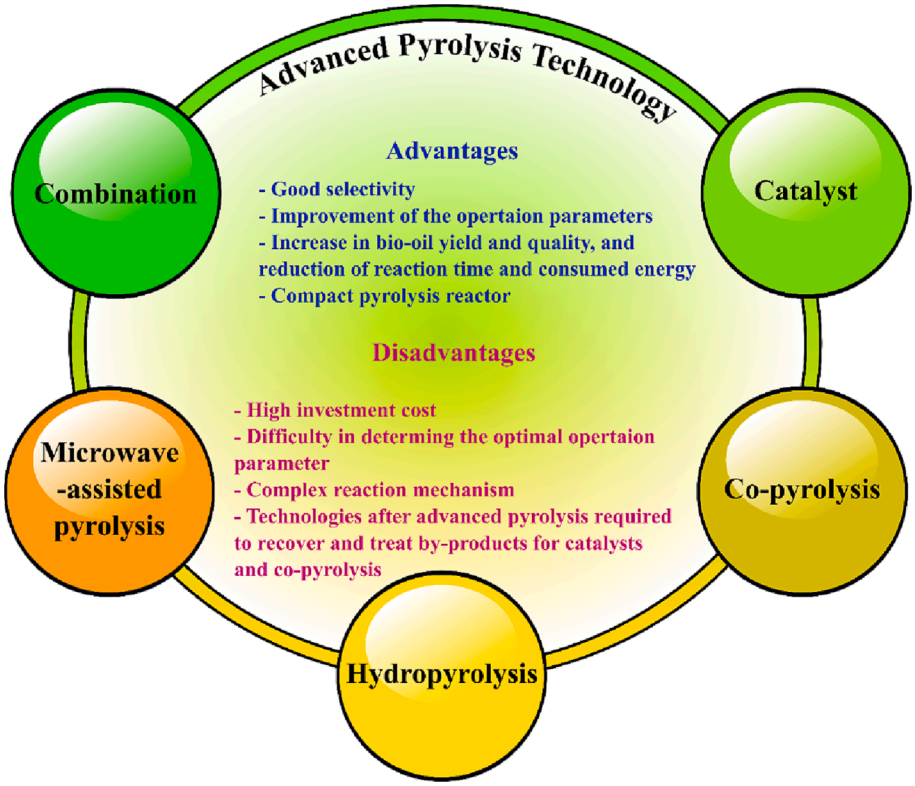

Fig. 3. Advantages and disadvantages of advanced microalgae pyrolysis.

Table 2
Relationship between bio-oil characteristics and operation conditions of microalgae pyrolysis.

Microalgae	Pyrolysis type	Pyrolysis conditions	Bio-oil yield and characteristics	Reference
C. vulgaris	Fast pyrolysis	550 °C	47.7 wt% of yield with HHV = 28 MJ/kg and %C = 30.7%	(Sotoudehniakarani et al., 2019)
Botryococcus braunii		600 °C	65 wt% of yield with HHV MJ/kg = 40 and %C = 75.7%	(Piloni et al., 2021)
S. obliquus		475 °C	50.9% with %C = 50.3%	(Ferreira and Soares Dias, 2020)
Dunaliella salina	Slow pyrolysis	500–550 °C	55.4 wt% with HHV = 24.1 MJ/kg and %C = 55.2%	(Yang et al., 2019)
Spirulina platensis		556 °C	66.04 wt%	(Rocha et al., 2020)
Spirulina platensis	Catalytic pyrolysis	450 °C with ZSM-5-MgO catalyst	46.8 wt% of yield with HHV = 36.8 MJ/kg and %C = 58.7%	(Mo et al., 2020)
Nannochloropsis sp.		500 °C with catalyst of HY, HZSM-5, Hβ, and Activated carbon	47.84 wt% of yield for Hβ; maximum aromatics = 96.27% for HY	(Tang et al., 2021)
Chlorella sorokiniana		450–550 °C, HZSM-5 catalyst	40 wt% of yield with %C = 52.5% and 87 wt% of aromatics	(Shirazi et al., 2020)
Chlorella sp.	Microwave-assisted pyrolysis with catalyst	CaO catalyst, microwave power of 600 W for 20 min	20.57 wt% of yield with HHV = 43 MJ/kg	(Qadariyah et al., 2021)
Chlorella vulgaris		Catalyst TiO_2	14.74 wt% of yield with %C = 47.62%	(Chen et al., 2021b)
C. vulgaris	Microwave-assisted pyrolysis without catalyst	300 °C for 40 –60 min	38 wt% of yield with %C = 50.3%	(Tsubaki et al., 2019)
Chlorella vulgaris	Co-pyrolysis with microwave	Co-pyrolysis with high-density polyethylene and 40% addition of Fe/AC catalyst	25.6 wt% of yield with LHV = 21.55 MJ/kg and %C = 47.62%	(Chen et al., 2022)
Chlorella vulgaris		Co-pyrolysis with rice straw	19.2 wt% of yield with hydrocarbon of 20.79% and %C = 47.62%	(Wei et al., 2023)
Nannochloropsis sp.	Co-pyrolysis without microwave	Co-pyrolysis with low-density plastic	65.17 wt% of yield with LHV = 19.51 MJ/kg and %C = 54.41%	(Tang et al., 2019)

in the range of temperature from 230 °C to 250 °C, and amino acids continue being decomposed to various products through deamination, decarboxylation, dehydration, oligomerization, and re-polymerization reactions at temperatures >250 °C (Akaberi et al., 2019). In addition, amino acids could react with esters/sugars to form N-containing compounds, and interact with lipids/polysaccharides to generate bio-oil

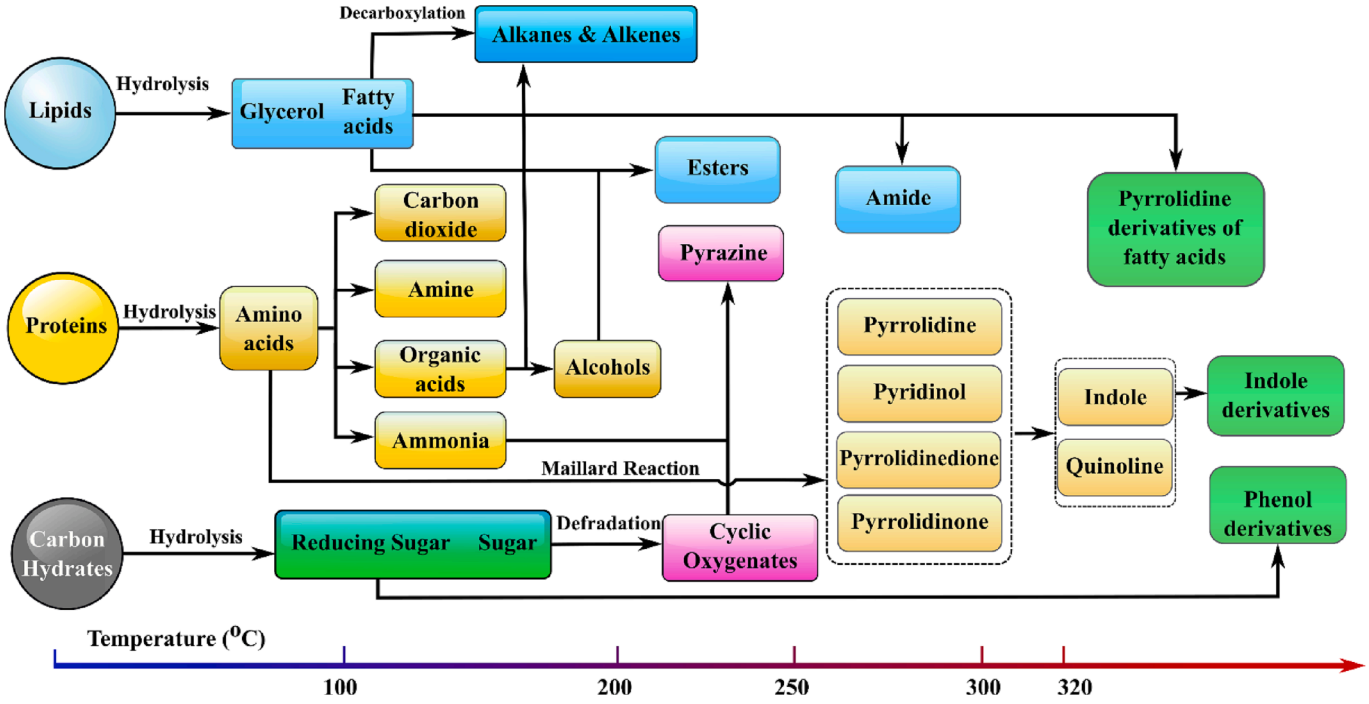

Fig. 4. Hydrothermal liquefaction mechanism for major components in microalgae with the evolution of temperature (Liu et al., 2022).

through reactions such as Maillard, Friedel-Crafts acylation, Beckmann rearrangement, (retro)-Aldol condensation, and other (Gu, 2020; Gu et al., 2020). For lipids, their hydrolysis process could generate acetic acid and ethanol at temperatures <400 °C, and gaseous products at temperatures >400 °C. Furthermore, triacylglycerides in lipids were also hydrolyzed to glycerol and free fatty acids under subcritical-water conditions in the HTL process (Hassan et al., 2020). For example, glycerol in *Spirulina* and *Nannochloropsis salina* microalgae could be decomposed and converted to acrolein, aldehyde, methanol, and gaseous products at temperatures >310 °C in the HTL. In the case of polar lipids, they could be decomposed into P-containing compounds and oleic acid (Toor et al., 2013). However, conventional HTL was found to be not suitable for recovering pigments of microalgae since microalgae pigments could be severely degraded into non-bioactive components (Gu et al., 2020). In summary, the mechanism of microalgae HTL could be illustrated in Fig. 4.

4.2. Hydrothermal liquefaction for bio-oil production

For studies on the MB yield using the HTL process, Khan et al. (2018) evaluated the MB yield through the HTL of *Chlorella vulgaris* using photobioreactors. They indicated that laboratory-scale trials produced 30% bio-oil. In addition, Nava-Bravo et al. (2021) revealed that the oxygenated compounds in MB attained from the HTL of *Desmodesmus* sp. were from 32.2% to 46.1%, and these oxygenated compounds were mainly formed through the decomposition process of lipids and carbohydrates, and a small part of ketones. However, it was also confirmed that carbohydrates account for the majority of generating O-containing compounds in MB through the HTL process (Zhang et al., 2021). Furthermore, Hietala et al. (2019) indicated that Maillard reactions were promoted by the HTL reactions, leading to increasing C and N content in bio-crude, improving bio-crude yield and HHV (up to 38.4 MJ/kg), and decreasing O content for the cases of *Nannochloropsis, Chlorella*, and *Spirulina* microalgae. More importantly, they reported that the biochemical composition of microalgae, reaction time, and HTL temperature were considered as the main factors affecting the yield and quality of bio-crude. As reported in the literature, the long HTL time was thought to offer a high MB yield for microalgae species containing low-protein and high-lipid contents. Indeed, the highest MB yield of 87.2% was indicated in a study by Li et al. (2014) when they used low-protein and high-lipid *Chlorella* sp. microalgae for the 90-minute HTL process. The reaction temperature was also found to be one of the important reaction parameters affecting the bio-oil yield and quality (Reddy et al., 2016). In the HTL process of microalgae with the presence of water, the ionic product of the water and the dielectric constant could be adjusted by the changes in temperature and pressure (Mathimani and Mallick, 2019). In the literature, most of the works indicated that the most suitable HTL temperature range for producing high-yield bio-oil from microalgae was from 250 to 375 °C depending on the content of proteins, lipids, and carbohydrates of microalgae (Mathimani and Mallick, 2019; Shahi et al., 2020; Zhang et al., 2022). This could be due to the reduction of the organic content when increasing the reaction temperature (Mathimani and Mallick, 2019). Besides, the solvents used for the HTL process were found to have a significant effect on O content in MB, thereby affecting HHV and the quality of MB (Liu et al., 2022). For example, reaction conditions of microalgae HTL using ethanol as solvent could be gentler than that of using water due to the lower critical point of ethanol compared to water. More importantly, it was revealed that ethanol could play a hydrogen donor, in which supplied hydrogen from ethanol could saturate the unsaturated C-N/C=O bonds in MB, leading to high H/C and low O/C ratios, thereby increasing HHV of MB to 35 MJ/kg (Zhang et al., 2022). Alternatively, ethanol could react with acids/amides to ethyl-esters in the HTL reactions, leading to the reduction of N-containing compounds in MB and an increase in MB yield (Liu et al., 2022). Interestingly, using co-solvents could also remove more oxygen in the HTL process, showing that produced MB had higher HHV and quality although the ratio between solvents should be optimized to ensure the economy aspect (Jena et al., 2022). Utilizing various solvents/co-solvents for the HTL process aiming to produce high-quality MB could be scrutinized in the works of Han et al. (2019) and Kostyukevich et al. (2019), while the effects of reactor types, reaction temperature, and other parameters on the MB yield and quality could be found in reference (Gu et al., 2020).

The yield and quality of MB through the HTL method could be enhanced with the support of the catalyst and pre-treatment process. Indeed, Zhang et al. (2018) pretreated *Spirulina platensis* microalgae by ultrasound before performing the HTL process. They indicated that the cell and link disruption in microalgae through ultrasonic pretreatment could facilitate the subsequent HTL, yielding a maximum MB of 50 wt%. In addition, the MB quality could also be improved by increasing the amount of compounds with lower boiling points. In another work, Mahima et al. (2021) evaluated the efficiency of various pretreatments in generating bio-oil before the HTL process. They showed that using post-HTL wastewater to pretreat *Scenedesmus obliquus* microalgae could offer bio-oil with higher yield (48.53%), higher HHV (36.19 MJ/kg), lower oxygenated compounds, and higher quality (C7-C21 hydrocarbon-rich bio-oil) than those of non-pretreated and acid-pretreated cases.

Catalysts were also found to play an important role in converting MB into long-chain hydrocarbons; however, the suitable catalyst for this purpose should contain both hydrogenation and deoxygenation sites aiming to break the link of C–O (Liu et al., 2021). Due to these reasons, noble/transition metals with d-orbital unfilled by electrons are usually used for deoxygenation, while zeolites could act as the acid center for hydrogenation reactions (Liu et al., 2022). In an investigation of Patel et al. (2017), they indicated that the Pt/γ-Al_2O_3 catalyst was the highest activity in deoxygenating among monometallic noble-based catalysts. Indeed, the use of Pt/γ-Al_2O_3 for the HTL of *Nannochloropsis* sp. could generate MB with high yield and low oxygen content (only 1.6%). The combination of CNT with transition metals such as Co, Fe, or Ni could also bring high-quality bio-oil although noble metals were found to be more active than transition metals. (Liu et al., 2021) reported that using Co/CNT for catalyzing the HTL of microalgae could reduce the oxygen content in MB by 25.5% compared to the case without a catalyst (45.2%). In addition, Ni/γ-Al_2O_3 catalyst could provide excellent efficiency in deoxygenating, yielding bio-oil with only 0.2% oxygen content for the HTL of *Nannochloropsis sp* (Pongsiriyakul et al., 2021). Adding the second metal to the base catalyst was found to produce MB with high quality because of the synergistic effect of the bimetallic catalyst. For example, NiMo/Al_2O_3 catalyst could deoxygenate completely and denitrogenate significantly in MB from the *Spirulina* HTL process (Castello et al., 2019). However, the use of second metal should be carefully considered because the reverse effect could occur (Ni–Cu/γ-Al_2O_3 as an example) due to the formation of metallic oxide covering the active sites of the catalyst, reducing deoxygenation activity of the catalyst, thereby reducing the bio-oil yield and quality (Pongsiriyakul et al., 2021). The effects of catalysts on bio-oil yield and quality from the HTL process of microalgae could also be presented and discussed in detail in a recent work of (Sharma et al., 2021).

Solid acid catalysts with special crystal structures and high surface area were also reported to generate MB with high yield and low oxygen content because solid acid catalysts could enhance the dehydration and deoxygenation through the promotion of the esterification reaction of carboxylic acids (Liu et al., 2022). Indeed, Shen et al. (2021) assessed the effects of MgAl-LDH_3 and MgAl-LDO_3 on the MB yield and oxygen content. As a result, the bio-oil yield increased by 12.98% for MgAl-LDH_3 and 9.72% for MgAl-LDO_3 compared to the case without catalysts. However, MgAl-LDO_3 possessing more basic sites than MgAl-LDH_3 could promote the reactions of decarboxylation/decarbonylation, and amidation of fatty acids in bio-oil, decreasing O/C to 22.6% and increasing N/C to 28.4%. The employment of base catalysts for the HTL of microalgae was also shown to enhance the alcohol deprotonazation

from nucleophilic activation, leading to the promotion of the deoxygenation reaction, thereby reducing oxygen content in MB (Jeon et al., 2019). In addition, zeolites-based catalysts could be found to have high efficiency in improving the selectivity of products, especially for increasing aromatic hydrocarbon and long-chain alkane content and reducing phenolic oxygen-containing compounds (Liu et al., 2022). For example, using pore size-turned HZSM-5 could generate aromatic products up to 44% (Lu et al., 2020). As mentioned above, microalgae contain carbohydrates, protein, and lipids that could be changed in a large range, causing difficulties in the complete understanding of the whole reactions in the HTL process; however, advantages of HTL could be the necessary evidence to make this method become a commercial process for MB production. In summary, bio-oil characteristics through the HTL of microalgae could be given in Table 3.

5. Challenges and opportunities

Although using bio-oil is environmentally safe, MB production using pyrolysis and HTL is challenging and necessitates the implementation of advanced technologies. Principally, due to the high amount of oxygen in MB, some properties make it difficult to use as fuel if it is not upgraded (Sánchez-Borrego et al., 2021). Moreover, high acidity, increased viscosity, and a relatively low heating value are key challenges for MB production using pyrolysis and HTL techniques. In addition, the presence of water and little amounts of reactive oxygenated and inorganic compounds generates complex matrices with low pH and thermal stability (Kazemi Shariat Panahi et al., 2019). As a consequence, developing the proper pyrolysis or HTL for microalgae could facilitate the overcoming of these challenges to produce high-yield and high-quality MB that could benefit combustion in boilers, stimulate engines and turbines, deliver transportation fuels, and provide a renewable feedstock for the chemical industry. Alternatively, catalyst systems with high efficiency and low cost should be developed to increase the yield, form the products with a proper distribution rate, and produce bio-oil with desirable components.

Since bio-oil is a complex mixture of different compounds, this means no particular system is accessible for the complete characterization of MB, which creates prospects for future research recommendations. Moreover, catalytic cracking and hydrodeoxygenation are very complicated processes that necessitate dependable and well-configured reactors. Thus, advanced technologies and optimization studies on reactor configuration/design and reaction parameters should be further studied in the future to minimize the processing time and limit the secondary degradation of highly unstable compounds (Lee et al., 2020b). For example, hydropyrolysis could be a promising emerging technology for producing high-quality bio-oil (up to 48 MJ/kg). Besides, a wide range of microalgae produced 5–25 wt% more bio-oil than their lipid content of biomass (Kim et al., 2019), indicating that in addition to lipids, proteins, and carbohydrates are also used to make bio-oils. Therefore, instead of being disposed of as waste after extracting oil, the biomass residue of microalgae can be utilized as feedstock for thermochemical conversion, increasing the economic benefits of using microalgae for sustainable and renewable biofuel production. Furthermore, it should have a thorough analysis and comprehensive evaluation of the energy aspect and life cycle assessment of pyrolysis and HTL system aiming to couple the pyrolysis and HTL system with biorefinery efficiently in optimizing the performance of output products. On the other hand, the by-products obtained after processing of pyrolysis and HTL should be recovered for other useful aims, increasing the economical capacity and reducing secondary pollution. For example, solid residues could be used to produce animal feed additives, while aqueous phases containing beneficial elements such as N, P, Ca, and Mg could be employed as the nutrient medium for cultivating algae or biofertilizers.

Table 3
Bio-oil characteristics through hydrothermal liquefaction process of microalgae.

Microalgae types	Hydrothermal liquefaction conditions	Bio-oil yield and characteristics	Reference
Spirulina platensis	CeO_2 catalyst for HTL at a temperature of 250 °C for 30 min	26% of yield with %C of 62.8 %and HHV of 27.15 MJ/kg	(Kandasamy et al., 2020)
Nannochloropsis sp.	No-catalyst at a temperature of 320 °C for 30 min	50% of yield with %C of 64.1%	(Pongsiriyakul et al., 2021)
Spirulina platensis	250 °C, 30 min, 0.20 g catalyst (CeO_2)	33 wt% of yield, HHV of 35.64 MJ/kg, and %C of 69.75%	(Kandasamy et al., 2021)
Spirulina platensis	320 °C, 0.75 g of catalyst (Fe_3O_4) for 37 min	32.33 wt% of yield, HHV of 30.98, and %C of 69.36%	(Kandasamy et al., 2019)
Scenedesmus obliquus	300 °C	48.53 wt%, HHV of 28.88 MJ/kg and %C of 48.11%	(Mahima et al., 2021)
Scenedesmus obliquus	250 to 350 °C, catalyst (Zr-HZSM-5)	52.8 wt% of yield, HHV of 43.56 MJ/kg, and %C of 45.03%	(Mustapha et al., 2022)
Chlorella pyrenoidosa	340 °C, 60 min, –COOH modified C nanotube	77.9 wt% of yield, HHV of 37.6 MJ/kg, and %C of 50.72%	(Lu et al., 2021)
Chlorella	280 °C- 400 °C, catalyst based porous silica	32.2 wt% of yield, HHV of 36.56 MJ/kg	(Lu et al., 2020)
Nostoc ellipsosporum	300 °C	24.62 wt% of yield with hydrocarbons of 25%	(Devi and Parthiban, 2020)
Spirulina Platensis	340 °C, 50 min, solid/water ratio of 1:10 (w/w)	30.07 wt% of yield with HHV of 34.76 MJ/kg and %C of 71.51%	(Chen et al., 2019)

6. Conclusion

This paper comprehensively reviewed the key mechanisms and technologies in generating microalgae bio-oil using pyrolysis and hydrothermal liquefaction. Generally, bio-oil produced by the two aforementioned approaches has a relatively high yield and quality while using co-materials (only for pyrolysis) or being supported by proper catalysts. More importantly, microalgae bio-oil produced by the above-mentioned technologies has a large potential in reducing greenhouse gas emissions relative to fossil fuels. Finally, this work recommends that advanced technologies of pyrolysis and hydrothermal liquefaction should be further investigated to overcome the challenges in producing high-quality and high-yield bio-oil from microalgae toward a sustainable circular economy.

Declaration of Competing Interest

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

Data availability

The authors do not have permission to share data.

References

Adamakis, I.-D., Lazaridis, P.A., Terzopoulou, E., Torofias, S., Valari, M., Kalaitzi, P., Rousonikolos, V., Gkoutzikostas, D., Zouboulis, A., Zalidis, G., Triantafyllidis, K.S., 2018. Cultivation, characterization, and properties of Chlorella vulgaris microalgae with different lipid contents and effect on fast pyrolysis oil composition. Environ. Sci. Pollut. Res. 25, 23018–23032. https://doi.org/10.1007/s11356-018-2368-5.

Adamczyk, M., Sajdak, M., 2018. Pyrolysis Behaviours of Microalgae Nannochloropsis gaditana. Waste Biomass Valor. 9, 2221–2235. https://doi.org/10.1007/s12649-017-9996-8.

Akaberi, S., Gusbeth, C., Silve, A., Senthilnathan, D.S., Navarro-López, E., Molina-Grima, E., Müller, G., Frey, W., 2019. Effect of pulsed electric field treatment on enzymatic hydrolysis of proteins of Scenedesmus almeriensis. Algal Res. 43, 101656 https://doi.org/10.1016/j.algal.2019.101656.

Akhtar, A., Jiříček, I., Ivanova, T., Mehrabadi, A., Krepl, V., 2019. Carbon conversion and stabilisation of date palm and high rate algal pond (microalgae) biomass through slow pyrolysis. Int. J. Energy Res. 43, 4403–4416. https://doi.org/10.1002/er.4565.

Alherbawi, M., Parthasarathy, P., Al-Ansari, T., Mackey, H.R., McKay, G., 2021. Potential of drop-in biofuel production from camel manure by hydrothermal liquefaction and biocrude upgrading: A Qatar case study. Energy 232, 121027. https://doi.org/10.1016/j.energy.2021.121027.

Andrade, L.A., Batista, F.R.X., Lira, T.S., Barrozo, M.A.S., Vieira, L.G.M., 2018. Characterization and product formation during the catalytic and non-catalytic pyrolysis of the green microalgae Chlamydomonas reinhardtii. Renew. Energy 119, 731–740. https://doi.org/10.1016/j.renene.2017.12.056.

Arif, M., Li, Y., El-Dalatony, M.M., Zhang, C., Li, X., Salama, E.-S., 2021. A complete characterization of microalgal biomass through FTIR/TGA/CHNS analysis: An approach for biofuel generation and nutrients removal. Renew. Energy 163, 1973–1982. https://doi.org/10.1016/j.renene.2020.10.066.

Auersvald, M., Macek, T., Schulzke, T., Staš, M., Šimáček, P., 2020. Influence of biomass type on the composition of bio-oils from ablative fast pyrolysis. J. Anal. Appl. Pyrolysis 150. https://doi.org/10.1016/j.jaap.2020.104838.

Aysu, T., Ola, O., Maroto-Valer, M.M., Sanna, A., 2017. Effects of titania based catalysts on in-situ pyrolysis of Pavlova microalgae. Fuel Process. Technol. 166, 291–298. https://doi.org/10.1016/j.fuproc.2017.05.001.

Aysu, T., Fermoso, J., Sanna, A., 2018. Ceria on alumina support for catalytic pyrolysis of Pavlova sp. microalgae to high-quality bio-oils. J. Energy Chem. 27, 874–882. https://doi.org/10.1016/j.jechem.2017.06.014.

Azizi, K., Moraveji, M.K., Arregi, A., Amutio, M., Lopez, G., Olazar, M., 2020. On the pyrolysis of different microalgae species in a conical spouted bed reactor: bio-fuel yields and characterization. Bioresour. Technol. 311, 123561.

Bakır, H., Ağbulut, Ü., Gürel, A.E., Yıldız, G., Güvenç, U., Soudagar, M.E.M., Hoang, A.T., Deepanraj, B., Saini, G., Afzal, A., 2022. Forecasting of future greenhouse gas emission trajectory for India using energy and economic indexes with various metaheuristic algorithms. J. Clean. Prod. 360, 131946 https://doi.org/10.1016/j.jclepro.2022.131946.

Basar, I.A., Liu, H., Carrere, H., Trably, E., Eskicioglu, C., 2021. A review on key design and operational parameters to optimize and develop hydrothermal liquefaction of biomass for biorefinery applications. Green Chem. 23, 1404–1446. https://doi.org/10.1039/D0GC04092D.

Bordoloi, N., Narzari, R., Sut, D., Saikia, R., Chutia, R.S., Kataki, R., 2016. Characterization of bio-oil and its sub-fractions from pyrolysis of Scenedesmus dimorphus. Renew. Energy 98, 245–253. https://doi.org/10.1016/j.renene.2016.03.081.

Castello, D., Haider, M.S., Rosendahl, L.A., 2019. Catalytic upgrading of hydrothermal liquefaction biocrudes: Different challenges for different feedstocks. Renew. Energy 141, 420–430. https://doi.org/10.1016/j.renene.2019.04.003.

Chakraborty, S., Dunford, N.T., Goad, C., 2021. A kinetic study of microalgae, municipal sludge and cedar wood co-pyrolysis. Renew. Energy 165, 514–524. https://doi.org/10.1016/j.renene.2020.11.012.

Chang, G., Miao, P., Wang, H., Wang, L., Hu, X., Guo, Q., 2018. A synergistic effect during the co-pyrolysis of Nannochloropsis sp. and palm kernel shell for aromatic hydrocarbon production. Energy Convers. Manag. 173, 545–554. https://doi.org/10.1016/j.enconman.2018.08.003.

Che, Q., Yang, M., Wang, X., Yang, Q., Rose Williams, L., Yang, H., Zou, J., Zeng, K., Zhu, Y., Chen, Y., Chen, H., 2019. Influence of physicochemical properties of metal modified ZSM-5 catalyst on benzene, toluene and xylene production from biomass catalytic pyrolysis. Bioresour. Technol. 278, 248–254. https://doi.org/10.1016/j.biortech.2019.01.081.

Chen, C., Qi, Q., Huang, D., Zeng, T., Bu, X., Huang, Y., Huang, H., 2021a. Effect of additive mixture on microwave-assisted catalysis pyrolysis of microalgae. Energy 229, 120752. https://doi.org/10.1016/j.energy.2021.120752.

Chen, C., Qi, Q., Zeng, T., Fan, D., Zhao, J., Qiu, H., Huang, H., 2021b. Effect of compound additive on microwave-assisted pyrolysis characteristics and products of Chlorella vulgaris. J. Energy Inst. 98, 188–198. https://doi.org/10.1016/j.joei.2021.06.019.

Chen, C., Zeng, T., He, J., Qi, Q., Feng, J., Zhao, J., Fan, D., 2021c. Microwave pyrolysis characteristics and product of Chlorella vulgaris under compound additives and optimization by Box-Behnken design. J. Environ. Chem. Eng. 9, 106762 https://doi.org/10.1016/j.jece.2021.106762.

Chen, C., Fan, D., Ling, H., Huang, X., Yang, G., Cai, D., Zhao, J., Bi, Y., 2022. Microwave catalytic co-pyrolysis of Chlorella vulgaris and high density polyethylene over activated carbon supported monometallic: Characteristics and bio-oil analysis. Bioresour. Technol. 363, 127881 https://doi.org/10.1016/j.biortech.2022.127881.

Chen, H., He, Z., Zhang, B., Feng, H., Kandasamy, S., Wang, B., 2019. Effects of the aqueous phase recycling on bio-oil yield in hydrothermal liquefaction of Spirulina Platensis, α-cellulose, and lignin. Energy 179, 1103–1113. https://doi.org/10.1016/j.energy.2019.04.184.

Chen, H., Xie, Y., Chen, W., Xia, M., Li, K., Chen, Z., Chen, Y., Yang, H., 2019. Investigation on co-pyrolysis of lignocellulosic biomass and amino acids using TG-FTIR and Py-GC/MS. Energy Convers. Manag. 196, 320–329. https://doi.org/10.1016/j.enconman.2019.06.010.

Chen, R., Zhang, S., Yang, X., Li, G., Zhou, H., Li, Q., Zhang, Y., 2021. Thermal behaviour and kinetic study of co-pyrolysis of microalgae with different plastics. Waste Manag. 126, 331–339. https://doi.org/10.1016/j.wasman.2021.03.001.

Choudhary, S., Tripathi, S., Poluri, K.M., 2022. Microalgal-based bioenergy: strategies, prospects, and sustainability. Energy Fuels 36, 14584–14612. https://doi.org/10.1021/acs.energyfuels.2c02922.

Chowdhury, M.S., Rahman, K.S., Selvanathan, V., Nuthammachot, N., Suklueng, M., Mostafaeipour, A., Habib, A., Akhtaruzzaman, M., Amin, N., Techato, K., 2021. Current trends and prospects of tidal energy technology. Environ. Dev. Sustain. 23, 8179–8194.

Derakhshandeh, M., Ateş, F., Tezcan Un, U., 2021. Renewable bio-oil from pyrolysis of synechocystis and scenedesmus wild-type microalgae biomass. BioEnergy Res. 14, 991–1001.

Devi, T.E., Parthiban, R., 2020. Hydrothermal liquefaction of Nostoc ellipsosporum biomass grown in municipal wastewater under optimized conditions for bio-oil production. Bioresour. Technol. 316, 123943 https://doi.org/10.1016/j.biortech.2020.123943.

Escalante, J., Chen, W.-H., Tabatabaei, M., Hoang, A.T., Kwon, E.E., Andrew Lin, K.-Y., Saravanakumar, A., 2022. Pyrolysis of lignocellulosic, algal, plastic, and other biomass wastes for biofuel production and circular bioeconomy: A review of thermogravimetric analysis (TGA) approach. Renew. Sustain. Energy Rev. 169, 112914 https://doi.org/10.1016/j.rser.2022.112914.

Fakayode, O.A., Wahia, H., Zhang, L., Zhou, C., Ma, H., 2023. State-of-the-art co-pyrolysis of lignocellulosic and macroalgae biomass feedstocks for improved bio-oil production- A review. Fuel 332, 126071. https://doi.org/10.1016/j.fuel.2022.126071.

Fang, S., Gu, W., Dai, M., Xu, J., Yu, Z., Lin, Y., Chen, J., Ma, X., 2018. A study on microwave-assisted fast co-pyrolysis of chlorella and tire in the N2 and CO2 atmospheres. Bioresour. Technol. 250, 821–827. https://doi.org/10.1016/j.biortech.2017.11.080.

Ferreira, A.F., Soares Dias, A.P., 2020. Pyrolysis of microalgae biomass over carbonate catalysts. J. Chem. Technol. Biotechnol. 95, 3270–3279. https://doi.org/10.1002/jctb.6506.

Foong, S.Y., Chan, Y.H., Loy, A.C.M., How, B.S., Tamothran, A.M., Yip, A.J.K., Liew, R.K., Peng, W., Alstrup, A.K., Lam, S.S., Sonne, C., 2022. The nexus between biofuels and pesticides in agroforestry: Pathways toward United Nations sustainable development goals. Environ. Res. 214, 113751 https://doi.org/10.1016/j.envres.2022.113751.

Gao, W., Zhang, M., Wu, H., 2022. Bed agglomeration during fast pyrolysis of bio-oil derived fuels in a fluidized-bed reactor. Fuel 328, 125359.

Gu, X., 2020. Fractionation of Biomass Via Sequential Hydrothermal Liquefaction to Produce Value-Added Products and Techno-Economic Analysis. Washington State University.

Gu, X., Martinez-Fernandez, J.S., Pang, N., Fu, X., Chen, S., 2020. Recent development of hydrothermal liquefaction for algal biorefinery. Renew. Sustain. Energy Rev. 121, 109707 https://doi.org/10.1016/j.rser.2020.109707.

Han, Y., Hoekman, K., Jena, U., Das, P., 2019. Use of co-solvents in hydrothermal liquefaction (HTL) of microalgae. Energies 13, 124. https://doi.org/10.3390/en13010124.

Hassan, A.A., Alhameedi, H.A., Smith, J.D., 2020. Two-step sub/supercritical water and ethanol processes for non- catalytic biodiesel production. Chem. Eng. Process. - Process Intensif. 150, 107881 https://doi.org/10.1016/j.cep.2020.107881.

Hietala, D.C., Godwin, C.M., Cardinale, B.J., Savage, P.E., 2019. The independent and coupled effects of feedstock characteristics and reaction conditions on biocrude production by hydrothermal liquefaction. Appl. Energy 235, 714–728. https://doi.org/10.1016/j.apenergy.2018.10.120.

Hoang, A.T., Sirohi, R., Pandey, A., Nižetić, S., Lam, S.S., Chen, W.-H., Luque, R., Thomas, S., Arıcı, Ü., Pham, V.V., 2022. Biofuel production from microalgae: Challenges and chances. Phytochem. Rev. https://doi.org/10.1007/s11101-022-09819-y.

Hong, Y., Xie, C., Chen, W., Luo, X., Shi, K., Wu, T., 2020. Kinetic study of the pyrolysis of microalgae under nitrogen and CO2 atmosphere. Renew. Energy 145, 2159–2168. https://doi.org/10.1016/j.renene.2019.07.135.

Hu, Y., Gong, M., Feng, S., Xu, C. (Charles), Bassi, A., 2019. A review of recent developments of pre-treatment technologies and hydrothermal liquefaction of microalgae for bio-crude oil production. Renew. Sustain. Energy Rev. 101, 476–492. doi: 10.1016/j.rser.2018.11.037.

Hu, Y., Li, J., Wang, S., Xu, L., Barati, B., Cao, B., Wang, H., Xie, K., Wang, Q., 2021. Catalytic fast hydropyrolysis of seaweed biomass with different zeolite catalysts to produce high-grade bio-oil. Process Saf. Environ. Prot. 146, 69–76. https://doi.org/10.1016/j.psep.2020.08.019.

Huang, Z., Zhang, J., Pan, M., Hao, Y., Hu, R., Xiao, W., Li, G., Lyu, T., 2022. Valorisation of microalgae residues after lipid extraction: Pyrolysis characteristics for biofuel production. Biochem. Eng. J. 179, 108330 https://doi.org/10.1016/j.bej.2021.108330.

Jena, U., Eboibi, B.E., Das, K.C., 2022. Co-solvent assisted hydrothermal liquefaction of algal biomass and biocrude upgrading. Fuels 3, 326–341. https://doi.org/10.3390/fuels3020020.

Jeon, Y., Chi, W.S., Hwang, J., Kim, D.H., Kim, J.H., Shul, Y.-G., 2019. Core-shell nanostructured heteropoly acid-functionalized metal-organic frameworks: Bifunctional heterogeneous catalyst for efficient biodiesel production. Appl. Catal. B Environ. 242, 51–59. https://doi.org/10.1016/j.apcatb.2018.09.071.

Kandasamy, S., Zhang, B., He, Z., Chen, H., Feng, H., Wang, Q., Wang, B., Bhuvanendran, N., Esakkimuthu, S., Ashokkumar, V., Krishnamoorthi, M., 2019. Hydrothermal liquefaction of microalgae using Fe3O4 nanostructures as efficient catalyst for the production of bio-oil: Optimization of reaction parameters by

response surface methodology. Biomass Bioenergy 131, 105417. https://doi.org/10.1016/j.biombioe.2019.105417.
Kandasamy, S., Zhang, B., He, Z., Chen, H., Feng, H., Wang, Q., Wang, B., Ashokkumar, V., Siva, S., Bhuvanendran, N., Krishnamoorthi, M., 2020. Effect of low-temperature catalytic hydrothermal liquefaction of Spirulina platensis. Energy 190, 116236. https://doi.org/10.1016/j.energy.2019.116236.
Kandasamy, S., Devarayan, K., Bhuvanendran, N., Zhang, B., He, Z., Narayanan, M., Mathimani, T., Ravichandran, S., Pugazhendhi, A., 2021. Accelerating the production of bio-oil from hydrothermal liquefaction of microalgae via recycled biochar-supported catalysts. J. Environ. Chem. Eng. 9, 105321 https://doi.org/10.1016/j.jece.2021.105321.
Kazemi Shariat Panahi, H., Tabatabaei, M., Aghbashlo, M., Dehhaghi, M., Rehan, M., Nizami, A.-S., 2019. Recent updates on the production and upgrading of bio-crude oil from microalgae. Bioresour. Technol. Reports 7, 100216. doi: 10.1016/j.biteb.2019.100216.
Khan, S., Gholkar, P., Shastri, Y., Shah, N.G., Bhartiya, S., 2018. Hydrothermal liquefaction of chlorella SP for biocrude oil production: Comparison of experimental and modeling results. Int. Agric. Eng. J. 27, 8–16.
Kim, S., Tsang, Y.F., Kwon, E.E., Lin, K.-Y.-A., Lee, J., 2019. Recently developed methods to enhance stability of heterogeneous catalysts for conversion of biomass-derived feedstocks. Korean J. Chem. Eng. 36, 1–11. https://doi.org/10.1007/s11814-018-0174-x.
Koley, S., Khadase, M.S., Mathimani, T., Raheman, H., Mallick, N., 2018. Catalytic and non-catalytic hydrothermal processing of Scenedesmus obliquus biomass for bio-crude production – A sustainable energy perspective. Energy Convers. Manag. 163, 111–121. https://doi.org/10.1016/j.enconman.2018.02.052.
Kostyukevich, Y., Vlaskin, M., Zherebker, A., Grigorenko, A., Borisova, L., Nikolaev, E., 2019. High-resolution mass spectrometry study of the bio-oil samples produced by thermal liquefaction of microalgae in different solvents. J. Am. Soc. Mass Spectrom. 30, 605–614. https://doi.org/10.1007/s13361-018-02128-9.
Kumar, A., Yan, B., Cheng, Z., Tao, J., Hassan, M., Li, J., Kumari, L., Oba, B.T., Aborisade, M.A., Jamro, I.A., Chen, G., 2023. Co-pyrolysis of hydrothermally pre-treated microalgae residue and polymeric waste (plastic/tires): Comparative and dynamic analyses of pyrolytic behaviors, kinetics, chars, oils, and in-situ gas emissions. Fuel 331, 125814. https://doi.org/10.1016/j.fuel.2022.125814.
Lee, J., Kwon, E.E., Park, Y.-K., 2020. Recent advances in the catalytic pyrolysis of microalgae. Catal. Today 355, 263–271. https://doi.org/10.1016/j.cattod.2019.03.010.
Lee, X.J., Ong, H.C., Gan, Y.Y., Chen, W.-H., Mahlia, T.M.I., 2020a. State of art review on conventional and advanced pyrolysis of macroalgae and microalgae for biochar, bio-oil and bio-syngas production. Energy Convers. Manag. 210, 112707 https://doi.org/10.1016/j.enconman.2020.112707.
Lee, X.J., Ong, H.C., Gan, Y.Y., Chen, W.H., Mahlia, T.M.I., 2020b. State of art review on conventional and advanced pyrolysis of macroalgae and microalgae for biochar, bio-oil and bio-syngas production. Energy Convers. Manag. https://doi.org/10.1016/j.enconman.2020.112707.
Li, H., Liu, Z., Zhang, Y., Li, B., Lu, H., Duan, N., Liu, M., Zhu, Z., Si, B., 2014. Conversion efficiency and oil quality of low-lipid high-protein and high-lipid low-protein microalgae via hydrothermal liquefaction. Bioresour. Technol. 154, 322–329. https://doi.org/10.1016/j.biortech.2013.12.074.
Li, C., Zhu, L., Ma, Z., Yang, Y., Cai, W., Ye, J., Qian, J., Liu, X., Zuo, Z., 2021. Optimization of the nitrogen and oxygen element distribution in microalgae by ammonia torrefaction pretreatment and subsequent fast pyrolysis process for the production of N-containing chemicals. Bioresour. Technol. 321, 124461 https://doi.org/10.1016/j.biortech.2020.124461.
Liu, X., Guo, Y., Xu, D., Guan, Q., 2022. A review on recent advances in clean microalgal bio-oil production via catalytic hydrothermal deoxygenation. J. Clean. Prod. 366, 132978 https://doi.org/10.1016/j.jclepro.2022.132978.
Liu, L., Liu, Y., Wang, W., Wang, Y., Li, G., Hu, C., 2021. Pyrolysis of high-ash natural microalgae from water blooms: effects of acid pretreatment. Toxins (Basel). 13, 542. https://doi.org/10.3390/toxins13080542.
Liu, B., Wang, Z., Feng, L., 2021. Effects of reaction parameter on catalytic hydrothermal liquefaction of microalgae into hydrocarbon rich bio-oil. J. Energy Inst. 94, 22–28. https://doi.org/10.1016/j.joei.2020.10.008.
Lu, Q., Gong, Y., Lu, J., Liu, J., Wu, Y., 2020. Hydrothermal catalytic upgrading of model compounds of algae-based bio-oil to monocyclic aromatic hydrocarbons over hierarchical HZSM-5. Ind. Eng. Chem. Res. 59, 20551–20560. https://doi.org/10.1021/acs.iecr.0c03439.
Lu, J., Wu, J., Zhang, L., Liu, Z., Wu, Y., Yang, M., 2020. Catalytic hydrothermal liquefaction of microalgae over mesoporous silica-based materials with site-separated acids and bases. Fuel 279, 118529. https://doi.org/10.1016/j.fuel.2020.118529.
Lu, J., Zhang, Z., Fan, G., Zhang, L., Wu, Y., Yang, M., 2021. Enhancement of microalgae bio-oil quality via hydrothermal liquefaction using functionalized carbon nanotubes. J. Clean. Prod. 285, 124835.
Maheria, K.C., Lodhi, A., Sharma, G., 2021. Microalgae oil upgrading over zeolite-based catalysts. pp. 89–124. doi: 10.1021/bk-2021-1379.ch004.
Mahima, J., Sundaresh, R.K., Gopinath, K.P., Rajan, P.S.S., Arun, J., Kim, S.-H., Pugazhendhi, A., 2021. Effect of algae (Scenedesmus obliquus) biomass pre-treatment on bio-oil production in hydrothermal liquefaction (HTL): Biochar and aqueous phase utilization studies. Sci. Total Environ. 778, 146262 https://doi.org/10.1016/j.scitotenv.2021.146262.
Majid, M., Chin, B.L.F., Jawad, Z.A., Chai, Y.H., Lam, M.K., Yusup, S., Cheah, K.W., 2021. Particle swarm optimization and global sensitivity analysis for catalytic co-pyrolysis of Chlorella vulgaris and plastic waste mixtures. Bioresour. Technol. 329, 124874 https://doi.org/10.1016/j.biortech.2021.124874.
Maliutina, K., Tahmasebi, A., Yu, J., Saltykov, S.N., 2017. Comparative study on flash pyrolysis characteristics of microalgal and lignocellulosic biomass in entrained-flow reactor. Energy Convers. Manag. 151, 426–438. https://doi.org/10.1016/j.enconman.2017.09.013.
Masoumi, S., Dalai, A.K., 2021. Techno-economic and life cycle analysis of biofuel production via hydrothermal liquefaction of microalgae in a methanol-water system and catalytic hydrotreatment using hydrochar as a catalyst support. Biomass and Bioenergy 151, 106168. https://doi.org/10.1016/j.biombioe.2021.106168.
Mathimani, T., Mallick, N., 2019. A review on the hydrothermal processing of microalgal biomass to bio-oil - Knowledge gaps and recent advances. J. Clean. Prod. 217, 69–84. https://doi.org/10.1016/j.jclepro.2019.01.129.
Miliotti, E., Rosi, L., Bettucci, L., Lotti, G., Rizzo, A.M., Chiaramonti, D., 2020. Characterization of chemically and physically activated carbons from lignocellulosic ethanol lignin-rich stream via hydrothermal carbonization and slow pyrolysis pretreatment. Energies 13, 4101. https://doi.org/10.3390/en13164101.
Mo, L., Dai, H., Feng, L., Liu, B., Li, X., Chen, Y., Khan, S., 2020. In-situ catalytic pyrolysis upgradation of microalgae into hydrocarbon rich bio-oil: Effects of nitrogen and carbon dioxide environment. Bioresour. Technol. 314, 123758 https://doi.org/10.1016/j.biortech.2020.123758.
Mustapha, S.I., Rawat, I., Bux, F., Isa, Y.M., 2021. Catalytic pyrolysis of nutrient-stressed Scenedesmus obliquus microalgae for high-quality bio-oil production. Renew. Energy 179, 2036–2047. https://doi.org/10.1016/j.renene.2021.08.043.
Mustapha, S.I., Mohammed, U.A., Bux, F., Isa, Y.M., 2022. Catalytic hydrothermal liquefaction of nutrient-stressed microalgae for production of high-quality bio-oil over Zr-doped HZSM-5 catalyst. Biomass Bioenergy 163, 106497. https://doi.org/10.1016/j.biombioe.2022.106497.
Mustapha, S.I., Mohammed, U.A., Rawat, I., Bux, F., Isa, Y.M., 2023. Production of high-quality pyrolytic bio-oils from nutrient-stressed Scenedesmus obliquus microalgae. Fuel 332, 126299. https://doi.org/10.1016/j.fuel.2022.126299.
Nava-Bravo, I., Velasquez-Orta, S.B., Monje-Ramírez, I., Güereca, L.P., Harvey, A.P., Cuevas-García, R., Yáñez-Noguez, I., Orta-Ledesma, M.T., 2021. Catalytic hydrothermal liquefaction of microalgae cultivated in wastewater: Influence of ozone-air flotation on products, energy balance and carbon footprint. Energy Convers. Manag. 249, 114806 https://doi.org/10.1016/j.enconman.2021.114806.
Nazem, M.A., Tavakoli, O., 2017. Bio-oil production from refinery oily sludge using hydrothermal liquefaction technology. J. Supercrit. Fluids 127, 33–40. https://doi.org/10.1016/j.supflu.2017.03.020.
Ni, J., Qian, L., Wang, Y., Zhang, B., Gu, H., Hu, Y., Wang, Q., 2022. A review on fast hydrothermal liquefaction of biomass. Fuel 327, 125135. https://doi.org/10.1016/j.fuel.2022.125135.
Nishu, Liu, R., Rahman, M.M., Sarker, M., Chai, M., Li, C., Cai, J., 2020. A review on the catalytic pyrolysis of biomass for the bio-oil production with ZSM-5: Focus on structure. Fuel Process. Technol. 199, 106301. doi: 10.1016/j.fuproc.2019.106301.
Norouzi, O., Tavasoli, A., Jafarian, S., Esmailpour, S., 2017. Catalytic upgrading of bio-products derived from pyrolysis of red macroalgae Gracilaria gracilis with a promising novel micro/mesoporous catalyst. Bioresour. Technol. 243, 1–8. https://doi.org/10.1016/j.biortech.2017.06.072.
Nyoni, B., Duma, S., Bolo, L., Shabangu, S., Hlangothi, S.P., 2020. Co-pyrolysis of South African bituminous coal and Scenedesmus microalgae: Kinetics and synergistic effects study. Int. J. Coal Sci. Technol. 7, 807–815. https://doi.org/10.1007/s40789-020-00310-7.
Oasmaa, A., Lehto, J., Solantausta, Y., Kallio, S., 2021. Historical review on VTT fast pyrolysis bio-oil production and upgrading. Energy and Fuels 35. https://doi.org/10.1021/acs.energyfuels.1c00177.
Ong, H.C., Chen, W.-H., Singh, Y., Gan, Y.Y., Chen, C.-Y., Show, P.L., 2020. A state-of-the-art review on thermochemical conversion of biomass for biofuel production: A TG-FTIR approach. Energy Convers. Manag. 209, 112634 https://doi.org/10.1016/j.enconman.2020.112634.
Palumbo, A.W., Bartel, C.J., Sorli, J.C., Weimer, A.W., 2019. Characterization of products derived from the high temperature flash pyrolysis of microalgae and rice hulls. Chem. Eng. Sci. 196, 527–537. https://doi.org/10.1016/j.ces.2018.11.029.
Patel, B., Arcelus-Arrillaga, P., Izadpanah, A., Hellgardt, K., 2017. Catalytic Hydrotreatment of algal biocrude from fast Hydrothermal Liquefaction. Renew. Energy 101, 1094–1101. https://doi.org/10.1016/j.renene.2016.09.056.
Piloni, R.V., Daga, I.C., Urcelay, C., Moyano, E.L., 2021. Experimental investigation on fast pyrolysis of freshwater algae. Prospects for alternative bio-fuel production. Algal Res. 54, 102206 https://doi.org/10.1016/j.algal.2021.102206.
Pongsiriyakul, K., Kiatkittipong, W., Adhikari, S., Lim, J.W., Lam, S.S., Kiatkittipong, K., Dankeaw, A., Reubroycharoen, P., Laosiripojana, N., Faungnawakij, K., Assabumrungrat, S., 2021. Effective Cu/Re promoted Ni-supported γ-Al2O3 catalyst for upgrading algae bio-crude oil produced by hydrothermal liquefaction. Fuel Process. Technol. 216, 106670 https://doi.org/10.1016/j.fuproc.2020.106670.
Pourkarimi, S., Hallajisani, A., Alizadehdakhel, A., Nouralishahi, A., 2019. Biofuel production through micro- and macroalgae pyrolysis – A review of pyrolysis methods and process parameters. J. Anal. Appl. Pyrolysis 142, 104599. https://doi.org/10.1016/j.jaap.2019.04.015.
Qadariyah, L., Aswie, V., Widjaya, H.V., Aditya, K.H., Mahfud, M., 2021. Microwave-assisted pyrolysis of microalgae in producing bio-oil using CaO catalyst and charcoal as heat absorber. IOP Conf. Ser. Earth Environ. Sci. 765 https://doi.org/10.1088/1755-1315/765/1/012095.
Reddy, H.K., Muppaneni, T., Ponnusamy, S., Sudasinghe, N., Pegallapati, A., Selvaratnam, T., Seger, M., Dungan, B., Nirmalakhandan, N., Schaub, T., Holguin, F. O., Lammers, P., Voorhies, W., Deng, S., 2016. Temperature effect on hydrothermal liquefaction of Nannochloropsis gaditana and Chlorella sp. Appl. Energy 165, 943–951. https://doi.org/10.1016/j.apenergy.2015.11.067.

Rocha, K.C., Alonso, C.G., Leal, W.G.O., Schultz, E.L., Andrade, L.A., Ostroski, I.C., 2020. Slow pyrolysis of Spirulina platensis for the production of nitrogenous compounds and potential routes for their separation. Bioresour. Technol. 313, 123709 https://doi.org/10.1016/j.biortech.2020.123709.

Sabariswaran, K., Zhang, B., He, Z., Bhuvanendran, N., EL-Seesy, A.I., Wang, Q., Narayanan, M., Thangavel, P., Dar, M.A., 2022. Microalgae as a multipotential role in commercial applications: Current scenario and future perspectives. Fuel 308, 122053. doi: 10.1016/j.fuel.2021.122053.

Said, Z., Nguyen, T.H., Sharma, P., Li, C., Ali, H.M., Nguyen, V.N., Pham, V.V., Ahmed, S. F., Van, D.N., Truong, T.H., 2022. Multi-attribute optimization of sustainable aviation fuel production-process from microalgae source. Fuel 324, 124759. https://doi.org/10.1016/j.fuel.2022.124759.

Salbitani, G., Carillo, P., Di Martino, C., Bolinesi, F., Mangoni, O., Loreto, F., Carfagna, S., 2022. Microalgae cross-fertilization: short-term effects of Galdieria phlegrea extract on growth, photosynthesis and enzyme activity of Chlorella sorokiniana cells. J. Appl. Phycol. 34, 1957–1966.

Saleh Khodaparasti, M., Reza Shirazvatan, M., Tavakoli, O., Ali Khodadadi, A., 2022. Co-pyrolysis of municipal sewage sludge and microalgae Chlorella vulgaris: Products' optimization; thermo-kinetic study, and ANN modeling. Energy Convers. Manag. 254, 115258 https://doi.org/10.1016/j.enconman.2022.115258.

Sánchez-Borrego, F.J., Álvarez-Mateos, P., García-Martín, J.F., 2021. Biodiesel and other value-added products from bio-oil obtained from agrifood waste. Processes 9, 797.

Sathya, A.B., Thirunavukkarasu, A., Nithya, R., Nandan, A., Sakthishobana, K., Kola, A. K., Sivashankar, R., Tuan, H.A., Deepanraj, B., 2023. Microalgal biofuel production: Potential challenges and prospective research. Fuel 332, 126199. https://doi.org/10.1016/j.fuel.2022.126199.

Shahi, T., Beheshti, B., Zenouzi, A., Almasi, M., 2020. Bio-oil production from residual biomass of microalgae after lipid extraction: The case of Dunaliella Sp. Biocatal. Agric. Biotechnol. 23, 101494 https://doi.org/10.1016/j.bcab.2020.101494.

Sharma, N., Jaiswal, K.K., Kumar, V., Vlaskin, M.S., Nanda, M., Rautela, I., Tomar, M.S., Ahmad, W., 2021. Effect of catalyst and temperature on the quality and productivity of HTL bio-oil from microalgae: A review. Renew. Energy 174, 810–822. https://doi.org/10.1016/j.renene.2021.04.147.

Shen, Z., Ma, T., Fei, L., Li, A., Liu, J., Xu, Z., Hu, X., Sun, Y., 2021. MgAl-LDH/LDO-catalyzed hydrothermal deoxygenation of microalgae for low-oxygen biofuel production. ACS ES&T Eng. 1, 989–999. https://doi.org/10.1021/acsestengg.1c00024.

Shirazi, Y., Viamajala, S., Varanasi, S., 2020. In situ and ex situ catalytic pyrolysis of microalgae and integration with pyrolytic fractionation. Front. Chem. 8, 1–12. https://doi.org/10.3389/fchem.2020.00786.

Siddiki, S.Y.A., Mofijur, M., Kumar, P.S., Ahmed, S.F., Inayat, A., Kusumo, F., Badruddin, I.A., Khan, T.M.Y., Nghiem, L.D., Ong, H.C., Mahlia, T.M.I., 2022. Microalgae biomass as a sustainable source for biofuel, biochemical and biobased value-added products: An integrated biorefinery concept. Fuel 307, 121782. https://doi.org/10.1016/J.FUEL.2021.121782.

Sotoudehniakarani, F., Alayat, A., McDonald, A.G., 2019. Characterization and comparison of pyrolysis products from fast pyrolysis of commercial Chlorella vulgaris and cultivated microalgae. J. Anal. Appl. Pyrolysis 139, 258–273. https://doi.org/10.1016/j.jaap.2019.02.014.

Söyler, N., Goldfarb, J.L., Ceylan, S., Saçan, M.T., 2017. Renewable fuels from pyrolysis of Dunaliella tertiolecta: An alternative approach to biochemical conversions of microalgae. Energy 120, 907–914. https://doi.org/10.1016/j.energy.2016.11.146.

Su, G., Ong, H.C., Cheah, M.Y., Chen, W.-H., Lam, S.S., Huang, Y., 2022a. Microwave-assisted pyrolysis technology for bioenergy recovery: Mechanism, performance, and prospect. Fuel 326, 124983. https://doi.org/10.1016/j.fuel.2022.124983.

Su, G., Ong, H.C., Gan, Y.Y., Chen, W.-H., Chong, C.T., Ok, Y.S., 2022b. Co-pyrolysis of microalgae and other biomass wastes for the production of high-quality bio-oil: Progress and prospective. Bioresour. Technol. 344, 126096 https://doi.org/10.1016/j.biortech.2021.126096.

Sun, J., Norouzi, O., Mašek, O., 2022. A state-of-the-art review on algae pyrolysis for bioenergy and biochar production. Bioresour. Technol. 346, 126258 https://doi.org/10.1016/j.biortech.2021.126258.

Tang, Z., Chen, W., Chen, Y., Yang, H., Chen, H., 2019. Co-pyrolysis of microalgae and plastic: Characteristics and interaction effects. Bioresour. Technol. 274, 145–152. https://doi.org/10.1016/j.biortech.2018.11.083.

Tang, Z., Chen, W., Chen, Y., Hu, J., Yang, H., Chen, H., 2021. Preparation of low-nitrogen and high-quality bio-oil from microalgae catalytic pyrolysis with zeolites and activated carbon. J. Anal. Appl. Pyrolysis 159, 105182. https://doi.org/10.1016/j.jaap.2021.105182.

Tang, F., Yu, Z., Li, Y., Chen, L., Ma, X., 2020. Catalytic co-pyrolysis behaviors, product characteristics and kinetics of rural solid waste and chlorella vulgaris. Bioresour. Technol. 299, 122636 https://doi.org/10.1016/j.biortech.2019.122636.

Thanigaivel, S., Vickram, S., Dey, N., Gulothungan, G., Subbaiya, R., Govarthanan, M., Karmegam, N., Kim, W., 2022. The urge of algal biomass-based fuels for environmental sustainability against a steady tide of biofuel conflict analysis: Is third-generation algal biorefinery a boon? Fuel 317, 123494. https://doi.org/10.1016/j.fuel.2022.123494.

Toor, S.S., Reddy, H., Deng, S., Hoffmann, J., Spangsmark, D., Madsen, L.B., Holm-Nielsen, J.B., Rosendahl, L.A., 2013. Hydrothermal liquefaction of Spirulina and Nannochloropsis salina under subcritical and supercritical water conditions. Bioresour. Technol. 131, 413–419. https://doi.org/10.1016/j.biortech.2012.12.144.

Tsubaki, S., Oono, K., Onda, A., Kadono, T., Adachi, M., Mitani, T., 2019. Microwave-assisted solubilization of microalgae in high-temperature ethylene glycol. Biomass Bioenergy 130, 105360. https://doi.org/10.1016/j.biombioe.2019.105360.

Varsha, S.S.V., Vuppaladadiyam, A.K., Shehzad, F., Ghaedi, H., Murugavelh, S., Dong, W., Antunes, E., 2021. Co-pyrolysis of microalgae and municipal solid waste: A thermogravimetric study to discern synergy during co-pyrolysis process. J. Energy Inst. 94, 29–38. https://doi.org/10.1016/j.joei.2020.10.010.

Vuppaladadiyam, A.K., Antunes, E., Sanchez, P.B., Duan, H., Zhao, M., 2021. Influence of microalgae on synergism during co-pyrolysis with organic waste biomass: A thermogravimetric and kinetic analysis. Renew. Energy 167, 42–55. https://doi.org/10.1016/j.renene.2020.11.039.

Wang, Y., Akbarzadeh, A., Chong, L., Du, J., Tahir, N., Awasthi, M.K., 2022. Catalytic pyrolysis of lignocellulosic biomass for bio-oil production: A review. Chemosphere 134181.

Wang, K., Brown, R.C., Homsy, S., Martinez, L., Sidhu, S.S., 2013. Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production. Bioresour. Technol. 127, 494–499. https://doi.org/10.1016/j.biortech.2012.08.016.

Wang, X., Sheng, L., Yang, X., 2017. Pyrolysis characteristics and pathways of protein, lipid and carbohydrate isolated from microalgae Nannochloropsis sp. Bioresour. Technol. 229, 119–125. https://doi.org/10.1016/j.biortech.2017.01.018.

Wang, S., Yerkebulan, M., Abomohra, A.-E.-F., El-Khodary, S., Wang, Q., 2019. Microalgae harvest influences the energy recovery: A case study on chemical flocculation of Scenedesmus obliquus for biodiesel and crude bio-oil production. Bioresour. Technol. 286, 121371 https://doi.org/10.1016/j.biortech.2019.121371.

Wang, X., Zhao, B., Yang, X., 2016. Co-pyrolysis of microalgae and sewage sludge: Biocrude assessment and char yield prediction. Energy Convers. Manag. 117, 326–334. https://doi.org/10.1016/j.enconman.2016.03.013.

Wang, S., Zhao, S., Uzoejinwa, B.B., Zheng, A., Wang, Q., Huang, J., Abomohra, A.E.F., 2020. A state-of-the-art review on dual purpose seaweeds utilization for wastewater treatment and crude bio-oil production. Energy Convers. Manag. 222, 113253 https://doi.org/10.1016/j.enconman.2020.113253.

Wei, D., Chen, C., Huang, X., Zhao, J., Fan, D., Zeng, T., Bi, Y., 2023. Products and pathway analysis of rice straw and chlorella vulgaris by microwave-assisted co-pyrolysis. J. Energy Inst. 101182. https://doi.org/10.1016/j.joei.2023.101182.

Wu, H., Wang, L., Ji, G., Lei, H., Qu, H., Chen, J., Wang, F., Liu, J., 2020. Renewable production of nitrogen-containing compounds and hydrocarbons from catalytic microwave-assisted pyrolysis of chlorella over metal-doped HZSM-5 catalysts. J. Anal. Appl. Pyrolysis 151, 104902. https://doi.org/10.1016/j.jaap.2020.104902.

Xiong, Z., Fang, Z., Jiang, L., Han, H., He, L., Xu, K., Xu, J., Su, S., Hu, S., Wang, Y., 2022. Comparative study of catalytic and non-catalytic steam reforming of bio-oil: Importance of pyrolysis temperature and its parent biomass particle size during bio-oil production process. Fuel 314, 122746.

Xu, S., Hu, Y., Wang, S., He, Z., Qian, L., Feng, Y., Sun, C., Liu, X., Wang, Q., Hui, C., Payne, E.K., 2019. Investigation on the co-pyrolysis mechanism of seaweed and rice husk with multi-method comprehensive study. Renew. Energy 132, 266–277. https://doi.org/10.1016/j.renene.2018.08.002.

Xu, K., Li, J., Zeng, K., Zhong, D., Peng, J., Qiu, Y., Flamant, G., Yang, H., Chen, H., 2023. The characteristics and evolution of nitrogen in bio-oil from microalgae pyrolysis in molten salt. Fuel 331, 125903. https://doi.org/10.1016/j.fuel.2022.125903.

Yang, C., Li, R., Zhang, B., Qiu, Q., Wang, B., Yang, H., Ding, Y., Wang, C., 2019. Pyrolysis of microalgae: A critical review. Fuel Process. Technol. 186, 53–72.

Yuan, C., Jiang, D., Wang, S., Barati, B., Gong, X., Cao, B., Zhang, R., Zhang, C., Odey, E. A., 2020. Study on catalytic pyrolysis mechanism of seaweed polysaccharide monomer. Combust. Flame 218, 1–11. https://doi.org/10.1016/j.combustflame.2020.04.022.

Yuan, T., Tahmasebi, A., Yu, J., 2015. Comparative study on pyrolysis of lignocellulosic and algal biomass using a thermogravimetric and a fixed-bed reactor. Bioresour. Technol. 175, 333–341. https://doi.org/10.1016/j.biortech.2014.10.108.

Zainan, N.H., Srivatsa, S.C., Li, F., Bhattacharya, S., 2018. Quality of bio-oil from catalytic pyrolysis of microalgae Chlorella vulgaris. Fuel 223, 12–19. https://doi.org/10.1016/j.fuel.2018.02.166.

Zhang, B., Feng, H., He, Z., Wang, S., Chen, H., 2018. Bio-oil production from hydrothermal liquefaction of ultrasonic pre-treated Spirulina platensis. Energy Convers. Manag. 159, 204–212. https://doi.org/10.1016/j.enconman.2017.12.100.

Zhang, C., Wang, C., Cao, G., Chen, W.-H., Ho, S.-H., 2019. Comparison and characterization of property variation of microalgal biomass with non-oxidative and oxidative torrefaction. Fuel 246, 375–385. https://doi.org/10.1016/j.fuel.2019.02.139.

Zhang, C., Gong, X., Peng, Y., Feng, T., Li, X., 2022. Transformation of nitrogen during microalgae model compounds liquefaction in sub-/supercritical ethanol. Fuel 311, 122616. https://doi.org/10.1016/j.fuel.2021.122616.

Zhang, W., Li, J., Liu, T., Leng, S., Yang, L., Peng, H., Jiang, S., Zhou, W., Leng, L., Li, H., 2021. Machine learning prediction and optimization of bio-oil production from hydrothermal liquefaction of algae. Bioresour. Technol. 342, 126011 https://doi.org/10.1016/j.biortech.2021.126011.

Zhang, X., Zhan, L., Lin, M., Zeng, Y., Li, R., Wu, Y., 2022. Production of acid-free bio-oil through improved co-HTL of sludge and microalgae: Experiment and life cycle assessment. J. Clean. Prod. 379, 134668 https://doi.org/10.1016/j.jclepro.2022.134668.

Zhong, D., Zeng, K., Li, J., Qiu, Y., Flamant, G., Nzihou, A., Vladimirovich, V.S., Yang, H., Chen, H., 2022. Characteristics and evolution of heavy components in bio-oil from the pyrolysis of cellulose, hemicellulose and lignin. Renew. Sustain. Energy Rev. 157, 111989.