

State of art review on conventional and advanced pyrolysis of macroalgae and microalgae for biochar, bio-oil and bio-syngas production

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ABSTRACT

Algal biomass including macroalgae and microalgae show great potential as pyrolysis feedstock in generating energy-dense and valuable pyrolytic products such as bio-oil, biochar and bio-syngas. The chemical constituents of macroalgae and microalgae show great variations, especially their lipid, carbohydrate and protein contents, which could affect the qualities of the pyrolytic products. From the established conventional pyrolysis, the products produced from both macroalgae and microalgae show moderate energy contents (< 34 MJ/kg). The review identifies the issues associated with development of conventional pyrolysis such as flash and intermediate pyrolysis. To enhance the production of biofuels from algal biomass, advanced or non-conventional pyrolysis techniques have been employed. Catalytic pyrolysis on algal biomass could reduce the nitrogenates and oxygenates in the biofuels. On top of that, co-pyrolysis with suitable feedstock shows great enhancement on the bio-oil yield. As for hydrolypyrolysis of algal biomass, their generated biofuels can produce up to 48 MJ/kg with high yield of bio-oil up to 50 wt%, comparable to conventional fuels. Microwave-assisted pyrolysis of algal biomass greatly shortens the processing time through advanced heating; however, favours the formation of bio-syngas by improving the yield up to 84 wt% depending on the feedstock used. Therefore, formation of biofuel fraction suitable for energy generation highly depends on the selected pyrolysis technologies.

1. Introduction

Global energy consumption has increased considerably mainly because of the increase in world population as well as the rapid industrialisation over the years. To accommodate such development, generation of energy from conventional fuel combustion has created high level of greenhouse gases (GHG) emissions such as methane (CH₄), carbon dioxide (CO₂), carbon monoxide (CO), nitrogen oxide (NO_x), sulphur oxide (SO_x) and other hydrocarbons [1,2]. Especially the emission of CO₂, about 18.6% of the CO₂ (approx. 2 billion tons of CO₂) generated from the power generation sector contributed greatly to the global warming issue [3,4]. Furthermore, fossil fuels are finite resources which might be depleted in the near future with the current application and usage. Greener fuel type with low carbon emission is desirable, such as biofuels due to their renewable, biodegradable, and low GHG

emission natures as well as comparable energy content with conventional fuels [5]. The derivation of biofuel from biomass is especially attractive because biomass are low-cost, abundant and can be replenished by themselves over time.

Biomass can be produced from both living and dead organisms as well as non-living materials which are mostly non-fossil in nature and can be in liquid, solid or semi-solid forms [6]. Structurally, biomass is a complex and heterogeneous biopolymer, which may consist of carbohydrates, cellulose, hemicellulose, proteins, lignin, lipids, extractives, water, ash and other trace components [7-9]. Therefore, depending on their chemical constituents, there are two main groups of biomass, namely the non-lignocellulosic and waste biomass, and lignocellulosic biomass, respectively, as summarised in Table 1 [10,11]. Non-lignocellulosic and waste biomass refer to materials mainly comprise of proteins, lipids, polysaccharides or carbohydrates (holocellulose),

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Table 1
Classification of biomass materials and their fuel type [6,10,13–17].

Biomass Group	Diversities and Species	Type of Fuel
<i>Non-Lignocellulosic and Waste Materials</i>		
Algal biomass	<ul style="list-style-type: none"> • Macroalgae (seaweed): Red algae (Rhodophyta), green algae (Chlorophyceae) and brown algae (Phaeophyceae) • Microalgae (microphyte): Green algae (Chlorophyceae), blue-green algae (Cyanobacteria/ Cyanophyceae), Yellow-green algae (Xanthophyceae), golden algae (Chrysophyceae) and diatom (Bacillariophyceae) 	3rd Generation
Human and animal waste	<ul style="list-style-type: none"> • Human wastes: Faeces/ manures and hair • Animal wastes: Faeces/ manures, bone, poultry wastes, feather and meat 	2rd Generation
Industrial and municipal waste	<ul style="list-style-type: none"> • Sludge wastes, municipal solid wastes, refused fuel, hospital waste, tyre wastes and tannery wastes 	2rd Generation
Contaminated biomass and semi-biomass waste	<ul style="list-style-type: none"> • Demolition wood, paper industry wastes, paperboard wastes, chipboard residue, fibreboard residue and plywood residue. 	2rd Generation
<i>Lignocellulosic Materials</i>		
Aquatic biomass	<ul style="list-style-type: none"> • Water fern (Azolla) 	3rd Generation
Wood and plant residue	<ul style="list-style-type: none"> • Wood/plant species: Soft and hard wood species, coniferous and deciduous plants, angiosperms and gymnosperms • Plant residue: foliage/ leaf, chips, stems, bark, branches, lumps, sawdust and sawmill 	2rd Generation
Herbaceous biomass (grasses and flowers)	<ul style="list-style-type: none"> • Lemongrass, alfalfa, switchgrass, bamboo, brassica, miscanthus, reed canary grass, Eastern gamagrass and others. 	2rd Generation
Non-food agricultural biomass and residue	<ul style="list-style-type: none"> • Castor, jatropha, polanga and karanj • Coconut wastes, oil palm wastes and agricultural residues such as husks, root, branch, shells, peels and others. 	2rd Generation
Edible agricultural crops and food sources	<ul style="list-style-type: none"> • Edible parts of agricultural crops: Corn, hemp, soybean, rapeseed, sunflower seeds, palm oil, coconut kernel, peanut and canola • Food sources: Fruits, animal fats or intestines 	1st Generation

inorganics, minerals and photosynthetic pigments along with a minor fraction of lignocellulosic contents [11,12]. Due to the broad definition of non-lignocellulosic and waste biomass, most of the materials not categorised under lignocellulosic materials can be classified under this group which includes aquatic biomass, human and animal waste, industrial and municipal waste and contaminated biomass and semi-biomass waste. While, lignocellulosic biomass materials primarily consists of lignin, hemicellulose, cellulose, extractives and ash [11]. Emerging aquatic biomass such as azolla, wood, plant, herbaceous materials, agricultural crops, oils and residues are mostly considered to be lignocellulosic biomass based on their chemical constituents such as the presence of holocellulose and lignin (Table 1).

Among those biomass feedstock, algae as relatively new form of energy plant or crop, have shown great potential as thermochemical feedstock because algae grow faster and mature with abundant mass generation in matter of days when compared to terrestrial crops and plants which may take months to years [18–20]. By converting algal biomass into biofuel forms, these are regarded as 3rd generation biofuels. The main advantages of 3rd generation biofuels are non-potable water requirement, non-arable land cultivation, simple nutrient requirement such as CO₂ and sunlight, non-herbicide/pesticide cultivation, carbon-neutral feedstock usage and high quality production of pyrolytic materials [16,18,21–23]. Furthermore, the high photosynthetic efficiency of algae (6–8%) compared to terrestrial biomass (1.8–2.2%), as well as high CO₂ fixation by algae, make them excellent thermochemical feedstocks and natural environment remediators [4,19,24,25]. In the long term, the generation of viable feedstock and reduction of GHG (e.g. CO₂) can be achieved through algae cultivation.

The emerging thermochemical conversion techniques have generated great attention and interest from the science and research communities in recent years due to the technological advances and economical approaches [26,27]. Thermochemical conversion techniques produce higher yield of energy products compared to biochemical technologies (fermentation, anaerobic digestion and others) [28,29]. The establishment of these technologies such as combustion and co-firing, gasification, torrefaction and liquefaction has been well-reviewed on algal biomass as feedstock [10,13,19,24,30–34]. The main advantages of thermochemical conversion techniques are versatile with wet or dry biomass (moisture content > 50%), fast processing time (from second to minute) and generation of different products (liquid, solid and gas phase products) [13,30].

Algal biomass including macroalgae and microalgae are emerging as

one of the most studied and most potential biomass to date as the 3rd generation biofuel feedstock. This work investigates the chemical constituents including moisture, volatile matter, carbon content, ash content lipid, protein and carbohydrate of both microalgae and macroalgae as pyrolysis feedstock, which is lacking in the current literature. Numerous reviews are available and focus on mainly microalgae as the pyrolysis feedstock [10,31]. However, as part of algal family, macroalgae or seaweed as pyrolysis feedstock have been neglected over the years. Thus, a critical review which assesses and compares both macroalgae and microalgae as pyrolysis feedstock is important to identify the research gap in the current community. This is especially important because despite being in the algae family, the pyrolysis on both macroalgae and microalgae generates very different pyrolytic products distribution in term of yields, and product characteristics in term of physicochemical properties, as highlighted in this review.

1.1. Thermochemical conversion techniques

In thermochemical conversion, algal biomass is subjected to decomposition via thermal treatments to produce different energy products such as heat, steam, syngas, bio-liquid and biochar products, as shown in Fig. 1. Combustion technology is an established technique which can be applied directly on algal biomass under high temperature (800–1000 °C) with the presence of excessive air [35,36]. However, direct combustion of algal biomass for energy generation might not be applicable to all algal species even though this practice can reduce CO₂ emission as feedstock with high moisture content (> 50%) would create fumes of white smoke [37]. Nonetheless, to date, microalgae such as *Enteromorpha* and *Chlorella* [36] and macroalgae such as *Ulva lactuca* [38] both show great energy content; however, their high ash, alkaline salts and moisture content affect their direct usage. Thus, usually, they can be used as co-feedstock in combustion (co-firing) without any modification due to their compatibility with the existing conventional coal boiler [31,39].

Gasification is a well-known thermochemical technique which applies O₂, CO₂, steam or supercritical water treatments on algal biomass at an elevated temperature between 800 and 1000 °C [40,41]. When the algal biomass reacts with the O₂/CO₂/steam system/supercritical water, the generation of syngas occurs and its composition mainly consists of H₂, CO, CO₂, N₂, water vapour, CH₄ and tar by-products [40,42,43]. The main issue with gasification is the formation of tar or hydrocarbon condensate affecting the syngas combustion quality but

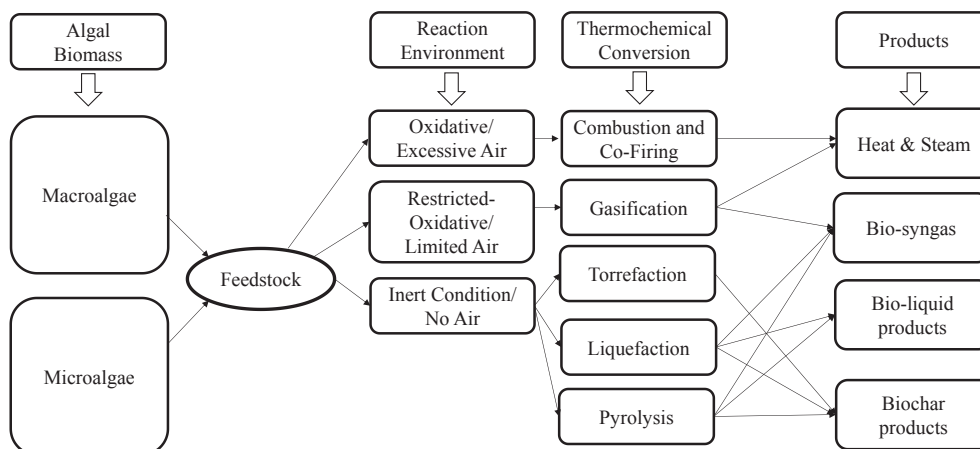


Fig. 1. Thermochemical conversion techniques using algal biomass as feedstock [32,34,35,50,54].

these issues can now be overcome by the use of Fe-based catalysts [42]. Dry and wet torrefaction, as emerging techniques, exert mild thermal treatment (160 – 300 °C) on algal biomass under the inert condition to produce energy dense solid fuels [21,44]. While dry torrefaction resembles pyrolysis technology, wet torrefaction shares similar experimental settings as hydrothermal carbonisation [11,45]. The resulted product known as torrefied biomass overcomes the disadvantages of direct usage of biomass as energy solid fuels such as high heterogeneity, short storage life and relatively higher moisture content [46,47]. Sub-critical water liquefaction can handle high moisture or wet biomass without energy-intensive pre-treatment such as drying, into liquid fuel (bio-crude) at moderate temperature (280 – 370 °C) and at applied pressure between 10 and 25 MPa [48,49]. In addition to pure water solvolysis, different solvents such as tetralin, toluene, acetone and alcohols (ethanol, methanol, propanol, butanol and pentanol) can be used as solvolysis media [49]. Besides bio-oil, biochar produced from the liquefaction can be used as soil conditioner [50], electrodes for supercapacitor [51] and lithium batteries [52], while the gaseous phase may be used as syngas fuel directly [50]. Generally, the yield of bio-oil generated from seaweed macroalgae is lower compared with microalgae feedstock as their high AC and carbohydrate contents do not favour the formation of bio-oil [53].

Among those thermochemical conversion techniques, pyrolysis has been regarded as one of the most developed and robust methods in transforming biomass into energy products. Pyrolysis is a form of thermolysis or carbonisation that uses intense heat under low or absence of oxygen (O_2) environment to thermally decompose a variety of biomass to different pyrolytic products such as solid products (biochar), liquid products (bio-oil) and gas products (bio-syngas) suitable for applications such as energy generation and environmental remediation [28,35]. As shown in Fig. 2, conventional pyrolysis techniques such as slow, intermediate, fast and flash pyrolysis are regarded as feasible and effective synthesis routes which can be applied impartially on different

biomass materials [28]. For instance, non-lignocellulosic and waste materials [14,55–58] and lignocellulosic biomass [59–61] have since been utilised and studied as pyrolysis feedstock in great details. To enhance the pyrolysis process, advanced modification can be performed on conventional pyrolysis, resulting in progressive techniques such as catalytic pyrolysis, co-pyrolysis, hydro-pyrolysis and microwave-assisted pyrolysis [10,30]. Pyrolysis technologies are therefore considered to be highly flexible and not limited to certain types of biomass, as long as the pyrolysis feedstock fits the criteria such as renewable, sustainable and abundant in supply sufficiently to support the continuous synthesis of pyrolytic products [55].

2. Overview of algal biomass characteristics

Algae are common aquatic organisms which can be found in marine area (coastal, shallow sea and deep sea), freshwater (lake, river), brackish water (estuaries, lagoon) and minority in sediments and soils. The categorisation of algae species has been diverse in accordance with pigment colours, membrane structures and others, without a uniform taxonomical classification [23]. Currently, the main types of algae can be commonly grouped as macroalgae (seaweed) and microalgae based on their biological structures as well as their differences in chemical constituents [10,19]. Thus, their inherent properties may influence their desirability and suitability as pyrolysis feedstock.

2.1. Algal biomass natural growth and artificial cultivation

Algae can grow naturally in different aquatic environments and can be found in different climatic regions such as Asia, New Zealand, Australia, Central and South America and Africa. The rapid growth rate of algae along with their high adaptability to extreme conditions have caused the occurrence of algal bloom to the water environment in lakes, estuaries and coastal water, resulting in eutrophication which

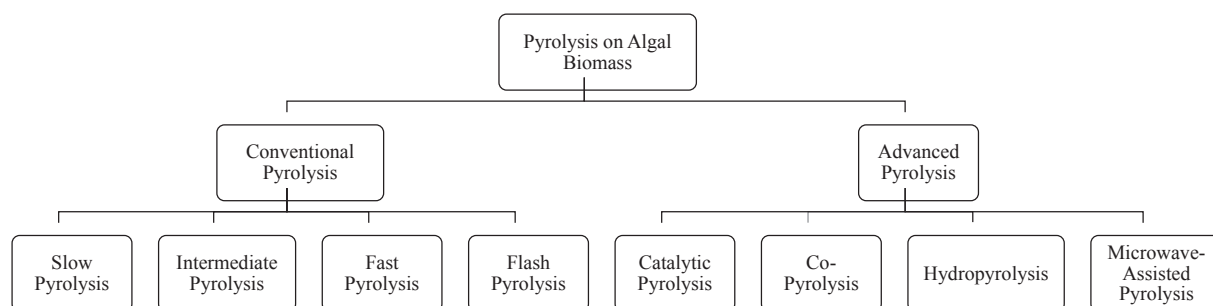


Fig. 2. Pyrolysis techniques grouped under conventional and advanced pyrolysis.

contributes to the deterioration of water qualities and the demise of biodiversity [20,62,63]. Algal colonisation usually consists of microalgae such as cyanobacteria, chlorophytes, diatoms and macroalgae such as green tide algae which can grow rapidly in almost any salinity and nutrient contents [62,64]. The presence of cyanobacteria can be toxic to the aquatic organisms and human health as they excrete cyanotoxins or algal toxins [65]. In China, the growth of blooming algae can reach uncontrollable states. For examples, about 13,600 and 26,000 tons per year of algae are generated in Dianchi Lake and Taihu Lake, respectively [65,66]. Such aquatic pollution can be contributed by discharges from both anthropogenic and industrial activities as well as natural decomposition of living organisms in the water environment. The accumulation of phosphorus (P) and nitrogen (N) in those water media creates unintended nutrients for algae blooming [67]. To counter the algal bloom issue, algicidal remediation can be applied by growing seaweed at the affected area to create nutrient competition against the unwanted algae [20]. By harvesting grown seaweed and extracting nuisance-causing algae from water media, they can be re-used and post-processed as a valuable feedstock for pyrolysis, thereby curbing the eutrophication process [63,67–69].

In artificial cultivation, algae can be farmed through three types of system *viz* open cultivation system, closed cultivation system and their hybrids under sufficient nutrients, CO₂ and sunlight, which are well-reviewed in these reports [13,70–72]. Generally, each system possesses its pros and cons, but all of which do not require an arable area for cultivation offering a great advantage in term of land usage. In open cultivation system, natural or abandoned waters such as lakes, ponds and lagoons can be converted into algae farms with simple setup while raceway ponds, shallow ponds, circular ponds as well as tanks are mainly manmade systems which require construction and commissioning [71]. High rate algae ponds (HRAPs) are technological open cultivation system which can be arranged in three geometries such as circular ponds, sloping ponds and raceway ponds, with mechanical parts for the generation of hydrodynamic conditions [73]. Typically, to ensure sufficient light for algal photosynthesis process, the liquid level of the open cultivation ponds are kept low (15 – 35 cm) in most setups [73,74]. The advantages of open cultivation system are high mass production of algal biomass, low capital cost, ease of maintenance and low energy requirement [13]. However, open cultivation system of algal biomass is associated with issues such as external contamination, high harvesting cost, batch-to-batch variation and weather factors such as limited sunlight due to seasonal change or rainy season [70]. Furthermore, the setting up of open pond system requires greater area-to-volume ratio (relatively 4 – 10 times greater) and is inherently more difficult in parametric controls such as temperature, CO₂ concentration, nutrient delivery and others, when compared to closed cultivation system [71,75]. However, in term of energy consumption, open cultivation system generally utilises less energy (0.12 – 1 W/m³), whereas close cultivation setup (photobioreactors) can consume about 200 to 1000 W/m³ for the cultivation of algal biomass at the similar productivity rates of 10 – 27 g/m² day [76].

Closed cultivation system normally uses transparent reactors or vessels such as tubular photobioreactor (vertical, horizontal, helical and α -shaped configurations), flat-plate photobioreactor, column photobioreactor and fermenter-type reactors to overcome the shortcomings of open cultivation system [71,74,75]. Owing to their enclosed configurations, these bioreactors can provide more precise parametric control and even cultivate single-species algae at higher production rate with a lower possibility of contamination [13]. Nonetheless, closed cultivation system has its own disadvantages such as expensive setup, higher axillary energy demand, fouling issues, possible photoinhibition, benthic algae growth, built-up of dissolved O₂ and scaling-up difficulties [70,71,74]. The hybrid system thus combines the benefits of open and closed cultivation systems, which consists of two-stage cultivation [70,71]. The first stage of the cultivation involves the usage of photobioreactor to ensure the optimisation of algae mass growth and to limit contamination issue. When the cultivation achieves the desired algal mass production, the second stage of the cultivation system focuses on lipid enhancement through nutrients deprivation such as sodium (N), potassium (P), calcium (Ca) and magnesium (Mg) starvations for algae growth [70,72,77].

2.1.1. Macroalgae characteristics, cultivation and harvesting

Macroalgae are represented by seaweed with different colour varieties or photosynthesis pigments such as red algae (Rhodophyta) with approximately 4000 – 6000 species, green algae (Chlorophyceae) with approximate 700 – 7000 species and brown algae (Phaeophyceae) with approximately 2000 – 5000 species, which mostly found on coastal zones [20,69,78,79]. Macroalgae are multicellular and eukaryotic organisms which can grow in varying sizes from millimetres up to meters, with plant-like structures such as roots, leaves, branches as well as flagellums [10,18]. Due to its rapid growth rate, macroalgae can be cultivated with the rate of about 2 – 4 m per year depending on species and are capable of growing up to 60 m [80,81]. Despite being utilised mainly in food products, macroalgae are excellent ingredients containing vital vitamins, minerals and bioactive compounds such as laminarin, algalic acid, phycocolloids (algal colloids such as alginate and agar), fucoidan, mannitol and fucoxanthin suitable for additives, pharmaceutical and biomedical applications [64,78,82]. Macroalgae are although produced globally but their commodities are mainly marketed in Asian countries. To date, China and Indonesia, as the main producers, cultivated a combined seaweed yield of over 21 – 23 million tonnes [79,82]. The Philippines and Korean Republic produced over 1.0 million tonne per year of seaweed, respectively while Japan, Malaysia, Zanzibar and Chile generated over 0.1 million tonne per year of seaweed, respectively [79,82]. Majority of the macroalgae (94%) are cultivated via aquaculture while the remaining (6%) are harvested from nature [79]. Therefore, in term of unit price, macroalgae vary between US\$ 10 – 50 per tonne [80].

As shown in Table 2, aside from natural growth in rivers and sea, macroalgae can be cultivated through open systems for mass production at offshore or near shore areas. There are currently four

Table 2
Macroalgae and microalgae cultivation and harvesting techniques.

Algal Group	Macroalgae	Microalgae
Cultivation technique/ mechanism	<ul style="list-style-type: none"> ● Floating raft ● Tension-leg platform farming ● Fixed off-bottom long line ● Rock-based farming 	<ul style="list-style-type: none"> ● Phototrophic cultivation ● Heterotrophic cultivation ● Mixotrophic cultivation ● Photoheterotrophic cultivation
Harvesting/ collection technique	<ul style="list-style-type: none"> ● Manual harvest ● Mechanical (moving boat, mesh conveyor and dredge) ● Formaldehyde preservation ● Natural drying 	<ul style="list-style-type: none"> ● Physical treatment: Centrifugation, flotation (dissolved and dispersed method), gravitational sedimentation, filtration and screening ● Chemical treatment: flocculation (autoflocculation, bio-flocculation, chemical coagulation, inorganic coagulation) ● Electrical-assisted treatment: Electrophoresis, electro-flocculation and electro-flotation.
Reference	[69,79,82,83]	[71,72,77,84]

noteworthy techniques applied in the farming of macroalgae, which include floating raft, tension-leg platform farming, fixed off-bottom long line and rock-based farming [69,79,82,83]. As macroalgae require non-arable land cultivation, floating raft farming uses floats/ wooden boats to suspend the seaweed seedling on the sea surface. This cultivation of seaweed can be performed at deeper water area. Tension-leg platform farming can be quite costly because the vertically-moored floating structure is specifically designed for the cultivation of seaweeds. So far, this technique has successfully cultivated macroalgae such as *Myagropsis myagroides*, *Ecklonia cava*, *Saccharina japonica*, *E. stolonifera* and *Sargassum horneri*. Similar to floating raft farming but instead of floats/boats, macroalgae can be grown using a rope entity with the length of 10 – 20 m. They are firstly embedded on the rope which acts as support before being submersed into the offshore shallow waters. Rock-based farming involves the attachment of the seaweeds to rock media with the assistance of support band until their full growth.

After the full growth of macroalgae, they are harvested manually or with mechanical supports such as boats or dredgers [69,79]. Comparatively, harvesting of macroalgae is more direct and simpler due to their overall larger structure. Usually, the harvesting and post-processing of macroalgae involve either formaldehyde preservation for large quantities or natural drying for small processing mass [69]. Natural drying process performed under the open sun for less than 24 h can greatly reduce the moisture content of macroalgae from 90 to 10% for storage purposes, which can save significant processing cost compared to technological drying [69].

2.1.2. Microalgae characteristics, cultivation and harvesting

Microalgae, on the other hand, are unicellular microorganisms (1 – 400 μm) with about 20,000 species available in the world, which include notable species such as green algae (Chlorophyceae), blue-green algae (Cyanobacteria/ Cyanophyceae), yellow-green algae (Xanthophyceae), golden algae (Chrysophyceae), diatom (Bacillariophyceae) and others [12,19]. So far, microalgae show great utilisation in product development such as pharmaceutical medicine, food ingredients, fertilizers, chemicals and biofuels due to their antimicrobial, anti-inflammatory, anti-cancer and biochemical properties [29]. From 1984 to 2016, the annual production of microalgae has increased steadily from 500 tonnes to 20,000 tonnes per annum, suggesting that microalgae as raw materials, products or feedstock increases consistently [85,86]. Despite their broad applications, the commercialisation of microalgae products remains to be challenging due to the expensive cultivation setup and harvesting process [87,88]. For the unit price of microalgae, they can easily reach up to US\$ 185 per tonne which are relatively more expensive compared to macroalgae [80].

As listed in Table 2, phototrophic, heterotrophic, mixotrophic and photoheterotrophic cultivations are regarded as the main mechanisms for microalgae cultivation, which have been well-discussed in these work [67,71]. These mechanisms differ in term of energy source (photo-based, organic-based or both), carbon supply (organic-based, inorganic-based or both), and reactor system (open pond system, photobioreactor or conventional fermenter) [19,72,89]. Currently, phototrophic cultivation, one of the most common used methods for microalgae growth, requires sources of radiation from sunlight or artificial light to affix CO_2 or soluble carbonates (inorganic carbon source) either in open (open pond) or closed (photobioreactor) systems [13]. Relatively, this method faces less contamination issue, low at cost with good lipid production. This is not the case for heterotrophic cultivation (conventional fermenter) whereby both energy and carbon sources are originated from organic carbon [19]. Usually, the cultivation can be performed in the fermenter with very limited light and generates very high lipid content of microalgae by assimilating different organic carbon sources such as glucose, glycerol, galactose and others. However, this form of cultivation is prone to contamination and also associated with high substrate cost. Mixotrophic cultivation is the combined

technique of phototrophic and heterotrophic cultivations under a closed photobioreactor system [71]. So far, this technique is rarely used due to its expensive equipment cost and high contamination risk. On the contrary to other mechanisms, photoheterotrophic cultivation refers to cultivation with light as energy supply while its carbon sources are mainly organic components, usually conducted in a closed photobioreactor. Generally, scaling-up of this method is not favourable due to the high equipment cost, expensive substrate and issues with contamination.

Differing from macroalgae, the resulted microalgal feedstock is usually dispersed in suspension, which requires harvesting and surface dewatering based on their density, size, desired yield and cell charge [77]. This presents certain challenges in harvesting and accounts high energy consumption for such a procedure to be performed. Several harvesting techniques have been detailed on microalgal biomass collection, which can be grouped in three main categories such as physical treatment, chemical treatment and electrical-assisted treatment [72,77,84]. Physical treatment dewater the microalgae by using centrifugation, flotation, gravitational sedimentation, filtration and screening. Centrifugation is a relatively simple method used to extract the microalgae, but generally, this process cannot handle mass amount of feedstock, is expensive, time-consuming and may cause damages to the microalgal cells [77]. Flotation in form of dissolved and dispersed methods have no problem in handling large amount of microalgae by applying air bubbles to create uplift force for particle separation. The extraction of microalgae can be enhanced with the usage of surfactant but comes with the price of higher processing cost. Another physical treatment involves the usage of gravitational force for sedimentation of microalgae may be low at cost with low energy consumption [77]. The use of a simple equipment with large processing volume is required to facilitate the process. However, due to the nature of the method, it is often time consuming for the completion of separation. Filtration and screening retain the microalgae by passing through the unwanted water, but over time, the system requires frequent maintenance due to saturation of modules. Therefore, mass extraction using filtration and screening system might not be feasible. Chemical-based dewatering can be performed through flocculation which may include autoflocculation, bio-flocculation, chemical coagulation and inorganic coagulation. This technique has been well-established in wastewater treatment, and can be used for large-scale extraction process of microalgae despite higher cost compared to other methods [72]. Other emerging techniques such as electrophoresis, electro-flocculation and electro-flotation are power-based technologies. These methods explore the negatively-charge microalgae by separating them based on the charge difference. Despite they are non-chemical process, the requirement of electricity will increase the cost of separation [77].

2.2. Other cultivation strategies

Currently, the idea of both macroalgae and microalgae cultivation in wastewater such as agricultural wastewater, municipal sewage wastewater, industrial wastewater and artificial wastewater has been found to be promising for mass production [19,64,67,69]. Such practice aims to reduce the pollutants contents of N and P in different wastewaters and to generate algal biomass for various applications. Microalgae such as *Botryococcus braunii*, *Microspora willeana*, *Ulothrix* sp., *Mucidosphaerium pulchellum*, *Chlorella vulgaris*, *Rhizoclonium hierglypticum* and microalgal consortia are some of the species which show consistency in nutrients removal from different wastewaters like slaughterhouse wastewater, dairy wastewater and fish farming wastewater [67,90,91]. In pilot-scale pond system, the removal of pollutants can reach between 65.1 and 97.5% for N and between 51.7 and 94.0% for P; whereas, photobioreactor is capable to removing about 29 – 83% of N and 59 – 89% of P, respectively [90]. Macroalgae can sequester metal ions through cellular surface bounding to its surface, followed by transport and storage in intracellular storage vacuoles, and formation of

an inert and non-toxic form of metal-protein compounds [92]. However, even though algae are known for their ability to sequester aquatic pollutants, the toxicity from the heavy metals (nickel (Ni), cadmium (Cd), chromium (Cr) and others) and organic pollutants (surfactants, pesticides and others) present in industrial wastewater may inhibit the growth of certain algae species [64,67]. Therefore, the analysis on wastewater content should be performed to determine their suitability as algae cultivation media before implementation.

The use of algae cultivation to treat the flue gas emission from industrial exhausts can be a feasible setup as algae are well-known for their ability in assimilating or mitigating CO₂. The cultivation of 1.0 tonne of algal biomass uptakes about 1.8 to 2.0 tonnes of CO₂ [3,93,94]. As CO₂ is well-known GHG, this requires an intermediate and effective way to reduce its generation. Typically, from the combustion flue gas, it comprises of SO_x, NO_x, volatile organic compounds (VOCs), CO, CO₂, hydrogen sulphide (H₂S), fine particulates and unburnt residues [94]. About 5 – 15% of the flue gas which is the CO₂ fraction can be channelled to either pond systems or photobioreactors as external sources for algal biomass cultivation. In addition, CO₂ from the atmosphere as well as other carbon sources (carbonates) can be mitigated as well through algae cultivation [95]. Such a strategy helps to curb CO₂ emission, improve algal biomass production, reduce chemical requirement and cost for cultivation purposes [3]. *Chlorella vulgaris*, *Chlorella pyrenoidosa*, *Dunaliella*, *Scenedesmus obliquus*, *Scenedesmus quadricauda* and *Synechococcus* spp. are some of the identified algae species which could perform well in high concentration CO₂ assimilation for cultivating purpose [95–98]. Similarly, macroalgae also have high carbon capture rate of 2 kt per annum for an area of 1 km², whereby its cultivation can produce food products and alleviate significant CO₂ emission [79].

By understanding the requirement of algae cultivation, the cultivation system can be constructed and configured to optimise the biomass production of algae. In the term of environmental perspective, algae biomass cultivation can be used for wastewater treatment and remediation of GHG emission such CO₂ through affixation from industrial exhausts [18,19].

2.3. Chemical constituents of algal biomass

Macroalgae and microalgae are both inherently comprised of carbohydrates, proteins, lipids, unsaturated fatty acids and nucleic acid, which can be potentially synthesised into different high value products [18,99]. However, their compositions can vary according to species, cultivation techniques, season and geography factors [100,101]. For instance, brown seaweeds harvested in the United Kingdom during summer possess higher energy content due to higher carbohydrates such as laminarin and mannitol while the same algal biomass collected during winter show lower energy content due to the presence of protein, ash and alginic acid [100]. The evaluation of chemical constituents such as lipid, carbohydrate and protein through chemical testing [102–104] as well as moisture content, volatile matter (VM), fixed carbon (FC) and ash content (AC) through proximate analysis via thermogravimetric analysis (TGA) [23,30,33] can provide insights of algal biomass as pyrolysis feedstock. Table 3 summarises some of the chemical constituents of macroalgae and microalgae, respectively. The following section correlates the chemical properties of algae biomass to their applications as raw material and feedstock for thermochemical processes.

2.3.1. Lipid

The molecular structure of lipid can be described as a long hydrocarbon chain attached with carboxyl functional group [23]. Typically, the types of lipid found in algal biomass differ from lignocellulosic biomass which are mostly triglycerides in nature [23]. Lipid contents in algal biomass can be diversifying in the forms of neutral lipids, phospholipids, sphingolipids, glycolipids, peptidolipids, peptidoglycolipids

and triglycerides [115]. Some of these lipids can be converted and formed into oil-based products which have higher fatty acid contents such as γ -linolenic, arachidonic, eicosapentaenoic, docosahexaenoic acids and others [31,93]. Based on Table 3, high oil or lipid contents (up to 51%) are detected in some microalgae (*Nannochloropsis* sp and *Schizochytrium limacinum*) whereby such chemical constituent is desirable for oil product synthesis through processes such as lipid extraction and transesterification [18,30,63]. The range of lipid content for microalgae however varies considerably from 1.10 to 51.00%, depending on the microalgal species and also relying heavily on the growth condition when more N₂ resources are exhausted, more lipids which can be accumulated up to 90% [29,89]. After oil extraction, these residue algal biomass can be used for pyrolysis feedstock instead of disposing of as waste materials [114,116]. For macroalgae, as observed, their lipid contents are mostly less than 5% (0.2 – 3.91%) which indicate that they are less suitable for direct oil extraction. However, the low lipid content of macroalgae will not hinder their direct application as pyrolysis feedstock [63].

2.3.2. Carbohydrate

Macroalgal and microalgal carbohydrate are usually made up of sugar monomers or polysaccharides such as glucose, cellulose and starch produced from their photosynthesis process. Generally, macroalgae possess higher carbohydrate contents ranging from 24.55 to 51.4% as compared to microalgae (3.28 – 30.21%) which are for extracellular protection and cell adhesion [23]. More specifically, different algal species contain a wide range of carbohydrate structures; for instance, laminarin, mannitol, fucans/fucoidan and alginic acid are found in brown algae; carrageenan, agar and cellulose are found in red algae; peptidoglycan and lipopolysaccharides are primarily sugars structures for blue algae [23,117]. Nonetheless, mannitol can be regarded as the main photosynthetic products found in algal biomass with the chemical structure of sugar alcohol formed from six sugar carbons of D-mannose [23]. Other forms of sugar such as glucuronic acid, mannosexylose and galactose are also found in algal biomass which can contribute to higher O₂ content when compared to cellulose [23]. As feasible feedstock, bioethanol and hydrogen (H₂) can be generated from glucose or starch while biologically active ingredients can be produced from polysaccharides [29]. In addition, carbohydrates are also raw materials for synthesising valuable chemicals such as cyclic ketones and phenols [31]. Under pyrolysis process, algal carbohydrates form light organics and polycyclic aromatic hydrocarbons (PAHs) in the composition of pyrolytic products [31,118].

2.3.3. Protein

Proteins are macromolecules that exist in the living organisms. Biologically, protein is made up of amino acid monomers in polymerised chains which are important substrates for plants and animals in maintaining their normal functionalities as well as in generating hormone and enzymes [23,29]. As observed from Table 3, protein content is exceptionally high in microalgae (14.00 – 65.20%) when compared with macroalgae (1.12 – 14.13%). With high protein content in microalgae biomass, large quantities of heterocycles such as pyrroles and indoles can be produced as valuable fine chemicals for applications such as herbicides, pharmaceutical ingredients and adhesives [31,119]. The protein content in algal biomass however also contributes to the N element in the products. Under pyrolysis process, N-based species such as nitriles, nitrites and nitrogenates will either devolatilised or remain in the pyrolytic bio-oil [12,113]. These N-based products are undesirable in pyrolytic bio-oil which may result in higher NO_x emission if combusted and eventually leaving behind ash in the form of metal oxides [23,113].

2.3.4. Moisture

The moisture content of algal biomass can affect the pyrolytic products in different ways. For bio-oil's moisture content, it is contributed

Table 3
Chemical constituents of algal biomass.

Algal Biomass	Species	Lipid (%)	Carbohydrate (%)	Protein (%)	Moisture (%)	Volatile Matter (%)	Fixed Carbon (%)	Ash Content (%)	Reference
<i>Macroalgae</i>									
<i>Dictyopteris australis</i>	Brown Algae	1.34	33.12	9.70	–	–	–	28.11	[102]
<i>Stoechospermum marginatum</i>	Brown Algae	3.91	33.58	10.90	–	–	–	35.83	[102]
<i>Lyngaria stellata</i>	Brown Algae	2.84	31.96	11.73	–	–	–	31.17	[102]
<i>Sargassum linearifolium</i>	Brown Algae	1.93	29.82	8.93	–	–	–	31.5	[102]
<i>Stypopodium schimperi</i>	Brown Algae	2.48 – 11.53	–	1.12 – 3.15	78.45	–	–	3.88 – 17.98	[78]
<i>Turbinaria turbinata</i>	Brown Algae	0.20 – 2.87	20.50 – 33.93	8.00 – 13.83	13.00	–	–	13.52 – 16.00	[102,105]
<i>Haloplegma duperreyi</i>	Red Algae	0.55	30.50	9.33	–	–	–	17.12	[102]
<i>Gracilaria gracilis</i>	Red Algae	1.70	28.6	13.70	5.88	53.1	10.9	36.00	[106]
<i>Spyridia filamentosa</i>	Red Algae	0.14 – 1.10	–	1.71 – 2.20	87.55	–	–	3.38 – 27.15	[78]
<i>Acanthophora nayadiformis</i>	Red Algae	0.29 – 2.19	–	1.71 – 1.76	86.83	–	–	3.22 – 24.47	[78]
<i>Halymenia venusta</i>	Red Algae	1.43	34.81	14.13	–	–	–	17.12	[102]
<i>Halymenia floresii</i>	Red Algae	0.12 – 2.46	–	0.95 – 3.05	95.00	–	–	0.96 – 19.16	[78]
<i>Enteromorpha prolifera</i>	Green Algae	1.1	51.4	11.8	7.99	59.41	4.90	27.70	[107]
<i>Ulva lactuca</i>	Green Algae	1.45	32.61	12.17	–	–	–	20.94	[102]
<i>Ulva reticulata</i>	Green Algae	2.50	33.35	6.90	–	–	–	19.88	[102]
<i>Acrosiphonia orientalis</i>	Green Algae	1.24	24.55	7.47	–	–	–	24.98	[102]
<i>Boodlea composita</i>	Green Algae	2.51	33.93	6.35	–	–	–	16.05	[102]
<i>Cladophora glomerata</i>	Green Algae	2.40	34.70	13.70	4.40	44.80	29.1	26.10	[106]
<i>Microalgae</i>									
<i>Spirulina platensis</i>	Cyanobacteria	10.30 – 13.30	12.00 – 30.21	48.36 – 65.20	4.54 – 7.48	79.14 – 82.03	5.43 – 15.24	5.06 – 6.56	[107,108]
<i>Laminaria japonica</i>	Phaeophyceae	1.10	7.40	45.20	–	69.60	16.00	14.40	[109]
<i>Nannochloropsis sp</i>	Eustigmatophyceae	30.00	19.20	40.80	4.01 – 7.00	63.50 – 79.61	10.38 – 19.6	6.00 – 9.90	[88,107]
<i>Nannochloropsis oculata</i>	Eustigmatophyceae	14.46	6.87	23.95	8.38	74.46 – 81.27	4.74 – 5.17	12.43 – 13.57	[110]
<i>Chlorella vulgaris</i>	Chlorellaceae	12.40 – 15.70	17.30 – 19.20	52.00 – 56.44	1.00 – 10.21	67.40 – 80.41	9.40 – 15.60	5.54 – 15.80	[103,104,111]
<i>Chlorella sp.</i>	Chlorellaceae	2.50 – 7.00	9.42 – 15.50	34.00 – 42.70	4.13 – 13.70	65.50 – 69.45	10.10 – 18.50	7.8 – 10.2	[33]
<i>Dunaliella tertiolecta</i>	Chlorophyceae	2.87	21.69	61.32	4.98	54.48	27.00	13.54	[112]
<i>Cladophora sp.</i>	Ulvophyceae	5.80	24.80	24.60	5.91	64.10	16.70	13.30	[63]
<i>Chlamydomonas reinhardtii</i>	Chlorophyceae	12.19	3.28	61.73	–	70.83	11.60	17.96	[12]
<i>Chlamydomonas debaryana</i>	Chlorophyceae	19.90	10.10	59.40	2.70	–	–	7.90	[113]
<i>Schizochytrium limacinum</i>	Thraustochytriaceae	51.00	24.00	14.00	–	89.4	1.70	8.90	[114]

Note: “–” Not available.

by its inherent moisture content of the biomass as well as the water formation mechanisms from pyrolysis reaction [120,121]. Due to high moisture content, flame temperature and heating value are usually reduced; however, viscosity and fluidity of bio-oil are often improved which can be beneficial for combustion process [120]. In term of syngas composition, higher moisture content of feedstock may favour the production of H₂ and CO₂ and reduce the CO generation depending on the overall composition of the algal feedstock used as well as the possible conversion of H₂O to H₂ by water-gas shift reaction (WGSR) [122–124]. In addition, the moisture content for macroalgae (4.4 – 95%) is higher than microalgae (2.7 – 13%) based on the literatures studied in Table 3. Majority of the macroalgae biomass are naturally high with moisture content up to 95% [78]. Therefore, the post-processing of macroalgae for long-term storage is required to improve storage life by reducing the moisture content [69]. If technological drying techniques are applied, the energy consumption can easily reach in between 3 and 5 MJ to reduce the moisture content from 50 – 60 wt% to 10 – 15 wt% [21]. Comparatively, microalgae possess lower moisture contents (1.00 – 13.01%), which are desirable for biofuel synthesis via pyrolysis. That is to say, less post-processing step and cost for dewatering process will be required for pyrolysis of microalgae to reduce their moisture content.

2.3.5. Volatile matter and fixed carbon

VM is measured based on the mass difference at the devolatilisation stage after dehydration stage, but before combustion stage in proximate analysis [59,60,125]. As the combustible fraction in the form of gas or vapour in algal biomass, VM also acts as an important index of biomass origin and coal quality characteristics [126–128]. From Table 3, both macroalgae and microalgae show high VM content which are mostly greater than 44.80%. The benefit of having high VM can be related to better biofuel conversion process [59,129]. In chemical composition, FC is regarded as the solid combustible composition measured under the oxidation condition [128,130,131]. From Table 3, FC varies considerably for both macroalgae (4.90 – 29.10%) and microalgae (1.70 – 27.00%), respectively. With higher FC, the produced biochar is beneficial for carbon sequestration [59,129].

Thus, by knowing the chemical contents such as VM and FC, the suitability of algal biomass as pyrolysis feedstock can be preliminarily assessed [59]. The ratio of VM to FC (VM:FC) of the raw algal biomass can provide conservative prediction on biochar yield which is mostly inversely proportional to the ratio [35,130,131]. By reversing the ratio to FC:VM, this gives the fuel ratio characteristics of the end products [132]. With higher fuel ratio, the end products are typically more desirable as biofuels due to high FC content [132,133]. Furthermore, the pyrolysis conditions (pyrolysis severity/ carbonisation severity) can be correlated with the fuel ratio, providing a simple assessment on the

pyrolytic products' quality. Therefore, both VM and FC contents may provide crucial information to assess the suitability of algal biomass as pyrolysis feedstock [134,135].

2.3.6. Ash content

During the growth of algal biomass, the assimilation of inorganic minerals from their cultivating environment can result in uptake of essential nutrients such as K, Na, Ca and Mg and trace elements such as iron (Fe), zinc (Zn), copper (Cu) and manganese (Mn) [79,134]. These alkali metals would eventually remain in the pyrolytic products especially in the biochar with AC being their grouped composition [118,135]. In addition, other elements such as halogens (Cl) and sulphur (S) are also found as part of the composition which are undesirable due to their environmental effects [136]. Nonetheless, the presence of undesirable ash in algal biomass can lower the yield of bio-oil and biochar [59,137]. For instance, K content can cause adverse catalytic impact on the pyrolysis process while P content might reduce the product yield and affect the products' structure [138]. Based on overall comparison between macroalgae and microalgae, the AC present in macroalgae can reach up to 35.83% whereas microalgae are about two times lesser. The issues associated with high AC in biofuels are erosion, corrosion on engines and valves, interference with burning rate, fouling and slagging problems [120,139]. Some of the conventional ways to reduce AC from the algal biomass feedstock are to pre-treat with water or acid-washing procedure prior pyrolysis process [138,140]. Especially acid-washing, ash elements such as Mg, K, Na and Ca were reduced up to 90% in some studies [100,141]. A recent study showed that pre-treatment with HCl can enhance the bio-oil quality by inhibiting the formation of phenols, carboxylic acid and water-based impurities while increasing the aliphatic hydrocarbon generation [142]. This however would increase the cost and time of processing for overall synthesis. Therefore, low AC is one of the critical criteria for biofuel synthesis.

3. Conventional pyrolysis

Among those thermochemical methods, pyrolysis can produce different forms of product from algal biomass into liquid, solid and gas products at varied pyrolysis conditions. Slow, intermediate, fast and flash pyrolysis are considered to be long-standing technologies and distinguished through several critical parametric controls such as pyrolysis temperature, pyrolysis time, heating rate, particulate size and inert gas sweeping rate [58,59]. In the pyrolysis experiment, the heating rate is the determining factor of the type of pyrolysis applied on the algal biomass as well as the distribution of the pyrolytic products [10,28]. There are numerous reviews and studies focus on microalgae pyrolysis [10,30,31,33,81]; however, for macroalgae or seaweeds, their pyrolysis studies have been lacking with research gaps to be addressed [58,69]. Table 4 summarises the critical experimental parameters for conventional pyrolysis experiments, whereby some of the values are extracted conservatively based on various research work. The following section provides the review on the conventional pyrolysis and their current applications on algal biomass.

3.1. Slow pyrolysis

Slow pyrolysis is an eminent synthesis method utilised mainly to generate biochar with by-products such as bio-oil and syngas. Slow pyrolysis conditions primarily focus on moderate temperatures (550 – 950 °C), slow heating rates (< 60 °C/min) and long pyrolysis times (> 5 min), as observed from Table 4 [130,144]. Such experimental settings are favourable for solid product formation. For moderate temperature requirement, this is to balance between low pyrolysis temperature which supports the development of more biochar and high pyrolysis temperature which inhibit the formation of undesired tar [35,145]. Generally, a low heating rate with longer residence time further promotes the formation of solid products. Furthermore, slow

pyrolysis can handle a wider range of biomass particle from 5 to 50 mm [28,59]. Thus, slow pyrolysis will have no issue in processing both macroalgae (mm to m) and microalgae (µm). Overall, optimisation of these pyrolysis parameters (pyrolysis time, temperature, heating rate, sweeping gas flowrate and others) need to be undertaken to enhance the production of solid products.

In a slow pyrolysis study, three macroalgae (*Undaria pinnatifida*, *Laminaria japonica*, *Porphyra tenera*) were pyrolysed under varying temperatures (300 – 600 °C) [80]. As the physicochemical properties of each macroalga differed in term of AC (10.44 – 28.28 wt%), H/C ratio (1.37 – 1.92), O/C ratio (0.88 – 1.53), the produced products also presented different yield values and compositions. As the pyrolysis temperatures were increased, the general trends observed for all macroalgae were the increasing yields of both bio-oil and syngas with the decrease of biochar production, agreeing with other studies [55,59,130,146]. Biochar fraction still constituted the largest portion of the product followed by liquid and gaseous product when the pyrolysis temperature was maintained below 400 °C [144]. Bio-oil produced from slow pyrolysis contained two phases (aqueous and organic phases) with different HHV values. The aqueous phase was analysed and found to have lower HHV values due to higher O₂ contents [68]. Among these macroalgae, *Laminaria japonica* showed the highest HHV values for both aqueous phases (12.24 MJ/kg) and organic phase (33.57 MJ/kg), respectively. The gaseous products from all three algal biomass displayed low yield values (10 – 25 wt%) predominantly with CO₂ as the main product, which were different from the terrestrial biomass-based syngas (CO and CO₂ as main products) [80]. A recent study investigated the biochar synthesis from six different macroalgae which included *Gracilaria*, *Euclima*, *Kappaphycus*, *Saccharina*, *Sargassum* and *Undaria* with slow pyrolysis [147]. It was found that the biochar synthesised from all macroalgae presented high yields of biochar (45.3 – 62.4 wt%) with moderate HHV values (10.7 – 17.8 MJ/kg). The minerals (Ca, K, Mg and Na) detected on all biochar samples could be crucial as soil fertiliser for agricultural applications [24,59,144]. Macroalgae-based biochars were also synthesised for wastewater treatment applications [146,148]. For instance, *Laminaria japonica* was carbonised under slow pyrolysis in between 300 and 600 °C before being mixed with alginate solution to optimise and form Ca-alginate beads for phosphate removal [146]. At increasing temperature, the yields of biochar were reduced from 78.34 to 27.05% while AC was increased from 22.92 to 64.19%. This was mainly due to the presence of the alkaline minerals in the raw algae. The Brunauer-Emmett-Teller (BET) surface area of the sample was generally improved with the increment of pyrolysis temperature. The experimental results as well as the characteristics of the pyrolytic products were in agreement with other macroalga study such as *Saccharina japonica* [149].

Six microalgae (*Chlorella like*, *Tetraselmis chui*, *Chaetoceros muelleri*, *Dunaliella tertiolecta*, *Chlorella vulgaris* and *Synechococcus*) were used as algal biomass pyrolysis feedstocks [150]. The study however focussed more on the bio-syngas with the detected composition of CO₂, CO, CH₄, C₂H₄, C₂H₆ and H₂. The dominant gaseous species from the produced syngas for all microalgae feedstock was CO₂ varying from 9 to 17.5%, followed by CO (1.0 – 2.2%) and other light hydrocarbons such as CH₄, C₂H₄, C₂H₆ and H₂. Based on the calorific value of combustible bio-syngas, *Tetraselmis chui* was found to have the highest value (3.4 MJ/kg) while *Chaetoceros muelleri* presented the lowest value (1.2 MJ/kg). In another study, *Tetraselmis chui* was investigated of its bio-oil and biochar properties through slow pyrolysis [151]. High HHV of bio-oil (27.9 MJ/kg) with high contents of C₁₆ – C₂₀ generated from *Tetraselmis chui* showed considerable energy potential. For biochar, its high carbon content can be useful in soil remediation and nutrient retention. Even though the bio-syngas contains relatively lower energy value (2.9 MJ/kg), its direct usage for combustion without other processing step can be an attractive option for energy generation [118]. In addition to the abovementioned microalgae, *Spirulina Spp* is also gaining attention in slow pyrolysis studies [108,129]. Typically, the biochar yields from

Table 4
Conventional pyrolysis of algal biomass.

Algal Biomass	Type of Pyrolysis	Heating Rate (°C/min)	Pyrolysis Time (min)	Pyrolysis Temperature (°C)	Pyrolysis Temperature	Particle Size (mm)	Carrier Gas Flowrate (mL/min)	Solid Product (wt%)	Liquid Product (wt%)	Gas Product (wt%)	HHV (MJ/kg)	Ref
Macroalgae												
<i>Undaria pinnatifida</i>	Slow	-	60	300 – 600	300 – 1600 µm	N ₂ : 50	40 – 60	22 – 40	15 – 25	Aqueous phase: 9.56 Organic phase: 23.33	[80]	
<i>Laminaria japonica</i>	Slow	-	60	300 – 600	300 – 1600 µm	N ₂ : 50	39 – 52	28 – 35	15 – 30	Aqueous phase: 12.24 Organic phase: 33.57	[80]	
<i>Porphyra tenera</i>	Slow	-	60	300 – 600	300 – 1600 µm	N ₂ : 50	35 – 60	30 – 48	10 – 20	Aqueous phase: 6.75 Organic phase: 29.74	[80]	
<i>Gracilaria</i>	Slow	-	60	450	1 – 2	N ₂ : 4000	59.8 – 61.8	-	-	Biochar: 11.1 – 16.1	[147]	
<i>Eucheuma</i>	Slow	-	60	450	1 – 2	N ₂ : 4000	57.2 – 61.7	-	-	Biochar: 14.6 – 17.2	[147]	
<i>Kappaphycus</i>	Slow	-	60	450	1 – 2	N ₂ : 4000	54.1 – 59.2	-	-	Biochar: 13.0 – 17.8	[147]	
<i>Saccharina</i>	Slow	-	60	450	1 – 2	N ₂ : 4000	45.3 – 49.7	-	-	Biochar: 11.4 – 14.8	[147]	
<i>Sargassum</i>	Slow	-	60	450	1 – 2	N ₂ : 4000	49.0 – 61.9	-	-	Biochar: 11.8 – 13.5	[147]	
<i>Undaria</i>	Slow	-	60	450	1 – 2	N ₂ : 4000	60.3 – 62.4	-	-	Biochar: 10.7 – 14.7	[147]	
<i>Lyngbya</i> sp.	Slow	30	20	600	~ 0.18	He: 200 cm ³ /min	17	12	44	Biochar: 16.4 – 25.0,6	[63]	
<i>Cladophora</i> sp.	Slow	30	20	600	~ 0.18	He: 200 cm ³ /min	26	20	38	Biochar: 17.4 – 22.7	[63]	
<i>Saccharina japonica</i>	Slow	-	4 – 10	425 – 530	3 – 5	N ₂ : 0.6 L/min	25.5 – 34.5	45.2 – 48.4	-	Bio-oil: 28.7 Biochar: 6.62 – 15.53	[149]	
<i>Prasiola crispa</i>	Intermediate	100	10	900	< 250 µm	He: 50	38.1	-	-	-	[101]	
<i>Monostroma arcticum</i>	Intermediate	100	10	900	< 250 µm	He: 50	35.0	-	-	-	[101]	
<i>Polysiphonia arctica</i>	Intermediate	100	10	900	< 250 µm	He: 50	46.0	-	-	-	[101]	
<i>Devalersea ramentacea</i>	Intermediate	100	10	900	< 250 µm	He: 50	33.0	-	-	-	[101]	
<i>Odonthalia dentata</i>	Intermediate	100	10	900	< 250 µm	He: 50	35.9	-	-	-	[101]	
<i>Phycodrys rubens</i>	Intermediate	100	10	900	< 250 µm	He: 50	39.4	-	-	-	[101]	
<i>Sphaelaria plumosa</i>	Intermediate	100	10	900	< 250 µm	He: 50	45.3	-	-	-	[101]	
<i>Gigartina skottsbergii</i>	Intermediate	100	10	900	< 250 µm	He: 50	39.8	-	-	-	[101]	
<i>Plocamium cartilagineum</i>	Intermediate	100	10	900	< 250 µm	He: 50	46.0	-	-	-	[101]	
<i>Myriogramme manginii</i>	Intermediate	100	10	900	< 250 µm	He: 50	35.0	-	-	-	[101]	
<i>Hymenocladopsis crustigena</i>	Intermediate	100	10	900	< 250 µm	He: 50	41.5	-	-	-	[101]	
<i>Kallymenia antarctica</i>	Intermediate	100	10	900	< 250 µm	He: 50	40.3	-	-	-	[101]	
<i>Saccharina japonica</i>	Fast	-	2 s	350 – 500	< 400 µm	N ₂ : 4500	30.4 – 50.0	25.0 – 45.0	20.8 – 34.2	Bio-oil: 24.8 – 28.3 Bio-syngas: 4.60 – 12.9	[158]	
<i>Saccharina japonica</i>	Fast	-	2 s	350 – 500	300 – 500 µm	N ₂ : 100 – 500	31.9 – 42.1	31.2 – 40.9	19.4 – 37.0	Bio-oil: 33.0 – 33.2 Biochar: 11.8 – 12.4	[158]	

(continued on next page)

Table 4 (continued)

Algal Biomass	Type of Pyrolysis	Heating Rate (°C/min)	Pyrolysis Time (min)	Pyrolysis Temperature (°C)	Pyrolysis Temperature (°C)	Particle Size (mm)	Carrier Gas Flowrate (mL/min)	Solid Product (wt%)	Liquid Product (wt%)	Gas Product (wt%)	HHV (MJ/kg)	Ref
<i>Ulva lactuca</i>	Fast	-	0.5–2 s	400–600	400–600	< 0.25	N ₂ : 50 L/h	20	65	15	Bio-oil: 18.9–25.7	[156]
<i>Enteromorpha clathrata</i>	Fast	-	-	400–600	400–600	< 0.25	N ₂ : 50 L/h	40.2–51.0	34.1–41.2	14.9–22.6	-	[164]
<i>Sargassum natans</i>	Fast	-	-	400–600	400–600	< 0.25	N ₂ : 50 L/h	46.9–52.9	28.8–33.7	15.3–24.1	-	[164]
Microalgae												
<i>Tetraselmis chui</i>	Slow	10	-	500	500	-	-	37	43	20	Bio-syngas: 3.4	[150]
<i>Chlorella like</i>	Slow	10	-	500	500	-	-	34	41	25	Bio-syngas: 1.8	[150]
<i>Chlorella vulgaris</i>	Slow	10	-	500	500	-	-	37	41	22	Bio-syngas: 4.8	[150]
<i>Chaetoceros muelleri</i>	Slow	10	-	500	500	-	-	53	33	14	Bio-syngas: 1.2	[150]
<i>Dunaliella tertiolecta</i>	Slow	10	-	500	500	-	-	63	24	13	Bio-syngas: 2.4	[150]
<i>Synechococcus</i>	Slow	10	-	500	500	-	-	44	38	18	Bio-syngas: 1.4	[150]
<i>Tetraselmis chui</i>	Slow	10	20	500	500	-	He: 50	37	-	-	Biochar: 14.5	[151]
<i>Tetraselmis chui</i>	Slow	10	20	500	500	-	N ₂ : 100	-	-	-	Bio-oil: 27.9	[151]
<i>Spirulina Sp. powder</i>	Slow	8	60	450–600	450–600	0.5–0.1	N ₂ : 30	31–32	40–45	24–27	Bio-oil: 21.68	[129]
<i>Spirulina platensis</i>	Slow	3.5–7.0	60	350–600	350–600	-	N ₂ : 250	23.8–28.2	25.6–39.7	19.2–28.0	Bio-oil: 29.30–33.62	[108]
											Biochar: 23.77–26.12	
<i>Chlamydomonas reinhardtii wild type</i>	Intermediate	100	10	900	900	< 250 µm	He: 50	25–27	-	-	-	[153]
<i>C. reinhardtii CW15+</i>	Intermediate	100	10	900	900	< 250 µm	He: 50	25–27	-	-	-	[153]
<i>Chlorella vulgaris</i>	Intermediate	100	10	900	900	< 250 µm	He: 50	30	-	-	-	[153]
<i>Chlorella protothecoides</i>	Fast	600 °C/s	2–3 s	500	500	0.18	N ₂ : 0.4 m ³ /h	54	17	29	Bio-oil: 30	[68]
<i>Microcystis aeruginosa</i>	Fast	600 °C/s	2–3 s	500	500	0.18	N ₂ : 0.4 m ³ /h	21	24	55	Bio-oil: 29	[68]
<i>Chlorella vulgaris</i> remnants	Fast	-	-	500	500	420–700 µm	-	31	53	10	Bio-oil: 24.57	[162]
Green algae	Fast	-	1.5 s	500	500	90–1000 µm	N ₂ : 250 CO ₂ : 250	24.6–26.0	56.2–58.6	16.8–17.8	Bio-oil: 26.7	[163]
Green-blue algae	Fast	-	1.5 s	500	500	90–1000 µm	Steam: 250 N ₂ : 250	24.4–28.4	54.4–56.8	16.4–19.9	Bio-oil: 26.8	[163]
<i>Chlorella</i>	Fast	-	1.5 s	500	500	< 90 µm	N ₂ : 250	29.0	53.9	17.3	Bio-oil: 25.5	[163]
<i>Scenedesmus</i> sp.	Fast	-	2 s	480	480	-	N ₂ : 250	-	55	-	Bio-oil: 18.4	[165]
											Biochar: 4.6	

these microalgae were reported to be moderate (23.8 – 32%) but the produced bio-oil yields were regarded to be high (25.6 – 45%). The HHVs of bio-oil and biochar from microalgae were high in energy contents (21.68 – 33.62 MJ/kg) with low S and N contents, comparable to coal.

3.2. Intermediate pyrolysis

A novel form of pyrolysis has been developed as an independent synthesis technology known as intermediate pyrolysis, which is carried out between the pyrolysis conditions of slow and fast pyrolysis [152]. This synthesis of intermediate pyrolysis has been patented with the following conditions: pyrolysis temperature: up to 500 °C; pyrolysis time: 30 – 1500 s; and vapour residence time: 2 – 4 s [101]. Through this process, the liquid remains as the largest product fraction (40 – 60%), followed by non-condensable bio-syngas (20 – 30%) and lastly solid products (15 – 25%) [153]. The bio-oil synthesised from intermediate pyrolysis shows lower tar concentration and reduced viscosity which can be directly used in boilers and engines [154,155].

Currently, the use of macroalgae as intermediate pyrolysis feedstock has either been lacking or incomplete in literature when compared to other forms of pyrolysis (Table 4) [69,101]. In a study on the thermochemical behaviour of polar seaweeds intermediate pyrolysis, biochar yields for the 12 types of macroalgae were considerably high (33 – 46%) at high pyrolysis temperature of 900 °C [101]. Furthermore, based on the Py-GC/MS compound analysis during the evolution of algal biomass, about 30 compounds were detected and categorised into aromatic compounds, acids, furans, pyrans aliphatic hydrocarbons, terpenes, anhydrosugars, monosaccharides and others, which were compounds found in algal bio-oil [20,81]. Even though the proximate analysis was not performed on the biochar formed, the raw microalgal biomass contained high AC (30 – 44.7%) which would eventually contribute to the composition of biochar in the form of minerals [38,133].

Intermediate pyrolysis was more commonly applied on microalgal feedstock which included *Chlamydomonas reinhardtii wild type*, *C. reinhardtii CW15⁺* and *Chlorella vulgaris* [153]. The biochar yields ranged from 25 to 30% while the bio-oil and bio-syngas were not quantified in this study. From Py-GC/MS in the form of pyrograms, various compounds were detected from protein pyrolysis into aromatic compounds, phenols and heterocyclic compounds while pyrolysis of lipid contributed to the formation of esters and hydrocarbons [128]. Nonetheless, the intermediate pyrolysis experimental parameters are not strongly established on the feedstock of algal biomass. The most obvious gap identified from the literature would be the measurement and analysis of yields and compositions for all product fractions. As this form of pyrolysis is currently uncommon, this presents great challenge in comparing different research findings. The gap should be minimised by more laboratory-scale work being conducted with comprehensive investigations on the intermediate pyrolysis parameters.

3.3. Fast pyrolysis

To maximise the bio-oil production, fast pyrolysis is often employed on biomass with the following pyrolysis conditions: high temperature (850 – 1250 °C), fast heating rate (> 60 °C/min) and short pyrolysis time (0.5 – 10 s) [28,58]. As fast pyrolysis operates with high pyrolysis temperature but short residence period, such settings can inhibit the secondary reactions of volatiles thereby preventing the cracking of the primary products, which eventually contribute to improve liquid product yields [58,68]. In other words, fast pyrolysis technology suppresses secondary reactions as well as polymerisation of volatile intermediates [10,33]. With fast pyrolysis processes, the algal biomass is directly converted into liquid and non-condensable gaseous products before the formation of biochar [28]. To accommodate such processing temperature and time, the particle size of biomass used in fast pyrolysis

is usually fine (< 1 mm) to ensure effective heating [28,30]. Furthermore, fast pyrolysis is capable of handling high AC feedstock such as macroalgae and microalgae by concentrating those minerals or inorganics into the portion of the biochar which can be used as soil fertiliser and conditioner [128,156]. Compared with other forms of pyrolysis, fast pyrolysis is considered to be an inexpensive way to produce pyrolytic liquid with good quality [157].

Fast pyrolysis was performed on *Saccharina japonica* using a bubbling fluidized-bed reactor for the synthesis of liquid product [158]. The study thoroughly investigated the effects of temperature and fluidisation on the yield and HHV of the pyrolytic products. By increasing the temperature from 350 to 500 °C, the conversion of macroalgal biomass to bio-oil was reduced from 44.99 to 26.67 wt%; biochar was improved from 34.20 to 39.18 wt%; and bio-syngas was enhanced from 20.81 to 34.15 wt%. For this particular macroalgae, the bio-oil was best produced at relatively low temperature (350 °C) in comparison with biomass such as palm kernel shells (490 °C) [159]. This indicates that macroalgae was less recalcitrant to thermal treatment. Higher pyrolysis temperature favours the secondary cracking reactions which shows consistency in the reducing trends of bio-oil yield and the increasing trends of bio-syngas yield [58,159,160]. As for the effect of fluidisation, the bio-oil yield was optimised at the rate of 4.0 × 4.5 L/min even though its HHV was not the highest (24.80 MJ/kg). In other study, the same macroalga was applied as fast pyrolysis feedstock using a fixed-bed reactor which could handle the formation of undesirable compounds such as tar, char as well as alginate without compromising the continuous process [161]. Both bio-oil (33.0 – 33.2 MJ/kg) and biochar (11.8 – 12.4 MJ/kg) derived from *Saccharina japonica* showed considerable energy contents with desirable yield values.

Miao et al. [68] performed one of the earliest fast pyrolysis study for renewable fuels synthesis from microalgae such as *Chlorella protothecoides* and *Microcystis aeruginosa*. As observed from Table 4, despite both microalgae were used as pyrolysis feedstock, their yield trends were completely different. For *Chlorella protothecoides*, the biochar production was the highest fraction (54 wt%) among the three products. The bio-syngas was produced the most (55 wt%) from *Microcystis aeruginosa* at 500 °C compared to other products. Thus, the types of microalgae used for the pyrolysis can greatly influence the yield of the pyrolytic products. Nonetheless, the bio-oils produced from both microalgae showed high HHV values (29 – 30 MJ/kg) indicating their great potential as biofuel products. In another study, *Chlorella vulgaris* as microalgal fast pyrolysis feedstock displayed the following product distribution [162]: biochar: 31 wt%; bio-oil: 53 wt%; and bio-syngas: 10 wt%. The remaining 6 wt% were mainly contributed by gas-phase products such as NH₃ and N₂. To investigate thoroughly the pyrolysis conditions on the pyrolytic product distribution, the effects of temperature, diameter of algal biomass, sweeping gas flowrate, biomass holdup and amount were varied accordingly on different microalgae such as green algae, green-blue algae and *Chlorella* [163]. Based on the products' yield analysis, they were not greatly influenced by the particle sizes using the falling solid reactor. In term of inert gas flowrate and type effects, the increasing sweeping inert gas rate decreased the biochar yield due to the rapid removal of uncondensed volatiles thereby reducing the secondary reactions such as condensation, oligomerisation and cracking [160,163]. All three types of microalgae-based bio-oil exhibited high HHV values (25.5 – 26.8 MJ/kg). Interestingly, the use of different inert gases (N₂, steam and CO₂) also affects the composition of the bio-oil significantly. Based on the GC/MS results, steam-based fast pyrolysis synthesised bio-oil with higher content of hydrocarbons, while N₂-based fast pyrolysis favoured the formation of alcohols and nitrogenates, and CO₂-based fast pyrolysis generated greater amount of oxygenates and compounds with O and N. The main reactions of steam-based fast pyrolysis were steam reforming and deoxygenation which led to the generation of H₂ contributing to high hydrocarbon contents [162,163]. CO₂-based fast pyrolysis contributed to the formation of waxy crystals in the aqueous phase which might pose clogging issue for

the downstream processing [163]. Thus, the study revealed that inert gas type selection is one of the crucial pyrolysis parameters to optimise the bio-oil qualities.

3.4. Flash pyrolysis

Flash pyrolysis can be referred as a more intensified form of fast pyrolysis with greater heating rate (> 1000 °C/s) [28,35]. The synthesis parameters of flash pyrolysis are usually performed in the following range: pyrolysis temperature: 700 – 1200 °C; particle size: < 0.1 mm; residence time < 2 s [10,33,143]. While many studies have grouped both fast and flash pyrolysis as similar technologies, the product fractions generated for flash pyrolysis are mainly two types of pyrolytic products such as oil and gas products by diminishing the solid products completely [143]. The extremely high conversion (up to 9%) of biomass to bio-oil by flash pyrolysis even though is attractive, the produced bio-oil can have several undesirable characteristics such as highly acidic, highly viscous, reactive, contain minor amount of residue solids and high aqueous contents [30].

Flash pyrolysis despite covered under numerous studies and reviews [28,30], up to date, there is no parametric study available on algal biomass feedstock. The most current studies only focused on the Py-GC/MS investigations of microalga *Botryococcus braunii* [166,167]. Both investigations focused on identifying the ether-linked alkyl chains isolated from algal biomass using flash pyrolysis conditions. The lack of laboratory scale or pilot scale experiments of flash pyrolysis of algal biomass can be related to the complexity of equipment setup [28]. For instance, entrained flow reactor and fluidised bed reactor are only a few of the pyrolysers which can handle extreme rapid heating with short residence time [30]. The design of those reactors is complicated and costly to be implemented. Due to such limitations, flash pyrolysis has not been widely applied at industrial scale. In laboratory scale, setting up a flash pyrolyser proves to be relatively more challenging due to safety and cost factors.

4. Advanced pyrolysis techniques

Non-conventional or advanced pyrolysis methods explore the modifications on these conventional techniques to improve the pyrolytic products' yields, qualities, characteristics and properties. Currently, advanced pyrolysis techniques involve several approaches, as follows:

- Use of catalysts to promote the pyrolysis process (catalytic pyrolysis)
- Mixture with other biomass/ materials/ wastes in the form of co-process to improve existing pyrolytic products (co-pyrolysis)
- Modification of the pyrolysis process by changing the pyrolysis conditions such as reaction environment and pyrolysis pressure (hydropyrolysis)
- Integration with other external technologies to improve the heating process (microwave-assisted pyrolysis)
- Combination of two or more technologies as listed above (catalytic co-pyrolysis, catalytic co-hydropyrolysis, microwave-assisted catalytic pyrolytic and others).

Advanced pyrolysis techniques aim to enhance better selectivity towards certain pyrolytic products (liquid, solid or gas) as well as improve the processing parameters by reducing pyrolysis temperature, processing time and by increasing desired product's yields [31,138]. The following section describes the pyrolysis settings and the advanced settings for each technology on the distribution of products for both macroalgae and microalgae as pyrolysis feedstock, respectively, for distinctive comparison of each technological contribution.

4.1. Catalytic pyrolysis

To enhance the pyrolysis process, different catalysts such as acid-type, base-type, metal-type, zeolite-type, carbon-type or mixture of different materials can be used to improve the existing pyrolysis process as well as the characteristics of the products [28,168–170]. There are two approaches in embedding the catalyst into the pyrolysis process, namely primary (in-situ) and secondary (ex-situ) catalytic pyrolysis.

Primary catalytic pyrolysis, also known as a catalyst-mixing method, blends the biomass with the dual-function catalysts (catalyst and heat carrier) with dry mixing (physical process) or wet mixing (chemical impregnation process) which can be directly used in conventional pyrolyser [31,171,172]. In-situ pyrolysis promotes liquid (e.g.: naphthalene and higher aromatic compounds) and gas (e.g.: CO) products generation [171]. The main advantages of primary catalytic pyrolysis are the inhibition of tar formation and the promotion of better catalytic effects [169]. Furthermore, relatively, in-situ pyrolysis requires lower equipment cost and spacing with simple one-reactor configuration. Nonetheless, simultaneous heating on incompatible biomass/catalyst system can lead to poor deoxygenation process due to ineffective solid/solid interaction caused by their respective different activation temperatures [171]. In addition, the primary catalytic pyrolysis is also associated with disadvantage such as the loss of catalytic activity caused by coke formation.

As for secondary catalytic pyrolysis (catalyst-bed method), the modified setup as shown in Fig. 3, separates the biomass at the upper train supported with quartz wool inside the reactor while the catalyst is fixed at the downstream of the pyrolyser [65,173,174]. The heating process will usually be performed stage-by-stage beginning with the catalyst activation, followed by the biomass thermal degradation process with the aid of a heat carrier (sand) [175]. This provides better control on pyrolysis and catalytic activities during the reaction as well as better optimisation process without interfering each other [171,176]. Due to such reactor configuration, longer residence time of pyrolysed vapour is anticipated which will stimulate secondary cracking reactions generating secondary solid products. Thus, ex-situ pyrolysis promotes solid (biochar) and gas (monocyclic aromatics) products generation [171]. Moreover, ex-situ system can reduce contamination of minerals (K, Na, Ca, Mg, etc.) from biomass to be deposited on the catalyst by retaining those elements into the biochar products instead [170,171]. More importantly, secondary catalytic process overcomes the difficulty of biochar-catalyst separation and recovery. This also improves the reusability of catalyst in the pyrolysis process.

From a chemistry perspective, the use of catalyst is more superior compared to non-catalytic pyrolysis, due to lower energy requirement, lower pyrolysis temperature and its ability to remove impurities such as solid residues, O, S, N and P contents in bio-oil as well as enhancement of product selectivity by changing the pyrolysis reaction pathways [10,168]. In term of process parameters, the catalyst is capable of reducing the overall pyrolysis temperature and time; thereby making the whole process more energy efficient and effective. Nonetheless, from economy perspective, catalytic reactions inevitably increase the cost of chemicals as some of the catalysts are quite expensive and difficult to retrieve especially in the form of the primary catalytic process [176]. Moreover, catalyst replacement for any pyrolysis process from time to time is common as part of the maintenance regime and also to ensure the consistency of the pyrolysis process. For pyrolysis system, higher reaction temperature despite can reduce tar products, the greater amount of pyrolytic vapour generated can also cause the coke to form on the catalyst's surface resulting in its deactivation [177,178]. Thus, poisoned or ineffective catalyst not only serves no purpose in the pyrolysis process, but it can also affect the process selectivity to undesired products [176]. As can be observed, a cost-effective catalyst which can efficiently promote the generation of preferred pyrolytic product without comprising the lifespan of the catalyst is highly desirable [178].

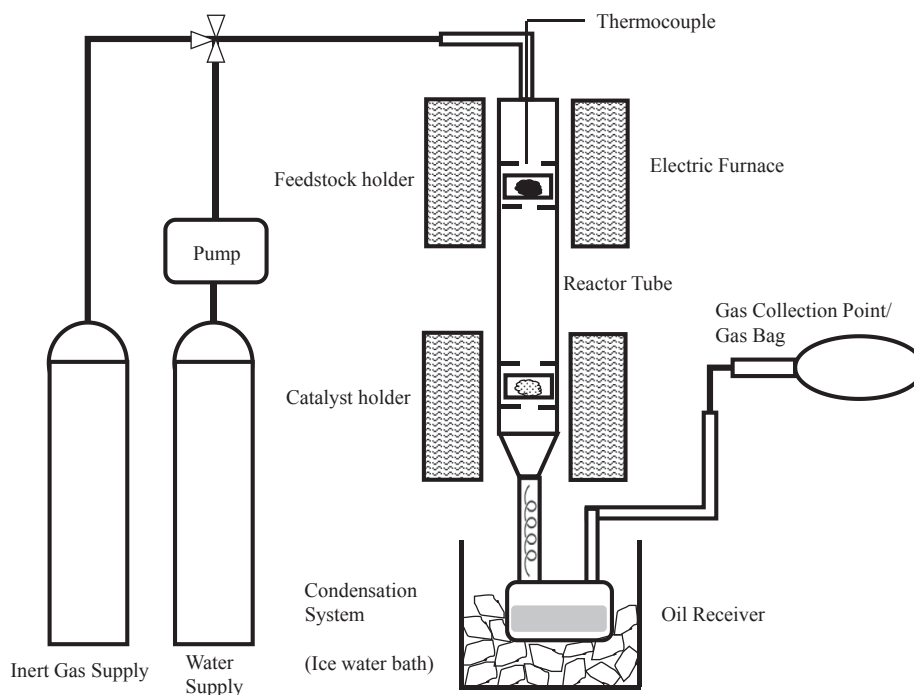


Fig. 3. General schematic diagram of ex situ catalytic pyrolysis [65,173].

In algal biomass pyrolysis, catalysts are used to achieve catalytic cracking to reduce both undesirable contents from the pyrolytic products such as oxygenated compounds and nitrogenates. Deoxygenation reaction eliminates oxygenated compounds from the pyrolysis vapours in the form of CO_2 , CO and H_2O whereas denitrogenation removes nitrogenates in other N-based species [176,179]. Catalytic-driven deoxygenation reactions such as hydrodeoxygenation, dehydration, decarboxylation, decarbonylation, cracking, aromatisation, condensation, alkylation and polymerisation reactions can also convert the oxygenates into useful hydrocarbons such as aromatic compounds and phenols [174,176]. Some of the deoxygenation and denitrogenation catalytic reactions may occur independently or simultaneously based on the catalyst applied during the pyrolysis process [128,178,179]:

- Dehydration removes H_2O
- Hydrodeoxygenation eliminates O_2 in the form of H_2O
- Decarboxylation generates CO_2 and CO from O_2 compounds
- Decarbonylation produces CO from O_2 compounds
- Denitrogenation forms ammonia (NH_3) and hydrogen cyanide (HCN) from N_2
- Ketonization and aldolcondensation remove O_2 and form C–C species.

Based on the available reactions above, the elimination of oxygenates in the form of CO_2 is mainly preferred [12]. The reason behind is because this reaction path can remove twice of oxygenates in the bio-oil compared to the elimination in the form of CO . The catalytic effects on the pyrolysis process can vary greatly depending on the catalyst used as well as the nature of the biomass. Selection of catalyst takes into account of several important criteria such as acidity, BET surface area, pore size as well as crystalline structure [168]. Table 5 summarises some of the catalysts used in the pyrolysis process. For instance, modified zeolite-based catalysts sometimes possess high acidity which can promote the generation of desired hydrocarbons. In some studies, metal-based/ metal supported catalysts show more superiority in resisting coke formation. Algal biochar has been another form of emerging catalyst, which shows excellent selectivity towards aromatic compounds through Diels-Alder reaction [180]. Iron (Fe) composite biochars can be used as catalyst to improve the generation of H_2 content

in syngas [181]. In another study, spent car catalytic converter has been successfully converted into multi-metal catalyst which promotes deoxygenation and ketonisation reactions [182]. CO_2 formation is favourably catalysed by basic catalysts leading to the removal of deoxygenates from bio-oil [12]. Therefore, catalyst and algal biomass must be compatible to ensure desirable catalytic effects and selectivity on the formation of products.

Despite catalytic pyrolysis of algal biomass has been discussed in several recent reviews [10,33], the correlation between the type of catalysts and the product characteristics still requires more deliberation. The current catalysts (zeolite and metal-based catalyst) and emerging catalyst (ceria-based) catalyst are extensively applied on algal biomass. Thus, the following section describes studies with respect to the catalysts used for different pyrolysis process (Table 6).

4.1.1. Zeolite-Based catalytic pyrolysis

Currently, over 60 natural zeolites and 230 synthetic zeolites and zeotype exist with different channel structures in one-, two- and three-dimensional orientations [188]. Pristine microporous zeolite is a highly tailorable silica-based material with aluminosilicate as a framework which can be modified into different catalyst forms such as ZSM-5, HZSM-5, H-Beta, H-Y Meso-MFI, HBEA, USY, SAPO5, SAPO11, MCM-41, Al-MCM-48 and others [128,188–190]. Up to date, ZSM-5 is one of the most applied pyrolytic catalysts on biomass due to its high resistance against deactivation [174]. However, zeolite-based catalyst suffers from an inability to process macromolecules and has minor denitrogenation effect [66,187].

As summarised in Table 6, the catalytic pyrolysis parametric studies on macroalgae are insufficient in the literature [184,185]. Catalytic pyrolysis over two different zeolite-based catalysts (hierarchical meso-MFI zeolite and nanoporous Al-MCM-48) were investigated using Py-GC/MS on *Laminaria japonica* [184]. The studies only focussed on identifying gas products and the composition of algal bio-oil as derived from two different catalytic processes. The results showed that the acidity of the catalyst played an important role in generating desired products. The acidic nature of Meso-MFI favoured the production of intermediate light hydrocarbons such as ethylene and propylene whereby these hydrocarbons were polymerised and aromatised into

Table 5
Characteristics of catalyst used for pyrolysis.

Catalyst	Si/Al	Average Pore Diameter (Å)	BET Surface Area (m ² /g)	Total Acidity (mmol/g)	Reference
ZSM-5 ammonium	50:1	88.73	335.47	0.4752	[183]
ZSM-5 ammonium	200:1	25.75	385.72	0.1058	[183]
Zeolite hydrogen	360:1	49.90	491.10	0.1739	[183]
Zeolite ammonium	38:1	54.94	512.40	0.4481	[183]
Zeolite Y ammonium	5.1:1	54.57	644.54	1.4373	[183]
Zeolite Y hydrogen	5.1:1	55.68	647.05	1.3614	[183]
Al-MCM-48	20:1	26	1219	–	[184]
Meso-MFI	20:1	41	471	–	[184]
Al-SBA-15	20:1	67	614	–	[185]
CeO ₂	–	71.04	18.69	–	[186]
TiO ₂	–	59.06	9.48	–	[186]
Ce/TiO ₂	–	29.68	126.8	–	[186]
Co/TiO ₂	–	31.32	278.5	–	[186]
Ni/TiO ₂	–	58.06	229.6	–	[186]
Co-Mo/HMS	–	25.6	714	1.07	[187]
Co-Mo/HZSM-5	–	< 10 ³ μm	256	2.24	[187]
Co-Mo/ZH-10	–	23.4	712	1.48	[187]
Co-Mo/ZH-20	–	23.1	711	1.86	[187]
Co-Mo/ZH-30	–	22.9	619	1.96	[187]
Co-Mo/ZH-40	–	22.8	524	2.10	[187]

aromatic hydrocarbons at the available pores of the catalyst. While, the less acidic Al-MCM-48-catalysed pyrolysis produced mainly paraffinic hydrocarbons. More gaseous pyrolytic products were produced from Meso-MFI-based catalytic process due to its higher acidic nature. This has indicated the significance of the catalyst acidity in the deoxygenation process. In another catalytic parametric studies using *Laminaria japonica* as macroalgal feedstock, the catalyst of Al-SBA-15 was employed to investigate its effects on the production distribution [185]. Even with the use of catalyst, the pyrolytic products (char: 42.23 wt%; bio-oil: 32.71 wt%; gas: 25.1 wt%) were not significantly improved compared to non-catalytic process (char: 42.12 wt%; bio-oil: 31.2 wt%; gas: 26.6 wt%). Nonetheless, the more apparent changes were detected in the composition of gas and bio-oil. Gas products with catalytic support generated a higher amount of C₁ – C₄ hydrocarbons. However, the large-pore catalyst used in the pyrolysis contributed to higher water content in bio-oil via dehydration reaction from 42.03 to 50.32 wt% which would be unfavourable. With the presence of the catalyst, oxygenates species such as 1,4-anhydro-D-galactitol and 1,5-anhydro-D-mannitol were eliminated completely from the bio-oil based on the GC data. To reduce the ash content of *Saccharina japonica* alga, an acid-pre-treatment was performed which was followed by HZSM-5 catalytic pyrolysis. At increasing temperature, the organic phase of bio-oil showed increase in HHV which correlated to the decrease in dianhydromannitol and 2-furyl methyl ketone, as well as to the increase in aromatic compounds such as derivatives of phenol, indole, and naphthalene [191].

Pan et al. [88] investigated the HZSM-5 catalyst-based pyrolysis of microalgae feedstock of *Nannochloropsis* sp. residue. The results indicated that the yield of bio-oil was reduced with the presence of a catalyst; however, the O₂ content was greatly reduced with improved HHV (32.2 MJ/kg). Comparing with direct pyrolysis, bio-oil derived from catalytic process mainly consisted of aromatic carbons. Furthermore, the change of catalyst to feedstock ratio from 0/1 to 1/1, the gas yield increased greatly due to the thermal cracking and secondary reactions catalysed by HZSM-5. A similar investigation was also performed on *Chlorella vulgaris*, as feedstock using the same catalyst (HZSM-5) with promising results [116]. Several types of zeolite-based catalysts (ZSM200, ZSM50, ZYAm, ZYH, ZβAm and ZβH) were applied in the fast pyrolysis of *Arthrospira platensis* at 600 °C [183]. It was found the application of zeolite-based catalyst had apparent impacts on the formation of nitriles, aromatics and cycloalkanes. By increasing the pyrolysis temperature (350 – 600 °C) and catalyst loading (2.1 to 50 wt %/wt%), the setting favoured the productions of aromatics (mono- and

poly-aromatics) and cycloalkanes.

4.1.2. Metal-Based and Ceria-Based catalytic pyrolysis

Zeolite-based catalysts possess great acidic sites on their surface which are preferred features to promote deoxygenation process [179]. However, such an advantageous feature can also be the cause of coke formation on the catalyst. To moderate the acidity in zeolite, transition metals such as Ni, cobalt (Co), molybdenum (Mo), gallium (Ga), palladium (Pd) and others are used as catalyst supports which could inhibit the catalyst deactivation due to the presence of coke [104]. In a recent work, cerium oxide (CeO₂) has gained huge attention in its application for heterogeneous catalysis, due to its diverse configurations in the forms of metal/oxide (conventional), oxide/metal (inverse) and (oxide + metal)/oxide (mixed-metal oxide) [197]. Ceria-based materials can catalyse processes such as CO oxidation, WGS as well as reforming of alcohols, which make them attractive catalysts in pyrolysis process [197].

Conversion of the macroalga, *Gracilaria gracilis* to pyrolytic products was catalytically pyrolysed with different catalysts such as HZSM-5, mesoporous silica (HMS) and their hybrid (ZH) with cobalt-molybdenum (Co-Mo) support [187]. The catalytic pyrolysis studies were performed under different catalysts (HMS, ZSM-5, ZH-10, ZH-20, ZH-30, ZH-40) [187]. The product distributions were summarised in Table 6. Based on the optimised results, ZH composites showed better deoxygenation on acetic acid and formic acid from 9.56 to 8.12 wt%. Overall, CoMo/ZH-20 was found to be most promising catalyst on this form of macroalga pyrolysis with high H₂ selectivity (6.08 mmol/g). Ceria-based catalyst (Ce/ZSM-5, MgCe/ZSM-5, CeNi/ZSM-1) and other metal catalyst (MgNi/ZSM-5) were also synthesised by varying the catalyst concentrations from 1 to 3 mmol in order to investigate their effects on bio-oil yields and compositions derived from *Enteromorpha clathrata* [193]. Among those metal-based catalysts, 1 mmol of MgCe/ZSM-5 produced a relatively higher concentration of C₅ – C₇ compounds, which indirectly reduced the generation of acidic compounds with the highest bio-oil yields (37.45 wt%) compared with other catalysts.

As one of the most common microalgae, *Chlorella vulgaris* was converted into pyrolytic products using Ni-supported zeolite (Si/Al = 30) at the temperature range of 300 – 600 °C with different catalyst to feedstock ratios (5:1, 2:1, 1:1 and 1:2) [104]. Ni-supported zeolite was prepared in two methods, ion-exchange (IE) and wet impregnation (WI), respectively. It was found that IE-based catalyst could reduce oxygenated and acidic compounds whereas WI-based catalyst

Table 6
Catalytic pyrolysis of algal biomass.

Algal Biomass	Type of Pyrolysis	Pyrolysis Parameter	Advanced Setting	Solid Product (wt%)	Liquid Product (wt%)	Gas Product (wt%)	HHV (MJ/kg)	Ref
Macroalgae <i>Laminaria japonica</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): 60 PT (°C): 500 PS (mm): - GF (mL/min):50 of N ₂	Catalyst: Al-SBA-15 Catalyst Dosage: 1 g catalyst: 10 g feedstock Catalyst Loading (wt%): -	42.12	31.2	25.1	-	[185]
<i>Cladophora glomerata</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): - PT (°C): 500 PS (mm): 150 μm GF (mL/min):30 of Ar	Catalyst: Biochar Catalyst Dosage: 0.4 g catalyst: 0.35 g feedstock Catalyst Loading (wt%): -	35	30	35	-	[192]
<i>Gracilaria gracilis</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 500 PS (mm): 150 μm GF (mL/min):30 of Ar	Catalyst: HMS Catalyst Dosage: 0.4 g catalyst: 1 g feedstock Catalyst Loading (wt%): -	35.5	38.65	26.85	-	[187]
<i>Gracilaria gracilis</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 500 PS (mm): 150 μm GF (mL/min):30 of Ar	Catalyst: ZSM-5 Catalyst Dosage: 0.4 g catalyst: 1 g feedstock Catalyst Loading (wt%): -	32.4	33.1	34.5	-	[187]
<i>Gracilaria gracilis</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 500 PS (mm): 150 μm GF (mL/min):30 of Ar	Catalyst: ZH-10 Catalyst Dosage: 0.4 g catalyst: 1 g feedstock Catalyst Loading (wt%): -	34.7	37.3	28	-	[187]
<i>Gracilaria gracilis</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 500 PS (mm): 150 μm GF (mL/min):30 of Ar	Catalyst: ZH-20 Catalyst Dosage: 0.4 g catalyst: 1 g feedstock Catalyst Loading (wt%): -	35.6	37.3	27.1	-	[187]
<i>Gracilaria gracilis</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 500 PS (mm): 150 μm GF (mL/min):30 of Ar	Catalyst: ZH-30 Catalyst Dosage: 0.4 g catalyst: 1 g feedstock Catalyst Loading (wt%): -	37.5	35.4	27.1	-	[187]
<i>Gracilaria gracilis</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 500 PS (mm): 150 μm GF (mL/min):30 of Ar	Catalyst: ZH-40 Catalyst Dosage: 0.4 g catalyst: 1 g feedstock Catalyst Loading (wt%): -	39.6	34.2	26.2	-	[187]
Acid-Washed <i>Saccharina japonica</i>	Catalytic Fast Pyrolysis	HR(°C/min): - Pt (min): - PT (°C): 400–500 PS (mm): 180 – 250 μm GF (mL/min):-	Catalyst: HZSM-5 Catalyst Dosage: - Catalyst Loading (wt%): -	21.7 – 24.2	35.4 – 39.1	39.3 – 40.5	Organic Phase: 25 – 27.2	[191]
<i>Enteromorpha clathrata</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): - PT (°C): 550 PS (mm): 0.3 GF (mL/min): 0.2 N ₂ L/min	Catalyst: Ce/ZSM-5 (1 – 3 mmol) Catalyst Dosage: 1 catalyst: 5 feedstock Catalyst Loading (wt%): -	40.15 – 46.25	33.60 – 36.74	20.15 – 23.11	-	[193]
<i>Enteromorpha clathrata</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): - PT (°C): 550 PS (mm): 0.3 GF (mL/min): 0.2 N ₂ L/min	Catalyst: MgCe/ZSM-5 (1 – 3 mmol) Catalyst Dosage: 1 catalyst: 5 feedstock Catalyst Loading (wt%): -	42.86 – 44.44	37.30 – 37.86	17.70 – 19.84	-	[193]
<i>Enteromorpha clathrata</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): - PT (°C): 550 PS (mm): 0.3 GF (mL/min): 0.2 N ₂ L/min	Catalyst: MgNi/ZSM-5 (1 – 3 mmol) Catalyst Dosage: 1 catalyst: 5 feedstock Catalyst Loading (wt%): -	45.20 – 46.80	35.06 – 35.60	17.60 – 19.34	-	[193]

(continued on next page)

Table 6 (continued)

Algal Biomass	Type of Pyrolysis	Pyrolysis Parameter	Advanced Setting	Solid Product (wt%)	Liquid Product (wt%)	Gas Product (wt%)	HHV (MJ/kg)	Ref
<i>Enteromorpha clathrata</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): - PT (°C): 550 PS (mm): 0.3 GF (mL/min): 0.2 N ₂ L/min	Catalyst: CeNi/ZSM-5 (1 – 3 mmol) Catalyst Dosage: 1 catalyst: 5 feedstock Catalyst Loading (wt%): -	40.80 – 44.79	34.80 – 35.04	18.92 – 24.40	-	[193]
<i>Ulva prolifera</i>	Catalytic Pyrolysis	HR(°C/min): 20 Pt (min): 60 PT (°C): 300 – 450 PS (mm): 0.3 GF (mL/min): 30 of N ₂	Catalyst: ZSM-5, Mordenite, Y-zeolite Catalyst Dosage: 0.2/0.5/1 catalyst: 10 feedstock Catalyst Loading (wt%): -	-	Y-zeolite 41.3	-	Bio-oil: 27.9	[194]
Microalgae <i>Nannochloropsis</i> sp. residue	Catalytic Slow Pyrolysis	HR(°C/min): 10 Pt (min): 120 PT (°C): 300–500 PS (mm): - GF (mL/min):30 of N ₂	Catalyst: HZSM-5 Catalyst Dosage: 1 catalyst: 1 feedstock Catalyst Loading (wt%): -	20.1 – 57.0	30.8 – 45.8	12.9 – 35.7	Bio-oil: 32.2	[88]
<i>Chlorella</i>	Catalytic Slow Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 350–450 PS (mm): - GF (mL/min):100 of Ar	Catalyst: Na ₂ CO ₃ Catalyst Dosage: - Catalyst Loading (wt%): 20	26.9 – 54.4	19.4 – 41.0	25.9 – 34.1	Bio-oil: 32.2	[172]
<i>Chlorella</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): - PT (°C): 500 PS (mm): < 90 μm GF (mL/min):125 of N ₂	Catalyst: Fe-ZSM-5 Catalyst Dosage: - Catalyst Loading (wt%): -	29.7	43.1	27.1	Bio-oil: 26.8	[163]
<i>Chlorella</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): - PT (°C): 500 PS (mm): < 90 μm GF (mL/min):125 of N ₂	Catalyst: Cu-ZSM-5 Catalyst Dosage: - Catalyst Loading (wt%): -	27.9	46.9	24.6	Bio-oil: 27.5	[163]
<i>Chlorella</i>	Catalytic Pyrolysis	HR(°C/min): - Pt (min): - PT (°C): 500 PS (mm): < 90 μm GF (mL/min):125 of N ₂	Catalyst: Ni-ZSM-5 Catalyst Dosage: - Catalyst Loading (wt%): -	30.1	45.1	25.4	Bio-oil: 28.2	[163]
<i>Pavlova</i>	Catalytic Fast Pyrolysis	HR(°C/min): 100 Pt (min): 60 PT (°C): 450–550 PS (mm): 105–174 μm GF (mL/min): 545 of N ₂	Catalyst: CeO ₃ Catalyst Dosage: 1 catalyst: 1 feedstock Catalyst Loading (wt%):-	36.23 – 47.96	15.10 – 21.07	36.94 – 45.92	Biochar: 5.93 Bio-oil: 35.56	[186]
<i>Pavlova</i>	Catalytic Fast Pyrolysis	HR(°C/min): 100 Pt (min): 60 PT (°C): 450–550 PS (mm): 105–174 μm GF (mL/min): 545 of N ₂	Catalyst: TiO ₃ Catalyst Dosage: 1 catalyst: 1 feedstock Catalyst Loading (wt%):-	37.76 – 48.18	14.4 – 20.04	37.38 – 45.10	Biochar: 6.94 Bio-oil: 35.21	[186]
<i>Pavlova</i>	Catalytic Fast Pyrolysis	HR(°C/min): 100 Pt (min): 60 PT (°C): 450–550 PS (mm): 105–174 μm GF (mL/min): 545 of N ₂	Catalyst: Ce/TiO ₃ Catalyst Dosage: 1 catalyst: 1 feedstock Catalyst Loading (wt%):-	36.36 – 47.44	15.46 – 21.67	37.10 – 46.26	Biochar: 6.74 Bio-oil: 37.07	[186]
<i>Pavlova</i>	Catalytic Fast Pyrolysis	HR(°C/min): 100 Pt (min): 60 PT (°C): 450–550 PS (mm): 105–174 μm GF (mL/min): 545 of N ₂	Catalyst: Ni/TiO ₃ Catalyst Dosage: 1 catalyst: 1 feedstock Catalyst Loading (wt%):-	35.90 – 47.66	15.30 – 22.55	37.04 – 45.39	Biochar: 4.84 Bio-oil: 36.95	[186]
<i>Pavlova</i>	Catalytic Fast Pyrolysis	HR(°C/min): 100 Pt (min): 60 PT (°C): 450–550	Catalyst: Co/TiO ₃ Catalyst Dosage: 1 catalyst: 1 feedstock	37.98 – 48.28	15.24 – 20.4	36.48 – 44.61	Biochar: 5.79	[186]

(continued on next page)

Table 6 (continued)

Algal Biomass	Type of Pyrolysis	Pyrolysis Parameter	Advanced Setting	Solid Product (wt%)	Liquid Product (wt%)	Gas Product (wt%)	HHV (MJ/kg)	Ref
		PS (mm): 105–174 μm GF (mL/min): 545 of N_2	Catalyst Loading (wt%):-				Bio-oil: 36.33	
<i>Cynobacteria</i>	Catalytic Slow Pyrolysis	HR($^{\circ}\text{C}/\text{min}$): 10 Pt (min): 30 PT ($^{\circ}\text{C}$): 550 PS (mm): - GF (mL/min): 40 of N_2	Catalyst: MgAl-LDH/ZSM-5 Catalyst Dosage: 1 catalyst: 1 feedstock Catalyst Loading (wt%):-	23.8	41.1	34.9	Bio-oil: 37.16	[66]
<i>Cynobacteria</i>	Catalytic Slow Pyrolysis	HR($^{\circ}\text{C}/\text{min}$): 10 Pt (min): 30 PT ($^{\circ}\text{C}$): 550 PS (mm): - GF (mL/min): 40 of N_2	Catalyst: MgAl-LDO Catalyst Dosage: 1 catalyst: 1 feedstock Catalyst Loading (wt%):-	24.2	35.9	39.3	Bio-oil: 38.2	[66]
<i>Cynobacteria</i>	Catalytic Slow Pyrolysis	HR($^{\circ}\text{C}/\text{min}$): 10 Pt (min): 30 PT ($^{\circ}\text{C}$): 550 PS (mm): - GF (mL/min): 40 of N_2	Catalyst: MgO/ZSM-5 Catalyst Dosage: 1 catalyst: 1 feedstock Catalyst Loading (wt%):-	22.0	37.1	40.6	Bio-oil: 38.0	[66]
<i>Arthrospira plantensis</i>	Catalytic Fast Pyrolysis	HR($^{\circ}\text{C}/\text{min}$): 100 Pt (min): 30 PT ($^{\circ}\text{C}$): 400 – 700 PS (mm): - GF (mL/min): 30 of Ar	Catalyst: Ni/HMS-ZSM5 Catalyst Dosage: 1 catalyst: 0.5 feedstock Catalyst Loading (wt%):-	32.52	33.44	27.67	-	[195]
<i>Arthrospira plantensis</i>	Catalytic Fast Pyrolysis	HR($^{\circ}\text{C}/\text{min}$): 100 Pt (min): 30 PT ($^{\circ}\text{C}$): 400 – 700 PS (mm): - GF (mL/min): 30 of Ar	Catalyst: Fe/HMS-ZSM5 Catalyst Dosage: 1 catalyst: 0.5 feedstock Catalyst Loading (wt%):-	30.01	38.15	58.94	-	[195]
<i>Arthrospira plantensis</i>	Catalytic Fast Pyrolysis	HR($^{\circ}\text{C}/\text{min}$): 100 Pt (min): 30 PT ($^{\circ}\text{C}$): 400 – 700 PS (mm): - GF (mL/min): 30 of Ar	Catalyst: Ce/HMS-ZSM5 Catalyst Dosage: 1 catalyst: 0.5 feedstock Catalyst Loading (wt%):-	31.80	36.41	28.58	-	[195]
<i>Oscillatoria</i>	Catalytic Pyrolysis	HR($^{\circ}\text{C}/\text{min}$): 20 Pt (min): 120 PT ($^{\circ}\text{C}$): 550 PS (mm): 75 – 250 μm GF (mL/min): -	Catalyst: TiO_2 , ZnO Catalyst Dosage: 1 TiO_2 : 1 ZnO Catalyst Loading (wt%): -	43.05	33.33	26.25	Bio-oil: 16.66 Biochar: 16.14	[196]

Note: HR = heating rate; Pt = pyrolysis/ process time; PT = pyrolysis/ process temperature; PS = particle size; GF = sweeping gas type and flowrate.

could eliminate nitrogenates as well as improve hydrocarbon ratio. Nonetheless, both forms of catalysts were found to have no apparent impacts on the yield values but rather on the composition of bio-oil. Based on the modification of metal-supported zeolite catalysts (Fe-ZSM-5, Cu-ZSM-5 and Ni-ZSM-5), microalga *Chlorella* catalytic pyrolysis generally reduced the liquid products (especially the bio-oil fraction), but increased both char and gas products as well as improved the HHV values of the bio-oil produced [163]. From the coke formation study, Fe-based modification catalysed highest dehydrogenation process among those metal-supported catalyst which in turn generated the most coke. Other forms of metal-supported catalyst (Ni/HMS-ZSM5, Fe/HMS-ZSM5 and Ce/HMS-ZSM5) were utilised in *Arthrospira plantensis* pyrolysis also showed similar products distribution trend [195]. In a Py-GC/MS study, the prepared catalyst of Co-Mo/ γ - Al_2O_3 was used for the pyrolysis of *Nannochloropsis oculata* [198]. The results revealed that the catalytic formation pathways included dehydration, isomerisation, ketonisation resulting in amide and carboxylic acids from protein and lipid of the feedstock. Nonetheless, compared with the non-catalytic study, the bio-oil showed lower moisture content with higher HHVs (33 – 39 MJ/kg). *Pavlova* microalga was studied as titania (Ti)-based catalytic pyrolysis feedstock [186]. The Ti-based catalyst was modified

with ceria, Ni and Co, respectively. Among these catalysts, Ni/ TiO_2 revealed to be the most resistance against coke formation with enhanced cracking activity. However, based on Table 6, the product distribution varied according to the catalysts used and pyrolysis temperature. It was observed that within the pyrolysis temperature of 450 – 550 $^{\circ}\text{C}$, Ni/ TiO_2 catalytic pyrolysis produced the most liquid fraction while Co/ TiO_2 catalytic pyrolysis generated the most solid products whereas Ce/ TiO_2 catalytic pyrolysis synthesised the most gas products. However, in term of HHV, Ce/ TiO_2 -based bio-oil was among the highest (37.07 MJ/kg). Despite most catalysts focus on the deoxygenation process, enhancement of denitrogenation is equally crucial. A Mg-Al layered double oxide/ ZSM composites was produced as a catalyst to aid the catalytic pyrolysis of cyanobacteria to focus on the less nitrogenous bio-oil generation [66]. The catalysts were prepared in several stages resulting in intermediate catalysts such as MgAl4-LDO and MgO/ZSM-5. Through the optimisation of several parameters such as pyrolysis temperature, heating rate and catalyst/feedstock ratio, the highest yield of liquid products was generated at 41.1% with the pyrolysis conditions as follows: PT: 550 $^{\circ}\text{C}$; HR: 10 $^{\circ}\text{C}/\text{min}$; catalyst:feedstock ratio = 0.75 with the catalyst of MgAl-LDO/ZSM-5 (Mg/Al = 4). Ceria-based catalysts (CeO_2 , Ce/ Al_2O_3 , NiCe/ Al_2O_3 , MgCe/ Al_2O_3 , Ce/

Table 7
Co-pyrolysis of algal biomass.

Algal Biomass	Type of Pyrolysis	Pyrolysis Parameter	Advanced Setting	Solid Product (wt %)	Liquid Product(wt %)	Gas Product (wt %)	HHV (MJ/kg)	Ref
Macroalgae <i>Laminaria japonica</i>	Co-Pyrolysis	HR(°C/min): - Pt (min): 60 PT (°C): 500 PS (mm): - GF (mL/min):50 of N ₂	Co-Material: Polypropylene (PP) Co-pyrolysis ratio: 2.5 g PP: 2.5 g feedstock	19.9	60.4	19.9	-	[185]
<i>Enteromorpha prolifera</i>	Co-Pyrolysis	HR(°C/min): 5 – 25 Pt (min): - PT (°C): 400–600 PS (mm): 0.18–0.45 GF (mL/min):100 of N ₂	Co-Material: Rice Husk Co-pyrolysis ratio: 0 to 100% of rice husk in mixture	22.8 – 31.4	39.2 – 47.2	28.7 – 31.4	Bio-oil: 25.5 – 30.6 Biochar: 26.9 – 31.6	[212]
<i>Sargassum</i>	Co-Pyrolysis	HR(°C/min): 10 Pt (min): - PT (°C): 400–700 PS (mm): 3–4 GF (mL/min):-	Co-Material: Polystyrene Co-pyrolysis ratio: 5 to 33% of polystyrene in mixture	31 – 40	19 – 48	24 – 28	Bio-oil: 25.5 – 30.6 Biochar: 26.9 – 31.6	[214]
<i>Laminaria japonica</i>	Catalytic Co-Pyrolysis	HR(°C/min): - Pt (min): 60 PT (°C): 500 PS (mm): - GF (mL/min):50 of N ₂	Co-Material: Polypropylene (PP) Co-pyrolysis ratio: 2.5 g PP: 2.5 g feedstock Catalyst: Al-SBA-15 Catalyst Dosage: 1 g catalyst: 10 g feedstock Catalyst Loading (wt%): -	20.5	57.1	22.6	-	[185]
Microalgae <i>Chlorella pyrenoidosa</i>	Co-Pyrolysis	HR(°C/min): - Pt (min): 10 – 120 PT (°C): 290 – 370 PS (mm): - GF (mL/min):-	Co-Material: Waste Rubber Tyre (WRT) Co-pyrolysis ratio: 5/0 – 0:5 (co-feedstock: feedstock) Solvent: feedstock: 5:5 – 30: 5	19 – 49.7	37.6 – 65.4	4.6 – 14	Bio-oil: 33.68 – 42.90	[204]
<i>Nannochloropsis</i> sp.	Co-Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 600 PS (mm): - GF (mL/min):150 of Ar	Co-Material: Polyethylene (LDPE) Co-pyrolysis ratio: 0 to 100% of LDPE in mixture	19.53	65.17	15	-	[215]
<i>Spirulina platensis</i>	Co-Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 600 PS (mm): < 120 μm GF (mL/min):200 of Ar	Co-Material: Bamboo waste Co-pyrolysis ratio: 1 bamboo waste :1 feedstock	23	68	12	-	[213]
<i>Nannochloropsis</i> sp.	Co-Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 600 PS (mm): < 120 μm GF (mL/min):200 of Ar	Co-Material: Bamboo waste Co-pyrolysis ratio: 1 bamboo waste :1 feedstock	22	67	13	-	[213]
<i>Spirulina platensis</i>	Catalytic Co-Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 600 PS (mm): < 120 μm GF (mL/min):200 of Ar	Co-Material: Bamboo waste Co-pyrolysis ratio: 1 bamboo waste :1 feedstock Catalyst: Biochar Catalyst Dosage: 1 g catalyst: 1 g feedstock Catalyst Loading (wt%): -	23	56	20	-	[213]
<i>Nannochloropsis</i> sp.	Catalytic Co-Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 600 PS (mm): < 120 μm GF (mL/min):200 of Ar	Co-Material: Bamboo waste Co-pyrolysis ratio: 1 bamboo waste :1 feedstock Catalyst: Biochar Catalyst Dosage: 1 g catalyst: 1 g feedstock Catalyst Loading (wt%): -	22	53	22	-	[213]

(continued on next page)

Table 7 (continued)

Algal Biomass	Type of Pyrolysis	Pyrolysis Parameter	Advanced Setting	Solid Product (wt %)	Liquid Product(wt %)	Gas Product (wt %)	HHV (MJ/kg)	Ref
<i>Nannochloropsis</i> sp.	Microwave-Assisted Catalytic Co-Pyrolysis	HR(°C/min): - Pt (min): 30 PT (°C): 450–650 PS (mm): 40 mesh GF (mL/min): Vacuum	Co-Material: Scum Co-pyrolysis ratio: 4:1; 2:1; 1:1; 1:2; 1:4 (feedstock: co-feedstock) Catalyst: ZSM5 Catalyst Dosage: 1:2; 1:1; 2:1 (catalyst: feedstock) Catalyst Loading (wt%):	33.0 – 53.8	16.7 – 26.7	30.3 – 45.7	–	[205]

Note: HR = heating rate; Pt = pyrolysis/ process time; PT = pyrolysis/ process temperature; PS = particle size; GF = sweeping gas type and flowrate.

ZrO₂, NiCe/ZrO₂ and MgCe/ZrO₂) were applied in the catalytic pyrolysis of several microalgae, *Nannochloropsis*, *Tetraselmis* sp., *Isochrysis* sp., *Thalassiosira weissflogii* [179,199,200]. Overall, ceria-based catalyst showed better denitrogenation ability compared with zeolite-based catalyst, with higher yield and better HHV of bio-oils.

4.1.3. Other catalytic pyrolysis

Carbon-based catalyst can be in the form of pure biochar or activated carbon. *Cladophora glomerata*, a type of green macroalga, was applied as catalytic pyrolysis feedstock with self-synthesised and self-sustained biochar catalyst [192]. As observed from the results, the use of biochar catalyst only promoted the formation of syngas products from 22 to 35 wt% while other products diminished considerably. More importantly, the work successfully improved the H₂ selectivity and production. Despite the yield reduction of bio-oil, catalytic pyrolysis by biochar enhanced phenols production greatly in bio-oil.

To overcome the acidity of the algal bio-oil as well as to encourage the decarboxylation process (CO₂ formation), a basic catalyst (Na₂CO₃) was used for the pyrolysis of *Chlorella* at varying temperatures [12,172]. Remarkably, the acetic acid in bio-oil decreased about 3 times resulting in low acidity value while aromatic hydrocarbons increased from 16.5 to 25.0 % when compared to direct pyrolysis. *Chlamydomonas reinhardtii* as algal feedstock was exposed to basic catalytic effect from hydrotalcite (Mg₆Al₂(OH)₁₆CO₃·4H₂O) [12]. The use of catalyst reduced the degradation temperature as well as the activation energy. Hydrotalcite, as a basic catalyst, encouraged the formation of hydrocarbon compounds, reduced some amount of oxygenates but greatly inhibited the formation of nitrogenates.

4.2. Co-Pyrolysis

The use of two or more biomasses as feedstock at a fixed and optimised ratio at a time can be regarded as co-pyrolysis which shares similar experiment settings with other form of pyrolysis [201,202]. Co-pyrolysis explores the synergistic effects and interactions between two or more materials under inert conditions. The synergistic effect is exerted when two or more biomasses interact which can generate greater impacts [203]. Due to the simplicity of the synthesis procedure which involves only blending and mixing, typically, no modification of existing equipment is required which can save equipment costing [202]. By using the suitable co-feedstock, both quantity and quality of the bio-oil can be improved significantly [202]. Technologically, co-pyrolysis can be performed without the requirement of catalysts or solvents [203]. However, in a recent development, catalytic or solvent co-pyrolysis seems to be viable and attractive options to improve the pyrolytic products [204].

Algae biomass can be directly co-pyrolysed with other biomasses and wastes based on the effective hydrogen index (EHI), which can be computed as follows (Eq. (1)) [33,205]:

$$EHI = \frac{H - 2O - 3N - 2S}{C} \quad (1)$$

where H, O, N, S and C represents the number of moles of hydrogen, oxygen, nitrogen, sulphur and carbon in the co-feedstock, respectively. For co-pyrolysis of algal biomass, its H₂-deficient composition as indicated by the low effective hydrogen index (EHI < 0.3) can have adverse effects in generating hydrocarbon-based compounds [206]. Therefore, co-pyrolysis with materials of high EHI such as alcohol, esters, polyethylene and others (EHI ~ 2) might promote effective reaction with algal biomass [205,207]. H/C ratio can also be used as an indicator of hydrogen content whereby a higher ratio is desirable as co-feedstock [208]. Moreover, higher C and H contents can encourage the generation of high HHV fuel and the effectiveness of their atomic exchange during the co-pyrolysis which can result in a more stable formation of intermediates [206]. As the direct pyrolysis of algal biomass can be challenging at times due to their high AC and moisture content, co-pyrolysis can overcome these issues by incorporating other biomass, wastes as well as plastics into the pyrolysis process. From waste management perspective, co-pyrolysis also helps to reduce wastes generated from other industries [209].

4.2.1. Co-Pyrolysis with biomass

As summarised in Table 7, *Enteromorpha clathrata* (EC) and *Sargassum fusiforme* (SF) were blended with risk husk (RH) biomass at 50:50 ratio [210]. The TG-FTIR analysis indicated that activation energy for EC/RH (84 – 107.39 KJ/mol) and SF/RH (77.46 – 114.85 KJ/mol) were reduced compared to their pristine forms (89.30 – 229.9 KJ/mol). This signifies that the co-pyrolysis enhances the synthesis process which requires lower energy input. *Enteromorpha prolifera* was co-pyrolysed with sugarcane bagasse as reported in the work of Hua and Li [211]. The optimised bio-oil yield (56.12 wt%) was at 50:50 blend ratio with 26.4 MJ/kg of HHV. The use of sugarcane bagasse as co-feedstock was able to reduce oxygenates species from the bio-oil by lowering the concentrations of acids, aldehydes, phenolic compounds and ketones. Desirable hydrocarbons, alcohols and esters were also detected in the bio-oil composition as synthesised from the co-pyrolysis of *Enteromorpha prolifera* and sugarcane bagasse. In a recent study, co-pyrolysis optimisation of macroalgae (*Enteromorpha prolifera*) with lignocellulosic biomass (RH) was performed using response surface methodology with central composite circumscribed model [212]. The results showed that all three parameters (co-material/biomass ratio, temperature and heating rate) were major factors which influenced the products' yields and HHV. The model optimisation further derived the maximum oil production at the following conditions: 455 °C, 20 °C/min and 80% of RH in the mixture. Both bio-oil (25.5 – 30.6 MJ/kg) and biochar (26.9 – 31.6 MJ/kg) produced exhibited remarkable HHV values suitable for power generation.

The use of two microalgae with very different chemical constituents was attempted in a co-pyrolysis process [208]. *Isochrysis* (lipid-rich alga) was co-pyrolysed with *Chlorella* (protein-rich alga) in the temperature range of 475 – 500 °C. The findings revealed that the yields of pyrolytic products were not greatly affected. However, the acidity of bio-oil could be reduced based on the elimination of carboxylic acids. Azizi et al. [206] revealed that the co-pyrolysis of three materials

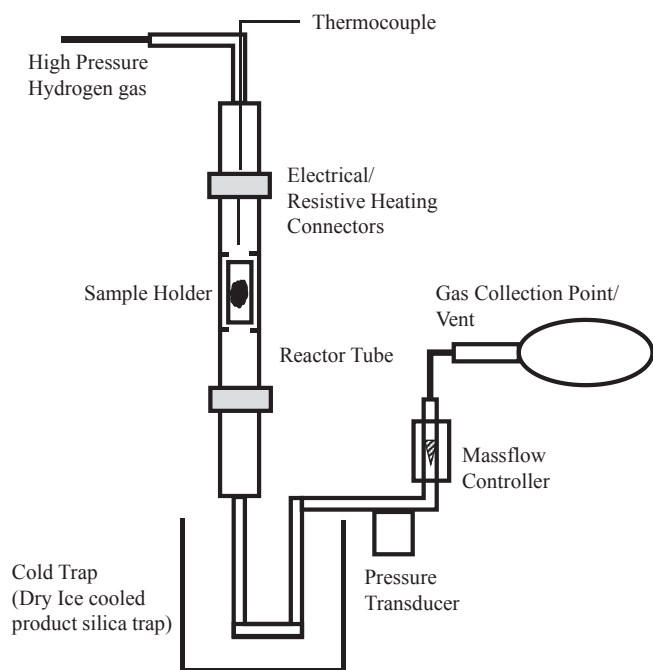


Fig. 4. General schematic diagram of hydro-pyrolysis [30].

(*Chlorella vulgaris*, wood and polymer) showed distinctive thermal degradation by varying the heating rates from 10 to 40 °C/min. Basically, microalgae and wood co-pyrolysed at the earlier stage of the pyrolysis followed by the degradation of the polymer. From a recent work by Chen et al. [213], it was found that co-pyrolysis of microalgae (*Spirulina sp.* or *Nannochloropsis sp.*) with bamboo could generate high bio-oil products (51 – 52 wt%). Nonetheless, under the biochar catalytic co-pyrolysis process, the bio-oil fractions reduced to 36 – 37 wt%. This was mainly due to the catalytic reactions that favoured formation of gas and water products. From the studies of different parameters, the synergistic interaction between feedstock and other biomass can be greatly influenced by the physicochemical properties of biomass as well as the selection of catalyst.

4.2.2. Co-Pyrolysis with wastes and other materials

Macroalgae representative (*Laminaria japonica*) was co-pyrolysed with polypropylene (PP) with and without catalyst (Al-SBA-15) [185]. Concerning its direct pyrolysis, a co-pyrolysis process greatly changed the product distribution by reducing the char yield and gas yield, but increasing the liquid yield up to two times. By comparing with catalytic co-pyrolysis process, the char and gas products were slightly improved while the overall liquid product was reduced from 60.4 to 57.1 wt%. Thus, the synergistic interaction can be affected by the presence of catalyst in this case.

Microalgae (*Nannochloropsis sp.*) co-pyrolysed with plastics (LDPE) at different mixing ratio was performed to study the production trends [215]. When the LDPE wt% was increased in the mixture, the gas product yields remained also constant; however, a significant increase in liquid products with great reduction in solid products were observed. This might be due to the volatiles contained in LDPE which could crack into both liquid and gas products. With LDPE addition, undesired oxygenates and nitrogenates were removed from the liquid products. In some studies, microalgae was blend with coal for co-pyrolysis, as a mean to reduce CO₂ emission [204,216–218]. By changing the temperature range (200 – 1000 °C), the synergistic interaction between *Chlorococcum humicola* and Victorian Brown coal was investigated [217]. However, no apparent interactive effect was observed between these two materials. In another study, *Spirulina* co-pyrolysed with low-rank coal revealed the synergistic mechanism lied on the integrative

action of glycine, medium chain triglyceride and starch [216]. Since co-pyrolysis can handle a wide range of materials as long as the EHI of the co-feedstock fulfils the requirement, wastes such scum can be co-pyrolysed with microalgae [205]. More importantly, the mixing ratio (microalgae: scum) can influence the EHI values significantly. With higher scum content, the EHI also increased from 0.4 to 1.4. It was found that only when EHI value > 7, the synergistic effect between microalgae and scum would be significant. Furthermore, it was found that such co-pyrolysis process favoured the formation of syngas (30.3 – 45.7 wt%) and char product (33 – 53.8 wt%) compared to liquid product (16.7 – 26.7 wt%). Sewage sludge was also utilised as a co-feedstock with *Isochrysis sp* [219]. Co-pyrolysis mechanistic reactions for microalgae and sewage sludge were contributed by random nucleation and growth reaction when below 550 °C. It was determined that N-heterocyclic compounds were the dominant species in the bio-crude. Waste rubber tyre (WRT) can be co-pyrolysed with microalgae (*Chlorella pyrenoidosa*) under the assistance of solvent (ethanol) [204]. Extensive parametric studies were performed at the following conditions: reaction temperature (290 – 370 °C), time (10 – 120 min), WRT/microalgae mass ratio (R/M, 5/0 – 0:5), and ethanol/feedstock ratio (EtOH/(R + M), 5:5 – 30:5). The presence of ethanol solvent provided lower effective co-pyrolysis temperature requirement favouring the overall synthesis process. Based on the results, a positive synergistic relationship (37.8%) was observed between WRT and microalgae at the R/M ratio of 1:1. The outcome of the pyrolytic products were energy-dense (33.68 – 42.90 MJ/kg) with high bio-oil yield (65.4 wt%).

4.3. Hydro-pyrolysis

Among those pyrolysis technologies, hydro-pyrolysis possesses very different system setup. As observed, the reactor setup of hydro-pyrolysis (Fig. 4) differs considerably from conventional pyrolysis setup. The relatively new pyrolysis technique applies the conversion process on the algal biomass with the utilisation of pressurised hydrogen or hydrogen-based (H₂) technologies to produce mainly high quality pyrolytic oil [30]. The advantages of using H₂-based technology include the reduction of O₂ content in bio-oil, the inhibition of char formation and the introduction of minor H₂ content in pyrolytic liquid products [28,31]. In addition to those advantages, the produced hydrocarbons from hydro-pyrolysis also show better stability in structural preservation [31].

As summarised in Table 8, the study on sole hydro-pyrolysis macroalgae is not available in the literature. However, a co-process of hydro-pyrolysis and hydroconversion through catalytic integration was led by Gas Technology Institute at pilot scale on natural-occurring ocean seaweed [220]. By applying CR1-2411 as catalyst and low pressure range (1.4 – 2.3 MPa), high yields (27 – 36 wt%) of bio-oil were produced with extensive removal of O₂ content due to the deoxygenation catalytic effects, whereby its O content was among the lowest (23.6 wt %). Furthermore, the composition of the gasoline derived from this process was analysed and found to be mainly made up of n-paraffin, i-paraffin, naphthenes and aromatics. Catalytic hydro-pyrolysis of macroalgae of *Enteromorpha prolifera*, *Laminaria japonica* Aresch, *Lemna minor* and *Porphyra yezoensis* were compared with catalytic co-hydro-pyrolysis with used engine oil (UEO) [221]. Generally, the catalytic co-hydro-pyrolysis products showed higher bio-oil yields (44.62 – 49.80 wt%) with reduced biochar yields (14.25 – 19.86 wt%) as compared to the bio-oil (12.89 – 22.29 wt%) and biochar (16.17 – 38.05 wt%) yields of catalytic hydro-pyrolysis products. A slight improvement was also observed on HHV of macroalgae-based bio-oil derived from catalytic co-hydro-pyrolysis of macroalgae feedstock with UEO. Based on the outcome, the removal of oxygenates from macroalgae induced by hydro-pyrolysis was inherently easier compared to microalgae. From the boiling point analysis, macroalgae-based bio-oils produced from direct hydro-pyrolysis contained lower naphtha fraction (50 – 140 °C), higher jet fuel fraction (140 – 230 °C) and lower diesel fraction (260 – 350 °C) except for *Porphyra yezoensis*, when compared to bio-oils produced from

Table 8
Hydrolysis of algal biomass.

Algal Biomass	Type of Pyrolysis	Pyrolysis Parameter	Advanced Setting	Solid Product (wt %)	Liquid Product (wt %)	Gas Product (wt %)	HHV (MJ/kg)	Ref
Macroalgae <i>Natural ocean seaweed</i>	Catalytic Hydrolysis/ Hydroconversion	HR(C/min): - Pt (min): - PT (C): 340–470 PS (mm): -	Applied Pressure (MPa): 1.4 – 2.3 H ₂ Catalyst: CR1-2411 Catalyst Loading (wt%): 1 – 60	6 – 23	27 – 36	19.6 – 22.7	-	[220]
<i>Enteromorpha prolifera</i>	Catalytic Hydrolysis	HR(C/min): - Pt (min): 240 PT (C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): 6.0 H ₂ Catalyst: Pt/C Catalyst Dosage: 0.3 g catalyst: 3 g feedstock Catalyst Loading (wt%): 10	38.05	12.89	6.33	Bio-oil: 46.35	[221]
<i>Enteromorpha prolifera</i> + Used Engine Oil	Catalytic Co-Hydrolysis	HR(C/min): - Pt (min): 240 PT (C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): H ₂ (1.4 – 2.3) Catalyst: Pt/C Catalyst Dosage: 0.6 g catalyst: 3 g feedstock: 3 g co-biomass Catalyst Loading (wt%): 10	19.86	45.88	6.00	Bio-oil: 48.16	[221]
<i>Laminaria japonica Aresch</i>	Catalytic Hydrolysis	HR(C/min): - Pt (min): 240 PT (C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): 6.0 H ₂ Catalyst: Pt/C Catalyst Dosage: 0.3 g catalyst: 3 g feedstock Catalyst Loading (wt%): 10	32.95	18.12	15.00	Bio-oil: 44.09	[221]
<i>Laminaria japonica Aresch</i> + Used Engine Oil	Catalytic Co-Hydrolysis	HR(C/min): - Pt (min): 240 PT (C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): H ₂ (1.4 – 2.3) Catalyst: Pt/C Catalyst Dosage: 0.6 g catalyst: 3 g feedstock: 3 g co-biomass Catalyst Loading (wt%): 10	15.83	47.29	11.59	Bio-oil: 47.63	[221]
<i>Lemna minor</i>	Catalytic Hydrolysis	HR(C/min): - Pt (min): 240 PT (C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): 6.0 H ₂ Catalyst: Pt/C Catalyst Dosage: 0.3 g catalyst: 3 g feedstock Catalyst Loading (wt%): 10	25.60	22.29	7.50	Bio-oil: 45.19	[221]
<i>Lemna minor</i> + Used Engine Oil	Catalytic Co-Hydrolysis	HR(C/min): - Pt (min): 240 PT (C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): H ₂ (1.4 – 2.3) Catalyst: Pt/C Catalyst Dosage: 0.6 g catalyst: 3 g feedstock: 3 g co-biomass Catalyst Loading (wt%): 10	14.25	49.80	5.34	Bio-oil: 47.62	[221]
<i>Porphyra yezoensis</i>	Catalytic Hydrolysis	HR(C/min): - Pt (min): 240 PT (C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): 6.0 H ₂ Catalyst: Pt/C Catalyst Dosage: 0.3 g catalyst: 3 g feedstock Catalyst Loading (wt%): 10	16.17	21.37	9.01	Bio-oil: 45.35	[221]
<i>Porphyra yezoensis</i> + Used Engine Oil	Catalytic Co-Hydrolysis	HR(C/min): - Pt (min): 240 PT (C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): H ₂ (1.4 – 2.3) Catalyst: Pt/C Catalyst Dosage: 0.6 g catalyst: 3 g feedstock: 3 g co-biomass Catalyst Loading (wt%): 10	15.07	44.62	7.00	Bio-oil: 48.13	[221]

(continued on next page)

Table 8 (continued)

Algal Biomass	Type of Pyrolysis	Pyrolysis Parameter	Advanced Setting	Solid Product (wt %)	Liquid Product (wt %)	Gas Product (wt %)	HHV (MJ/kg)	Ref
Microalgae <i>Chlorella pyrenoidosa</i>	Hydropyrolysis	HR(°C/min): - Pt (min): 5 – 120 PT (°C): 150 – 450 PS (mm): -	Applied Pressure (MPa): H ₂ (1 atm – 8)	12.3 – 74.0	12.2 – 53.2	2.2 – 21.2	Bio-oil: 32.8 – 38.9	[222]
<i>Oscillatoria</i>	Catalytic Hydropyrolysis	HR(°C/min): 20 Pt (min): 120 PT (°C): 550 PS (mm): 75 – 250 μm	Applied Pressure (MPa): - Catalyst: TiO ₂ , ZnO Catalyst Dosage: 1 TiO ₂ : 1 ZnO Catalyst Loading (wt%): -	44.14	31.94	23.92	Bio-oil: 16.66 Biochar: 16.14	[196]
<i>Chlorella pyrenoidosa</i>	Catalytic Hydropyrolysis	HR(°C/min): - Pt (min): 20 – 240 PT (°C): 200 – 410 PS (mm): -	Applied Pressure (MPa): H ₂ (2 – 10) Catalyst: Pd/C, Pt/C, Pt/C sulfided, Ru/C, Rh/C, Mo ₂ C, MoS ₂ , CoMo/γ-Al ₂ O ₃ , activated carbon Catalyst Dosage: 0.2 g catalyst : 2.0 g feedstock Catalyst Loading (wt%): 1 – 60	-	42.9 – 52.6	-	Bio-oil: 33.9 – 39.3	[190]
Microalgae mixture (27 Chlorophyta, 6 diatoms, 1 dinoflagellate, 11 cyanobacteria, 7 Euglenophycota, 1 Euglenozoa)	Catalytic Hydropyrolysis/ Hydroconversion	HR(°C/min): - Pt (min): - PT (°C): 340–470 PS (mm): -	Applied Pressure (MPa): 1.4 – 2.3 Catalyst: CR1-2411 Catalyst Dosage: -	1.1 – 5.2	46	20	-	[220]
<i>Nannochloropsis</i> species	Catalytic Hydropyrolysis	HR(°C/min): - Pt (min): 240 PT (°C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): 6.0 H ₂ Catalyst: Pt/C Catalyst Dosage: 0.3 g catalyst: 3 g feedstock Catalyst Loading (wt%): 10	15.77	39.20	5.00	Bio-oil: 45.05	[221]
<i>Nannochloropsis</i> species + Used Engine Oil	Catalytic Co-Hydropyrolysis	HR(°C/min): - Pt (min): 240 PT (°C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): H ₂ (1.4 – 2.3) Catalyst: Pt/C Catalyst Dosage: 0.6 g catalyst: 3 g feedstock: 3 g co-biomass Catalyst Loading (wt%): 10	9.45	52.88	4.91	Bio-oil: 47.35	[221]
<i>Chlorella pyrenoidosa</i>	Catalytic Hydropyrolysis	HR(°C/min): - Pt (min): 240 PT (°C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): 6.0 H ₂ Catalyst: Pt/C Catalyst Dosage: 0.3 g catalyst: 3 g feedstock Catalyst Loading (wt%): 10	6.95	33.09	7.67	Bio-oil: 46.44	[221]
<i>Chlorella pyrenoidosa</i> + Used Engine Oil	Catalytic Co-Hydropyrolysis	HR(°C/min): - Pt (min): 240 PT (°C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): H ₂ (1.4 – 2.3) Catalyst: Pt/C Catalyst Dosage: 0.6 g catalyst: 3 g feedstock: 3 g co-biomass Catalyst Loading (wt%): 10	6.79	54.98	7.83	Bio-oil: 46.83	[221]
<i>Spirulina platensis</i>	Catalytic Hydropyrolysis	HR(°C/min): - Pt (min): 240 PT (°C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): 6.0 H ₂ Catalyst: Pt/C Catalyst Dosage: 0.3 g catalyst: 3 g feedstock Catalyst Loading (wt%): 10	16.45	33.45	5.50	Bio-oil: 40.62	[221]

(continued on next page)

Table 8 (continued)

Algal Biomass	Type of Pyrolysis	Pyrolysis Parameter	Advanced Setting	Solid Product (wt %)	Liquid Product (wt %)	Gas Product (wt %)	HHV (MJ/kg)	Ref
<i>Spirulina platensis</i> + Used Engine Oil	Catalytic Co-Hydrolysis	HR(C/min): - Pt (min): 240 PT (°C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): H ₂ (1.4 – 2.3) Catalyst: Pt/C Catalyst Dosage: 0.6 g catalyst: 3 g feedstock: 3 g co-biomass Catalyst Loading (wt%): 10	8.29	50.88	7.67	Bio-oil: 46.98	[221]
<i>Schizochytrium limacinum</i>	Catalytic Hydrolysis	HR(C/min): - Pt (min): 240 PT (°C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): 6.0 H ₂ Catalyst: Pt/C Catalyst Dosage: 0.3 g catalyst: 3 g feedstock Catalyst Loading (wt%): 10	6.35	39.20	8.67	Bio-oil: 45.84	[221]
<i>Schizochytrium limacinum</i> + Used Engine Oil	Catalytic Co-Hydrolysis	HR(C/min): - Pt (min): 240 PT (°C): 400 – 450 PS (mm): < = 100 mesh	Applied Pressure (MPa): H ₂ (1.4 – 2.3) Catalyst: Pt/C Catalyst Dosage: 0.6 g catalyst: 3 g feedstock: 3 g co-biomass Catalyst Loading (wt%): 10	6.36	58.68	3.67	Bio-oil: 47.53	[221]

Note: HR = heating rate; Pt = pyrolysis/ process time; PT = pyrolysis/ process temperature; PS = particle size.

co-hydrolysis. Despite macroalgae being a suitable feedstock for bio-oil synthesis, additional processing steps such as deoxygenation, desulphurisation and denitrogenation are required to produce viable biofuels.

The catalytic hydrolysis/hydroconversion technology was applied on microalgae mixture (27 *Chlorophyta*, 6 *diatoms*, 1 *dinoflagellate*, 11 *cyanobacteria*, 7 *Euglenophycota*, 1 *Euglenozoa*) [220]. The liquid yields from microalgal mixture were more promising with 46 wt%, higher than of macroalgae-based (36 wt%) and wood-based bio-oils (25 – 28 wt%) [220]. However, the study did not report the parametric investigations. *Chlorella pyrenoidosa* was utilised as feedstock in a non-catalytic hydrolysis by studying the effects of different processing parameters on the products' yield and characteristics as well as the processing loss [222]. Based on the results, the effect of temperature exhibited greater impacts on the yield values when compared with the effect of processing time. As the hydrolysis temperature was increased, solid products started to reduce in term of yield with increasing generation of bio-oil products, which was in agreement with other form biomass pyrolysis studies [55,158,159]. Increasing pyrolysis temperature on algal biomass also contributes to the increase of N content in bio-oil due to the high conversion of protein fraction into liquid product. However, when above a certain temperature threshold, the denitrogenation or hydrodenitrogenation occurred which eventually reduced the N content in bio-oil. From the same study, the processing loss from hydrolysis was mainly due to the cracking of oil into light compounds which were released and uncaptured. Interestingly, the gas fraction produced from the hydrolysis process was maintained throughout the temperature change from low to high, which might be suppressed by the high pressure environment. Furthermore, the presence of H₂ at high pressure was found to promote the hydrocracking and hydrorefining processes which eventually improved the qualities (low viscosity and low O content) and quantities (high yield) of bio-oil derived from algal biomass using hydrolysis. To enhance the hydrolysis process, the effect of different catalysts (Pd/C; Pt/C, Pt/C sulfided, Ru/C, Rh/C, Mo₂C, MoS₂, CoMo/γ-Al₂O₃, activated carbon) was studied on the bio-oil yield generated from algal biomass [190]. Among those catalysts, MoS₂-aided hydrolysis generated the highest bio-oil yield (52.6 wt%), high HHV (37.8 MJ/kg) and high energy recovery (87%). The hydrolysis process parameters were further optimised by varying the temperature (200 – 410 °C), time (20 – 240 min), catalyst loading (1 – 60 wt%) and pressure (2 – 10 MPa). Based on the bio-oil yield and energy recovery measurements, temperature (15.7 – 52.7 wt%; 23.8 – 87.5%) has the greatest effect on yield as compared to time (50.2 – 54.6 wt%; 80.3 – 88.7%), catalyst loading (50.2 – 54.4 wt%; 77.8 – 89.0%) and H₂ pressure (52.0 – 52.9 wt%; 84.9 – 88.3%). Due to the flexible technological setup, the hydrolysis can be easily modified into catalytic co-hydrolysis system as well. Yan et al. [221] investigated the effect of Pt/C catalyst on hydrolysis of algal biomass as well as co-hydrolysis of algal biomass with UEO. As observed from Table 7, the bio-oil produced from microalgae with catalytic co-hydrolysis exhibited relatively higher yield values and slight improvement on their HHV values. The results also indicated that N and S were less recalcitrant in microalgae with the hydrolysis treatment compared to macroalgae. The use of catalytic media can also reduce the reliance on initial H₂ pressure as the controlling factors in hydrolysis [190,222]. With reference to catalytic co-hydrolysis of microalgae, boiling point distribution analysis revealed that lower naphtha fraction except *Spirulina platensis*, lower jet fuel fraction except *Schizochytrium limacinum* and lower diesel fraction except *Spirulina platensis* and *Schizochytrium limacinum* in bio-oils produced from hydrolysis. Therefore, as observed, the type of algal feedstock as well as their constituents still play a major role in producing the bio-oil with desirable properties.

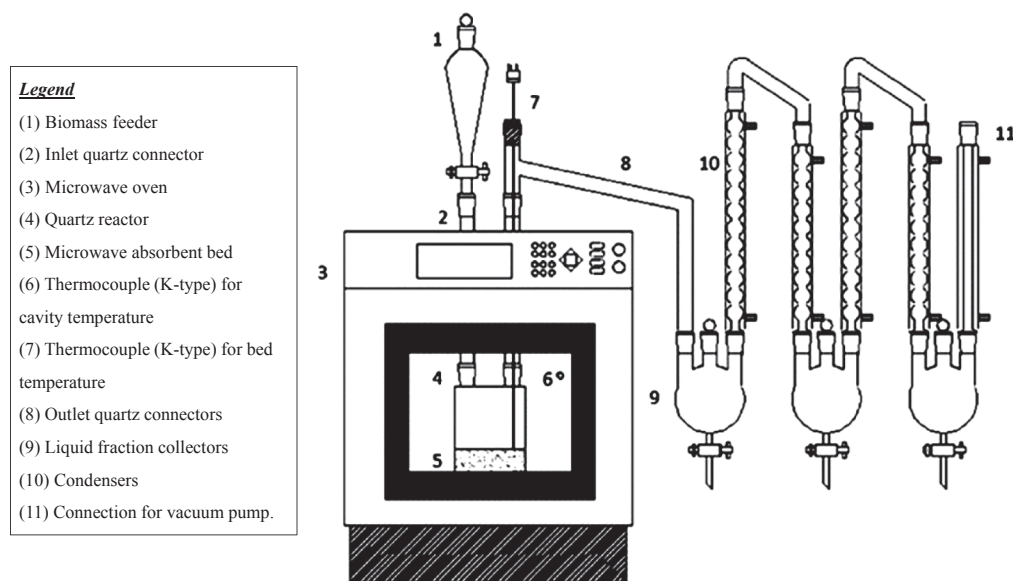


Fig. 5. General schematic diagram of microwave-assisted pyrolysis system. Reprinted from Xie, Addy [205], with permission from Elsevier.

4.4. Microwave-Assisted pyrolysis

Microwave-assisted pyrolysis has been gaining great development over the past 5 years, with strong research development in its principle, fundamental theory and mechanisms on different biomass [223,224]. Microwave energy is capable of providing effective, selective, rapid, consistent, hot-spot based, energy efficient and homogenous heating in the pyrolysis process [178,225,226]. In contrast, conventional heating through conduction, convection and radiation which are generally slow, non-selective, less control and inefficient [227–229]. As a form of electromagnetic irradiation, microwave energy works in the frequency range of 3×10^8 to 3×10^{11} Hz and in the wavelength of 1 to 10^{-3} m, respectively [225,227]. To ensure non-interference to other frequencies of different applications, all microwave devices including ovens and reactors have a dedicated operating frequency of 2.45 GHz (or wavelength of 12.25 cm) and an energy photon of 0.0016 eV, which only induce non-ionising radiation and non-chemical heating [227,229]. Microwave heating are generated by two mechanisms known as ionic migration/ conduction and dipolar polarisation, with the former playing a more major role in heat-producing capability [224]. Furthermore, the advantageous multimode and single-mode controls of microwave-assisted pyrolysis are considered to be simple modes of operation with direct control of pyrolysis time and power settings [205,225]. Through the rapid heating generated by microwave power, the microwave-assisted pyrolysis process heating can achieve the temperature requirement in shorter amount of time which eventually leads to energy saving. Overall, microwave-assisted pyrolysis can impartially handle various biomass with different particle sizes (2–4 mm), provides uniform pyrolytic heating and requires no mechanical parts for mixing [228,230]. Despite its advantages, the large-scale microwave system has yet to be industrialised in this current state.

As shown in Fig. 5, the laboratory-scale microwave system consists of a microwave oven which can house a microwave transparent reactor with high microwave penetration depth (d_p) such as quartz ($d_p = 75.73$ m) or borosilicate glass ($d_p = 15.7$ m), embedded with an absorbent bed [224]. Similar to the conventional setup, the outlet of the reactor is channelled to a series of condensers where the liquid collectors are attached. The pyrolysis heating in microwave system differs from the conventional system, whereby its heating rate is depending on the temperature (i.e.: °C mode) and power (i.e.: W mode) of the microwave settings as well as the microwave absorbability and chemical

constituents of the feedstock [118]. Thus, the heating rate might be changed over the pyrolysis process due initial moisture content of the feedstock at the early stage. Thereafter, heating rate might decrease and remain stable or fluctuate steadily at one point of the microwave-assisted pyrolysis process [118,231].

During the microwave heating operation, in its electromagnetic form, microwave irradiation propagates in two perpendicular fields known as electric and magnetic fields [227]. Due to its unique movements, microwave irradiation interacts differently with insulator (transparent), conductor (reflective) and absorber (dielectrics) [227,229]. To facilitate microwave heating, the feedstocks are either absorber themselves or are aided with absorbers which can absorb microwave energy and convert them into heating. To assess the microwave absorbability or loss tangent ($\tan \delta$) of a material, dielectric properties of the absorber such as the dielectric constant (ϵ') and the dielectric loss (ϵ'') can be correlated with the following relationship (Eq. (3)) [229]:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (3)$$

Whereby $\tan \delta < 0.1$ represents low microwave absorbability; $0.1 < \tan \delta < 0.5$ represent intermediate microwave absorbability; and $\tan \delta > 0.5$ represents high microwave absorbability. Basically, a higher value of $\tan \delta$ represents a better microwave absorbability of a material; thereby, promoting better microwave pyrolysis heating. In the algal biomass composition, carbohydrate ($\tan \delta = 0.035$) and protein ($\tan \delta = 0.068$) are inherently poor microwave absorbers as opposed to lipid ($\tan \delta \sim 0.105 - 0.424$) [228]. In some algal species, their lipid contents can be very low which hinder their direct pyrolysis under the utilisation of microwave power. Interestingly, the high water content in the algal biomass especially macroalgae (moisture content up to 95%) might be strong microwave absorbers which can facilitate the effective microwave heating. But, as discussed previously, high moisture content in the algal biomass can also result in poor bio-oil quality in most synthesis processes which needs to be balanced in the microwave-assisted pyrolysis. As for microalgae which are known for their poor microwave absorbing nature, they can be blended with strong microwave absorbers or dielectrics like activated carbon, some biomass and other solid residues to speed up the microwave heating for pyrolysis reaction [178,228,231]. Carbonaceous materials such as activated carbon ($\tan \delta = 0.31 - 1.646$) and biochars ($\tan \delta = 0.13 - 0.38$) show

Table 9
Microwave-assisted pyrolysis of algal biomass.

Algal Biomass	Type of Pyrolysis	Pyrolysis Parameter	Advanced Setting	Solid Product (wt %)	Liquid Product (wt %)	Gas Product (wt %)	HHV (MJ/kg)	Ref
Macroalgae <i>Gracilaria</i>	Microwave-Assisted Pyrolysis	HR(°C/min): - Pt (min):- PT (°C): 100 – 300 PS (mm): - GF (mL/min):-	Microwave Power (W): 200 – 300 Absorber: -	32.2 – 71.0	2.9 – 16.1	-	-	[232]
Algae Meal	Microwave-Assisted Pyrolysis	HR(°C/min): 5 Pt (min): 60 PT (°C): 750 PS (mm): - GF (mL/min): 100 of N ₂	Microwave Power (W): 200 – 300 Absorber: 1 g char : 1 g of feedstock	27.83	35.02	37.15	Bio-oil: 27.54 Biochar: 24.23 Syngas: 17.24	[233]
<i>Porphyra</i>	Microwave-Assisted Pyrolysis	HR(°C/min): - Pt (min): 20 PT (°C): 400 – 700 PS (mm): - GF (mL/min): 100 of N ₂	Microwave Power (W): - Absorber: 10 g SiC : 50 g of feedstock	10.2 – 12.2	2.2 – 3.0	85.6 – 87.1	Bio-oil: 2.4 – 3.3 Biochar: 13.8 – 18.2	[118]
Microalgae <i>Chlorella</i>	Microwave-Assisted Pyrolysis	HR(°C/min): - Pt (min): 20 PT (°C): - PS (mm): - GF (mL/min): 500 of N ₂	Microwave Power (W): 500 – 1250 Absorber: 6 g char : 30 g of feedstock	25.6 – 28.4	17.8 – 28.6	24.2 – 34.8	Bio-oil: 30.7	[230]
<i>Spirulina</i>	Microwave-Assisted Pyrolysis	HR(°C/min): - Pt (min): 20 PT (°C): 400 – 700 PS (mm): - GF (mL/min): 100 of N ₂	Microwave Power (W): - Absorber: 10 g SiC : 50 g of feedstock	5.1 – 9.6	6.6 – 13.1	80 – 84	Bio-oil: 2.9 – 3.3 Biochar: 13.5 – 14.4	[118]
<i>Chlorella</i>	Microwave-Assisted Pyrolysis	HR(°C/min): - Pt (min): 20 PT (°C): 400 – 700 PS (mm): - GF (mL/min): 100 of N ₂	Microwave Power (W): - Absorber: 10 g SiC : 50 g of feedstock	5.3 – 11.6	8.2 – 15.4	79.3 – 84	Bio-oil: 3.8 – 5.6 Biochar: 13.1 – 16.3	[118]
<i>Scenedesmus almeriensis</i>	Microwave-Assisted Pyrolysis	HR(°C/min): - Pt (min): - PT (°C): 400 – 800 PS (mm): - GF (mL/min): 20 of Ar	Microwave Power (W): 250 – 950 Absorber: 30 wt% biochar : 70 wt% feedstock	26.9 – 44.5	15.6 – 41.0	14.5 – 57.5	-	[223]
<i>Chlorella</i>	Catalytic Microwave-Assisted Pyrolysis	HR(°C/min): - Pt (min): 20 PT (°C): 400 – 700 PS (mm): < 0.2 GF (mL/min): 300 of N ₂	Microwave Power (W): 750 – 2250 Catalyst/ Absorber: Activated carbon; CaO; SiC; Solid Residue Catalyst/ Absorber Dosage: 5% catalyst: 30 g feedstock Absorber: -	-	35.83	52.37	-	[231]

Note: HR = heating rate; Pt = pyrolysis/ process time; PT = pyrolysis/ process temperature; PS = particle size; GF = sweeping gas type and flowrate.

high microwave absorbability which can be used as additives to algal biomass pyrolysis. Moreover, some of the additives also function as catalysts at the same time, whereby an absorber/catalyst system can be established to further enhance the microwave-assisted pyrolysis [231].

As microwave-assisted pyrolysis can be considered as new form of development based on the literature studies (Table 9), as such technologies are more commonly applied on lignocellulosic biomass and microalgae, rather than applied on macroalgae [232,233]. Macroalga, *Gracilaria* as microwave-assisted pyrolysis feedstock generated low bio-oil yield (2.9 – 16.1%) and high biochar yield (32.2 – 71.0%) [232]. From the mass loss profile, *Gracilaria* decomposed at low temperature

of 130 °C, compared to cellulose (~180 °C). The inherently high moisture of macroalgae (~7%) might be of good use in microwave-assisted synthesis as discussed, which produced higher bio-oil yield. Macroalgae microwave-assisted pyrolysis process was also applied on the algae meal (*Gelidium* variety) in between microwave power of 200 – 300 W [233]. It was found that microwave-assisted technology promoted the generation of syngas fraction (37.15 wt%) with lighter compounds. Despite the bio-oil yield generated was not satisfactory, its HHV was still the highest among all pyrolytic products. Similarly, the microwave-assisted pyrolysis tends to encourage the generation of gas product. In another study, the macroalgae (*porphyra*) generated the

highest syngas production (87 wt%) using microwave-based pyrolysis due to its high carbohydrate content [118]. More importantly, *porphyra* pyrolysis using microwave system showed the highest heating rate which could be related to its high combustible biomass fractions (VM and carbon content), moisture content, density and dielectric properties. Nonetheless, the bio-oil produced from this macroalgae over 400 – 700 °C showed low HHV values (2.4 – 3.3 MJ/kg) which were not favourable for energy application, as compared to its biochar products (13.8 – 18.2 MJ/kg).

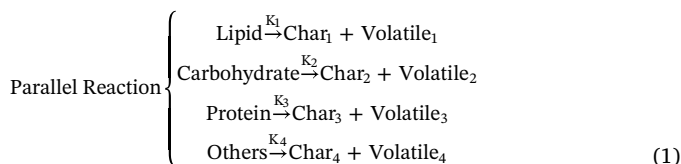
Comparatively, microwave-assisted pyrolysis is more commonly used in microalgae feedstock. *Chlorella* sp. was pyrolysed under microwave cavity in order to generate all three pyrolytic products [230]. From this study, it established the correlation between power setting and temperature setting. By increasing from 500 to 1250 W, the final temperatures measured by a thermocouple increased from 462 to 627 °C. This however would only serve as an approximation as the heating rates of the microwave-assisted pyrolysis are influenced by many other factors as discussed. At varying microwave settings, the pyrolytic products yields were reported as follows: biochar (25.6 – 28.4%), bio-oil (17.8 – 28.6% and syngas (24.2 – 34.8%). Its bio-oil was also reported to contain high HHV value up to 30 MJ/kg based on this feedstock. From another study, *Spirulina* and *Chlorella* used as feedstocks for microwave-assisted pyrolysis showed high generation of syngas products (up to 84 wt% of yield) [118]. From microwave-assisted pyrolysis, both microalgae could be used to generate bio-oil with yields in between 6.6 and 15.4% contributed mainly by their high protein content. *Scenedesmus almeriensis* was also found to be suitable feedstock for microwave-assisted pyrolysis to generate gas product [223]. At 800 °C, the maximum syngas yield was reported to be 94 vol% with the highest H₂/CO ratio through the reduction of CO₂ and light hydrocarbons. Zhang et al. [225] investigated the microwave-induced pyrolysis of naturally bloom algae. By increasing the microwave power from 400 to 800 W, the yield of the liquid product was improved from about 35 to 47 wt%. Gas product was also improved accordingly whilst biochar product was diminished drastically from about 47 to 25 wt%. The effect of microwave absorber or receptor type was also investigated on *Chlorella* and *Spirulina* [103]. It was found that receptor types (activated carbon or magnetite) had no significant impact on the bio-oil yield. However, magnetite catalysed the formation of aliphatic instead of aromatics while activated carbon enhanced dehydration reaction which formed nitrogen-containing aromatics. To enhance the bio-oil fraction using microwave-assisted pyrolysis, both *Chlorella* sp. and *Nannochloropsis* were investigated of their bio-oil productions with the use of SiC absorber as well as the presence of HZSM-5 catalyst [234]. Bio-oil yield obtained from *Chlorella* pyrolysis was optimised (57 wt%) without requiring catalyst whereas *Nannochloropsis* conversion to bio-oil was catalysed to generate higher bio-oil yield up to 59 wt%. Another catalytic microwave-assisted pyrolysis study was performed on *Chlorella vulgaris* by respective catalysts such as 5% of activated carbon, CaO, SiC and solid residue (char) [231]. From temperature rising rate, with the presence of those catalysts, the rates were increased by 174.30% (activated carbon), 140.84% (CaO), 116.39% (SiC) and 96.50% (solid residue) compared to pure microwave-assisted pyrolysis of *Chlorella vulgaris*. Polar molecules exist in the catalyst or microwave absorber such as activated carbon. With electromagnetic effect applied, those molecules would react and collide, generating heats for the pyrolysis process. Nonetheless, from the yield studies, the use of catalyst promoted the production of syngas yields (improvement of 24.49 – 75.66 wt%), but significantly reduced the bio-oil productions (reduction of 11.19 – 42.62 wt%), which showed agreement with other available studies. Such phenomena are common due to the competing nature between the gas and liquid products formation. At high temperature, the secondary cracking of bio-oil produced more gas fraction and with the presence of catalyst, the catalytic cracking favours the formation of incondensable gases. Compared with other forms of pyrolysis (catalytic, co-pyrolysis and others), microwave-assisted pyrolysis

seems to show high favourability in the formation of gas products from algal biomass.

5. Mechanisms and characteristics of algal biomass pyrolysis

Pyrolysis kinetics reaction implicates a series of endothermic mechanisms which decompose the biomass thermally at high temperature without the presence of O₂ to prohibit combustion process [56,235]. Pyrolysis decomposition kinetics of the respective component in biomass can be detected using TGA in term of weight loss to decipher the stepwise mechanism. Decomposition of lignocellulosic biomass has been investigated thoroughly. The process starts with the dehydration and extractive removal stage (100 – 250 °C), followed by the degradation of hemicellulose (250 – 350 °C) and cellulose and lignin (250 – 500 °C) [59,236]. Lignin is the most recalcitrant to thermal decomposition which can withstand up to 500 °C [236].

However, algal biomass shows very different thermal degradation profiles, with moisture removal stage in between 100 °C and 200 °C. More importantly, its chemical constituents differ greatly from lignocellulosic biomass, which consist of mainly lipid, carbohydrate, protein and others. The models of thermal degradation via pyrolysis of algae biomass can be represented with the following Eq. (1), comprising a series of parallel reactions [237]:



where K represents the rate of reaction to form the char and volatile. Based on the reaction scheme, the independent and simultaneous degradation of protein and carbohydrate occur in between 200 and 350 °C while only above 190 °C, lipids begin to breakdown [12]. When the temperature is in between 350 and 550 °C, most of the lipid structures degrade considerably at this stage [113,222]. During the same stage (350 – 550 °C), the devolatilisation process converts both carbohydrates and proteins into volatiles through depolymerisation, decarboxylation and cracking [184]. At intermediate temperatures (300 – 375 °C), the carbohydrates derivatives start to form as well [165,238]. In between 243 and 473 °C, gas products are generated from the protein present in the algal biomass [20]. Other more thermally-stable compounds such as residue lipid and non-volatile materials will only degrade and vaporise into CO₂ and CO when the temperature is > 550 °C [47,153]. Recalcitrant materials such as minerals and lipid will then be slowly transformed into carbonaceous materials like the solid products in the form of charcoals [113].

Generally, the favourability of bio-oil formation from algal biomass follows the trend: lipid > protein > carbohydrate. Therefore, lipid and protein can be converted efficiently into bio-oil fraction when compared to carbohydrate [30]. Chemical compositions (carbohydrate, lipid and protein) can be converted into oxygenate species or amino acids through thermal decomposition, and followed by the formation into different compounds such as aromatic, aliphatic, light hydrocarbons as well as non-condensable fractions of gaseous products such as CO, CO₂, H₂O, NH₃ and others [163]. To fully understand the pyrolysis conversion of algal biomass, compositional pyrolysis study of lipid, carbohydrates and protein into different products are described in the following sections.

5.1. Pyrolysis characteristics of algal biomass

Triglycerides represent the main composition of lipids in algal biomass during their pyrolysis. Usually, lipid undergoes decarboxylation, decarbonylation and fragmentation of glycerides [115]. This complex process primarily forms aldehydes, ketones, alcohols and acids

with long carbon chains from its triglycerides and fatty acids [165]. In addition, fatty olefins, paraffin and aromatic compounds are also formed from lipid constituents. From lipid pyrolysis, some of the acid products found in the pyrolytic products which may include 3,7,11,15-Tetramethyl-2-hexadecene ($C_{20}H_{40}O$); n-Hexadecanoic acid ($C_{16}H_{32}O_2$); Z-11,Hexadecenoic acid ($C_{16}H_{30}O_2$); cis-Vaccenic acid ($C_{18}H_{34}O_2$); 9,12-Octadecadienoic acid (Z, Z) ($C_{18}H_{32}O_2$); 9,12,15-Octadecatrienoic acid (Z, Z, Z) ($C_{18}H_{30}O_2$) [153,162]. Lipid contents from *Chlorella vulgaris* after undergoing pyrolysis are also converted into hydrocarbon compounds such as heptadecane, 1-nonadecene and heneicosane [153].

Multi-step pyrolysis degradation mechanism of carbohydrate differs greatly from cellulose pyrolysis process due to their different biopolymer structures. Based on Debiagi et al. [23], it was observed that alginic acid and mannitol only degraded at one major weight loss region while the degradation of fucoidan and laminarin generated two major weight loss regions. Thus, the thermal behaviours of each carbohydrate constituent react differently with respect to temperature gradient due to their chemical structures. Pyrolysis of carbohydrate can convert light organics, carbonyls, acids and alcohols that exist in the algae feedstock into deoxygenated olefins ($C_2 - C_6$) based on dehydration, glycosidic bond cleavage, rearrangement and ring scission [113,115]. Furans, pyrazines and pyrroles start to form from carbohydrate when the pyrolysis temperature is above 300 °C [165,238]. PAHs formation is also contributed by carbohydrate pyrolysis [118]. Based on the *Chlorella vulgaris* pyrolysis study, carbohydrate is the core ingredient to generate 2,5-dimethyl, furan (C_6H_8O); furfural ($C_5H_4O_2$); levoglucosenone ($C_6H_6O_3$); levoglucosan ($C_6H_{10}O_5$); 3-methyl-pentanoic acid ($C_6H_{12}O_2$); 5-methyl-2-furancarboxaldehyde ($C_6H_6O_2$); and acetic acid ($C_2H_4O_2$) [162]. At temperature > 500 °C, CO_2 evolution occurs which is attributed by the decomposition of saccharides [20].

Protein compositional pyrolysis exhibits multistep and multiphase kinetic behaviours [23]. Nitrogenous compounds such as amines, amides, pyridines, pyrroles, pyrazoles, pyrazines, polyheteroaromatics, nitriles, imidazoles and indoles are produced from the pyrolysis of protein-rich algae biomass [12,165]. More specifically, cyclic amides are products formed from intramolecular cyclisation process which differs from linear amines produced from the reaction between amino acids and carboxylic acid. Both imidazoles and indoles are built from different forms of amino acids during the pyrolysis of protein. At low temperature pyrolysis, hydrophobic protein fragments are formed as the main products. However, at high temperature range, the evolution of gaseous compounds such as NO, C_2H_6 and HCN can be related to the protein content present in the algal biomass [20]. From pyrolysis of *Chlorella vulgaris*, compounds such as 1H-indole; 1H-indole-3methyl, benzenepropanenitrile (C_9H_9N); benzyl nitrile (C_8H_7N); propanenitrile (C_3H_5N); 4-methyl-pentanenitrile ($C_6H_{11}N$), toluene, styrene, ethylbenzene, methylphenol, phenols were detected in the pyrolytic products as derived from protein fraction [153,162].

From the pyrolysis of algal biomass, a variety of organic and inorganic compounds are formed and distributed into three main pyrolytic products. The following section entails these products of different phases and their potential applications in power generation. Their advantages as well as disadvantages as biofuels, will be explained accordingly based on their physicochemical properties.

5.2. Pyrolytic product formation

The products derived from either conventional or advanced pyrolysis are value-added commodities as well as energy-dense biofuels. These pyrolytic products whether in liquid, solid or gas can be used in different fields and applications such as energy generation, transportation, wastewater treatment and agricultural sector [31,59,64,129]. Despite being the same species, macroalgae and microalgae share completely different chemical properties as discussed previously. Such variations can affect the properties and characteristics of the pyrolytic products. Table 10 summarises and compares all three products

synthesised from macroalgae and microalgae, respectively, from their physicochemical properties (pH, density, viscosity) as well as energy content (HHV).

5.2.1. Solid product

Solid residue collected from the pyrolyser is referred as charcoal, bio-charcoal or biochar, as formed from the primary and secondary pyrolysis reactions [164]. Biochar is a carbonaceous nutrient-retained material and stable under most conditions with high C contents [59,151]. Its long half-life delays the release of CO_2 to the atmosphere by gradually returning the CO_2 to the environment through decomposition, combustion and consumption [151]. Utilisation of biochar is diversifying due to its availability of functional groups, inert nature as well as its ability to sequester liquid or gas molecules [55,63]. Biochar is mainly produced from slow pyrolysis while in other forms of pyrolysis, its generation can be regarded as by-product. As main product, biochar is commonly used as a gasification substrate for energy generation [42]. In recent years, biochar shows great potential to be directly used for combustion as it emits far lesser CO_2 and contains similar or higher energy contents compared to fossil fuels [59]. As solid fuel, the main attraction of biochar is its direct application of biofuel without cumbersome extraction/ upgrading process as required by liquid-based biofuel [39]. Due to its richness in nutrients, biochar can be used as fertiliser as well as to retain water resources on plantations [239]. Even though some biochar might not have superior surface areas, their available functional groups can be useful for sequestering pollutants from water and gas environments [55]. As intermediary materials, biochar can be used as feedstock for nanotubes synthesis, activated carbon, carbon black, carbon fibres [63,105]

As observed from Table 10, the biochar produced from both microalgae and macroalgae shares similar pH (12 – 12.59) values exhibiting alkaline nature due to their inherently high ash content [38,90]. In term of energy potential, microalgae-based biochar seems to be more promising due its higher HHV range (14.5 – 36.67 MJ/kg). Nonetheless, macroalgae-based biochar possesses relatively higher surface area (up to 80 m^2/g), which can be crucial for catalysis and wastewater treatment [55,177]. Both algal biochar contain various functional groups and inorganic elements. These might be useful in adsorption process for environmental control [55,87].

5.2.1.1. Liquid product. From algal biomass pyrolysis, liquid products such as pyrolysis oil, pyrolytic oil, bio-oil and bio-crude can be obtained in the form of condensate. Bio-oil is formed with rapid quenching from the mixed volatiles at the outlet of the pyrolysis unit [120]. Typically, the bio-oil is produced from fast and flash pyrolysis, mostly with the appearance of dark brown, may be viscous or non-viscous and with strong, distinctive smell [238]. Chemically, bio-oil has high complexity containing organic compounds such as alcohols, acids, esters, aldehydes, ketones, phenols, guaiacols, syringols, furans, terpene and sugars whereby its composition is highly dependent on feedstock, pyrolysis process and synthesis operating conditions [120,238]. To date, many researchers focus on bio-oil synthesis as it has the potential to be a viable replacement for fossil fuels [152]. Bio-oil is made up of two different phases, namely organic phase and the aqueous phase (water soluble), along with negligible solid residues [128]. The organic phase usually possesses higher energy values compared to the aqueous phase. However, pyrolytic oil suffers from high viscosity, high acidity as well as high moieties which can cause bio-oil degradation over time [163].

Like other biomass-derived pyrolytic bio-oil, algal bio-oil contains high oxygenates in the forms of aldehydes, ketones, acids and phenols which can lead to low heating value, low thermal stability and low vapour pressure [155,170,176]. Due to its protein fraction, the nitrogen contents in algal bio-oil can reach up to 13% [8,31,155]. Furthermore, algal bio-oil is also associated with issues such as high distillate residue, immiscibility with petroleum products as well as reaction during

Table 10
Properties of bio-oil, biochar and bio-syngas derived from algal biomass pyrolysis.

Properties	Bio-oil			Bio-syngas
	Biochar	Microalgae Feedstock	Macroalgae Feedstock	
pH	11.06 – 12.00	7.6 – 12.59	4.30 – 9.52	-
Density	Skeleton Density: 3.28 g/mL Bulk Density: 0.78 g/mL	Bulk Density: 0.39 – 0.48 g/mL	0.98–1.20 kg/L	-
Viscosity (cP)	-	60 °C: 23.10 – 34.30 40 °C: 79.20 – 100.67 29 – 45.9	50 °C: 264 mm ² /s 40 °C: 101 6.75 – 33.57	-
HHV (MJ/kg)	14.5 – 36.67	6.47 – 17.8	-	4.60 – 12.55 MJ m ⁻³
Surface area/ Pore Area (m ² /g)	19.03	1.29 – 79.95	-	-
Elemental Composition wt %				
C	47.80 – 59.24	22.2 – 60.51	65.0 – 65.76	Gas Composition (%)
H	2.8 – 4.83	1.1 – 4.2	7.84 – 8.50	CO ₂ : 66.67 – 78.34
O	33.6	4.89 – 24.9	11.24 – 16.48	CO: 15.4 – 19.54
N	5.5 – 10.96	0.3 – 2.8	9.75 – 10.28	H ₂ : 8.49 – 21.40
S	0.3 – 0.91	0.6 – 9.3	0.45 – 0.81	Light hydrocarbons
Major Chemical Compound	<ul style="list-style-type: none"> Sulphide Silicates Inorganic compounds (P, K, Ca, Na, Al, Mg, B, Cu, Pb, Rb, Si, Fe, Ti, Cl, etc) Carboxylic group Isocyanate Inorganic compounds (P, K, Ca, Mg, Na, Al, Si, Fe, Cl, etc) 	<ul style="list-style-type: none"> Hydroxyl group Amide Amine Carboxylic group Isocyanate Inorganic compounds 	<ul style="list-style-type: none"> Aromatic hydrocarbons (toluene, ethylbenzene, styrene) Heterocyclic compounds (furan, benzene) Heterocyclic compounds (furan, pyrrole, indole) Phenols (4-Methyl-phenol, Phenol, 4-Ethyl-phenol) Acid (3-Methyl-pentanoic acid, n-Hexadecanoic acid, acetic acid, oleic acid) Ketone (3-Penten-2-one, 4-methyl-, 2-Pentanone, 4-hydroxy-4-methyl-, 2-hydroxy-4-methyl-, others) Amide (Acetamine, Picolinamide) Nitrile (Benzyl nitrile, Propanenitrile) Others (Levoglucosan, 3,7,11,15-Tetramethyl-2-hexadecen, Levoglucosenone) Aliphatics (1-Tridecene, Dodecane) Inorganic compounds (Na, Mg, Al, Si, P, Ca, Fe, Ni) 	<ul style="list-style-type: none"> CO₂: 52.67 – 70.70 CO: 15.4 – 19.54 H₂: 8.49 – 21.40 Light hydrocarbons CH₄: 0.47 – 6.50 C₂H₄: 0.92 – 2.22 C₂H₆: 4.97 – 7.41 C₃H₄: - C₂H₆: 0.16 – 1.72 C₃H₈: 0.10 – 0.77 Composition of species was converted into 100% basis based on gas yield fractions in between 13 and 25 %, the remaining (75 – 87%) are char and liquid yields.
Reference	[118,118,151]	[118,146-149,158]	[81,108,151,162,230]	[150,162] [158,233]

storage [171,240]. The macroalgae-based bio-oil shows narrow pH range (~pH 4 – 6) while bio-oil derived from microalgae exhibits greater pH range (~pH 4 – 9.5). In term of viscosity and density, both bio-oil shares similar properties. But, bio-oil synthesised from microalgae generally possesses higher HHV (29 – 46 MJ/kg). From the element composition analysis, bio-oil from macroalgae pyrolysis has high O% which is undesirable. Both macroalga-based and microalga-based bio-oils contain various oxygenates and nitrogenates which can lead to their ineffectiveness as biofuels. In current state, direct usage of algal bio-oil might not be feasible. Thus, these characteristics of bio-oil necessitate an upgrade process to eliminate the unfavourable compounds. Currently, there are three types of upgrade available for pyrolysed bio-oil which have been well-studied and can be summarised as follows [8,120,157,160,238]:

- Physical methods physical methods (filtration, solvent addition and emulsions/ emulsification)
- Catalytic methods (esterification/alcoholysis, zeolite cracking, vapour cracking, gasification, chemical extraction, aqueous phase reforming, steam reforming, hydro-deoxygenation and hydrotreating)
- Non-catalytic methods (hydrothermal and hydrothermal hydro-treating).

After the upgrade process, the bio-oil can be effectively used as biofuels in the existing boilers and combustors [138,160,238]. However, such upgrading step involves additional processing steps incurring additional equipment and chemical costs. Aside from its application as biofuels, bio-oil can be used in various applications such as wood flavourings, preservatives, resin, lubricants and adhesives synthesis [227].

5.2.1.2. Gas product. The gas product generated from pyrolysis can be referred as syngas and bio-syngas based on the biomass feedstock. Typically, the produced gas products have light-phase composition such as H₂, CO, CO₂, N₂, water vapour, CH₄, light hydrocarbons (ethane and propane) and heavy hydrocarbons (C₂ – C₃) and others [158,162]. Gas product has often been overlooked and considered as by-products from the pyrolysis process. Macroalgae and microalgae are regarded as suitable feedstock due to their inherently high moisture content. The water molecules can improve the gasification of char and promote the reforming process of hydrocarbon gas (C_nH_m) [241]. Until recently, microwave-assisted pyrolysis technique can generate a high yield of gas products with high HHV values [233]. By comparing both syngases derived, macroalgae-based syngas generates higher energy content (4.6 – 17.2 MJ/kg) which corresponds with the high H₂ (8.5 – 21.4%) and high CO (15.4 – 19.5%) when compared with microalgae-based syngas (1.2 – 5.1 MJ/kg). Moreover, pyrolysis of macroalgae can generate up to > C₄ species whereas microalgae pyrolysis can only produce up to ~ C₂ hydrocarbons, which significantly affects the overall HHV. Therefore, the chemical nature of macroalgae seems to be favourable for syngas production. Comparing with its two other counterparts (solid and liquid products), gas products as derived from pyrolysis process has the advantages such as it requires no additional upgrade process and its direct application as fuel feedstock for existing boilers, gas turbines and engine.

6. Summary of Findings, Challenges, recommendations and conclusions

6.1. Summary of findings

From the review of numerous manuscripts, we have identified the advantages and disadvantages of each technology, covering both conventional and non-conventional pyrolysis specifically for algal feedstocks, as listed in Table 11. Conventional pyrolysis, including slow and fast pyrolysis, despite being well-studied on algal biomass feedstock, they are associated with the main issues of the pyrolytic products, such

as low energy content (up to 34 MJ/kg), moderate yields as well as high O and N contents in the liquid products. Whilst, intermediate and flash pyrolysis are not thoroughly being developed as independent technologies at the moment. Their current experimental works were more to analytical studies as well as conceptual development whereby the actual designs of their respective pyrolyser are still in infancy. Bio-oil produced from intermediate pyrolysis shows favourable attributes while from flash pyrolysis, the bio-oil is associated with high acidity, high viscosity and unstable under ambient conditions.

Thus, the disadvantages conventional pyrolysis can be overcome by advanced pyrolysis in this case. Catalytic pyrolysis utilises different catalysts which could reduce the nitrogenates and oxygenates in the biofuels. Such enhancement can directly reduce the formation of GHG. As observed, the energy contents of biofuels produced from catalytic pyrolysis are only up to 38 MJ/kg which can be regarded as only moderate. While this form of technology does not improve the energy content, its pyrolytic oil is enhanced whereby other upgrading can be applied to generate feasible biofuels [157]. The use of co-pyrolysis technology is an attractive option due to its eco-friendliness as well as simplicity of operation. By selecting a suitable feedstock, the bio-oil yield generated from algal biomass can be higher than 55 wt%, with high energy content (> 40 MJ/kg). Hydro-pyrolysis, surprisingly, produces high energy content bio-oil (up to 48 MJ/kg) but with varying yield values. Nonetheless, this emerging technology can produce bio-fuel comparable to conventional fuels, and currently is in its pilot stage. Therefore, its commercialisation is more promising compared to other techniques. One of the major advantages of microwave-assisted pyrolysis is the reduction of synthesis time from hours to merely minutes. Furthermore, the heating rate of this technology can be easily influenced by the feedstock's physicochemical characteristics. Unlike other form of pyrolysis, microwave-assisted pyrolysis of algal biomass shows high selectivity towards gas products, for certain macroalgae and microalgae, up to 87 wt% of bio-syngas yield.

6.2. Challenges and recommendations

6.2.1. Algal feedstock

Based on the outcome of the review, there are several longstanding issues associate with macroalgae and microalgae biomass as pyrolysis feedstock. Even though algal biomass is regarded as 3rd generation biofuel feedstock which do not encounter the problems faced by 1st and 2nd generation biofuels, their cultivation and harvesting still pose great challenges in term of large scale farming and cost. While the cultivation studies via both open and closed systems are substantial with the current global productions, the cost of production especially technological drying and pre-treatment still remains expensive for industrialisation. Thus, wet biomass such as macroalgae and microalgae needs to be dewatered before pyrolysis process will increase the cost of production. With regards to this issue, microwave-assisted pyrolysis may be the solution to reduce the cost of pre-treatment as this technology is capable to handle moderately wet sample to produce pyrolytic products.

Secondly, numerous countries are still using algal biomass as food and pharmaceutical materials such as Korea, China, Philippines, Malaysia and others. Therefore, while non-arable cultivation can be achieved, algal biomass as pyrolysis feedstock can still create certain degree of food supply competition. Nonetheless, algal biomass are not regarded as the main food sources globally whereby as long as its cultivation can support the demand globally, the use of algal biomass as feedstock will not cause major food competition.

Based on the tabulated chemical data, the characterisation of algal feedstock especially macroalgae has been lacking literature and inconsistent in term of measurements. Thus, this undoubtedly creates huge research gap and presents high degree of difficulty in comparing different feedstock and correlating their chemical constituents to the synthesised products. Thus, researchers must fill in the missing gap for future development by performing relevant characterisation studies.

Table 11
Advantages and disadvantages of conventional and advanced pyrolysis techniques of algal biomass.

Technology	Advantages	Disadvantages
<i>Conventional Pyrolysis</i>		
Slow Pyrolysis	<ul style="list-style-type: none"> ● Established with comprehensive parametric studies ● Produces high yield and high quality biochar ● Highly scalable ● Simple equipment setup ● Ease of operation ● Can handle various particle size materials 	<ul style="list-style-type: none"> ● Long processing time ● Moderate energy content for biochar and for bio-oil ● Low energy content for bio-syngas
Intermediate Pyrolysis	<ul style="list-style-type: none"> ● Bio-oil with reduced tar and reduced viscosity ● Ease of operation 	<ul style="list-style-type: none"> ● Lack of parametric investigations ● Relatively new without proper equipment setting development
Fast Pyrolysis	<ul style="list-style-type: none"> ● Favours the formation of bio-oil with high yield ● Highly scalable ● Simple equipment setup ● Ease of operation 	<ul style="list-style-type: none"> ● Moderate energy content for biochar and for bio-oil ● Contain high N and O in bio-oil composition
Flash Pyrolysis	<ul style="list-style-type: none"> ● Only generates oil and gas products ● Rapid process 	<ul style="list-style-type: none"> ● Bio-oil may contain solid residue and high aqueous fraction ● Bio-oil may possess undesirable characteristics such as high acidic, high viscosity and chemically unstable. ● Complicated equipment design (safety and cost factors) ● Currently not feasible at industrial scale
<i>Advanced Pyrolysis</i>		
Catalytic Pyrolysis	<ul style="list-style-type: none"> ● In-situ configuration requires lower equipment cost and easier for scalability ● Ex-situ configuration reduces minerals in bio-oil ● Reduce synthesis temperature and time ● Promote deoxygenation and denitrogenation to generate higher quality of bio-oil with better energy content 	<ul style="list-style-type: none"> ● Use of catalyst may require higher production and maintenance costs ● Ex-situ configuration promotes char and gas generation
Co-Pyrolysis	<ul style="list-style-type: none"> ● Simple operation with blending and mixing ● No modification on existing pyrolyser ● Mean to reduce waste materials ● Significantly improves bio-oil yield ● High energy content bio-oil 	<ul style="list-style-type: none"> ● Inconsistency in feedstock supply may result in product variation
Hydropyrolysis	<ul style="list-style-type: none"> ● Generate high energy content and high yield products ● Reduced oxygenates and char formation in bio-oil ● Introduce minor H₂ into the pyrolytic products ● Commercialisable 	<ul style="list-style-type: none"> ● Expensive equipment setup ● Safety issue associating with the usage of H₂ at high temperature ● Complicated operation
Microwave-Assisted Pyrolysis	<ul style="list-style-type: none"> ● Rapid process ● Effective heating ● Excellent for gas product formation 	<ul style="list-style-type: none"> ● Unstable heating rate depending on the initial moisture content ● Some algal feedstock requires blending with microwave absorbers ● Scalable issues ● Expensive setup

These studies should be based on standards such as ASTM or BS whichever relevant. Furthermore, it is recommended to establish a concrete database on the physicochemical properties as well as taxonomy categorisation on algal biomass even though it can be challenging but it will benefit the development of 3rd generation biofuel significantly in the future.

6.2.2. Technology limitation

Conventional pyrolysis is established techniques for producing pyrolytic products. However, based on the literature review, especially on algal biomass, the parametric studies and product distribution records are still incomplete or not comprehensive in terms of product distribution data. Intermediate and flash pyrolysis of both algal biomass despite have been reviewed in several studies, a comprehensive and complete pyrolysis parametric investigation are still not available due to their complicated experimental setup or extreme pyrolysis settings.

The advanced pyrolysis is considered to be relatively new, especially hydropyrolysis. Nonetheless, the progress on these advanced or non-conventional pyrolysis technologies has been developed steadily over the past 5 years. As algal biomass has just recently emerged as one of the most studied feedstock in the world for various applications in pharmaceutical sector, fine chemical production as well as wastewater treatment, it is naturally that more investigations are required on their pyrolysis parameters as well as product characteristics by comparing to more common and developed lignocellulosic biomass pyrolysis process.

6.3. Conclusions

This manuscript critically investigated the experimental aspects of

both conventional and advanced pyrolysis studies on algal biomass such as macroalgae and microalgae, as well as their product distribution and characteristics. It was found that the chemical constituents of both macroalgae and microalgae are favourable as pyrolysis feedstock and could influence the product characteristics such as pH, viscosities, densities, HHV values and their compositions. By far, both macroalgae and microalgae show their suitability as pyrolysis feedstock to produce energy dense products, which can be commercialised in the future. Furthermore, advanced pyrolysis enhances the biofuels generated from algal biomass, by improving the qualities of bio-oil via catalytic pyrolysis, reducing the waste feedstock through co-pyrolysis, by generating energy dense biofuels from hydropyrolysis as well as by greatly reducing the energy consumption using microwave-assisted pyrolysis. Nonetheless, conventional pyrolysis still provides one of the most feasible technologies in term of process cost. Thus, by knowing the requirement of the energy products, the selection of a suitable pyrolysis method and appropriate feedstock can optimise the desired product fraction and produce high quality products in term of energy contents and characteristics.

Declaration of Competing Interest

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

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References

- Tekin K, Karagöz S, Bektaş S. A review of hydrothermal biomass processing. *Renew Sustain Energy Rev* 2014;40:673–87.
- Amini Z, Ilham Z, Ong HC, Mazaheri H, Chen W-H. State of the art and prospective of lipase-catalyzed transesterification reaction for biodiesel production. *Energy Convers Manage* 2017;141:339–53.
- Assis TCD, Calijuri ML, Assemany PP, Pereira ASADP, Martins MA. Using atmospheric emissions as CO₂ source in the cultivation of microalgae: Productivity and economic viability. *J Cleaner Prod* 2019;215:1160–9.
- Kumar G, Shobana S, Chen W-H, Bach Q-V, Kim S-H, Atabani AE, et al. A review of thermochemical conversion of microalgal biomass for biofuels: chemistry and processes. *Green Chem* 2017;19(1):44–67.
- Mahlia TMI, Syazmi ZAH, Mofijur M, Abas AEP, Bilad MR, Ong HC, et al. Patent landscape review on biodiesel production: Technology updates. *Renew Sustain Energy Rev* 2020;118:109526.
- Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the chemical composition of biomass. *Fuel* 2010;89(5):913–33.
- Hokkanen S, Bhatnagar A, Sillanpää M. A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. *Water Res* 2016;91:156–73.
- Xiu S, Shahbazi A. Bio-oil production and upgrading research: a review. *Renew Sustain Energy Rev* 2012;16(7):4406–14.
- Ahmed A, Abu Bakar MS, Azad AK, Sukri RS, Mahliah TMI. Potential thermochemical conversion of bioenergy from *Acacia* species in Brunei Darussalam: a review. *Renew Sustain Energy Rev* 2018;82:3060–76.
- Yu J, Maliutina K, Tahmasebi A. A review on the production of nitrogen-containing compounds from microalgal biomass via pyrolysis. *Bioresour Technol* 2018;270:689–701.
- Acharya B, Dutta A, Minaret J. Review on comparative study of dry and wet torrefaction. *Sustainable Energy Technol Assess* 2015;12:26–37.
- Andrade LA, Batista FRX, Lira TS, Barrozo MAS, Vieira LGM. Characterization and product formation during the catalytic and non-catalytic pyrolysis of the green microalgae *Chlamydomonas reinhardtii*. *Renewable Energy* 2018;119:731–40.
- Milano J, Ong HC, Masjuki HH, Chong WT, Lam MK, Loh PK, et al. Microalgae biofuels as an alternative to fossil fuel for power generation. *Renew Sustain Energy Rev* 2016;58:180–97.
- Li DC, Jiang H. The thermochemical conversion of non-lignocellulosic biomass to form biochar: A review on characterizations and mechanism elucidation. *Bioresour Technol* 2017;246:57–68.
- Isikgor FH, Becer CR. Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. *Polym Chem* 2015;6(25):4497–559.
- Lee, KT, Ofori-Boateng C. Sustainability of biofuel production from oil palm biomass, ed. K.T. Lee and C. Ofori-Boateng. 2013, Singapore: Springer.
- Pirbazari SM, Norouzi O, Kohansal K, Tavassoli A. Experimental studies on high-quality bio-oil production via pyrolysis of *Azolla* by the use of a three metallic/modified pyrochar catalyst. *Bioresour Technol* 2019;291:121802.
- Chia SR, Ong HC, Chew KW, Show PL, Phang S-M, Ling TC, et al. Sustainable approaches for algae utilisation in bioenergy production. *Renewable Energy* 2018;129:838–52.
- Yu KL, Show PL, Ong HC, Ling TC, Chi-Wei Lan J, Chen W-H, et al. Microalgae from wastewater treatment to biochar – Feedstock preparation and conversion technologies. *Energy Convers Manage* 2017;150:1–13.
- Wang S, Jiang XM, Wang N, Yu LJ, Li Z, He PM. Research on pyrolysis characteristics of seaweed. *Energy Fuels* 2007;21(6):3723–9.
- Gan YY, Ong HC, Show PL, Ling TC, Chen W-H, Yu KL, et al. Torrefaction of microalgal biochar as potential coal fuel and application as bio-adsorbent. *Energy Convers Manage* 2018;165:152–62.
- Singh A, Nigam PS, Murphy JD. Renewable fuels from algae: An answer to debatable land based fuels. *Bioresour Technol* 2011;102(1):10–6.
- Debiagi PEA, Trinchera M, Frassoldati A, Faravelli T, Vinu R, Ranzi E. Algae characterization and multistep pyrolysis mechanism. *J Anal Appl Pyrol* 2017;128:423–36.
- Yu KL, Show PL, Ong HC, Ling TC, Chen W-H, Salleh MAM. Biochar production from microalgae cultivation through pyrolysis as a sustainable carbon sequestration and biorefinery approach. *Clean Technol Environ Policy* 2018;20(9):2047–55.
- Brigljević B, Liu J, Lim H. Green energy from brown seaweed: Sustainable poly-generation industrial process via fast pyrolysis of *S. Japonica* combined with the Brayton cycle. *Energy Convers Manage* 2019;195:1244–54.
- Cheng J. Biomass to renewable energy processes. CRC Press; 2017.
- Ong HC, Chen W-H, Farooq A, Gan YY, Lee KT, Ashokkumar V. Catalytic thermochemical conversion of biomass for biofuel production: A comprehensive review. *Renew Sustain Energy Rev* 2019;113:109266.
- Tripathi M, Sahu JN, Ganesan P. Effect of process parameters on production of biochar from biomass waste through pyrolysis: a review. *Renew Sustain Energy Rev* 2016;55:467–81.
- Chew KW, Yap JY, Show PL, Suan NH, Juan JC, Ling TC, et al. Microalgae bio-refinery: high value products perspectives. *Bioresour Technol* 2017;229:53–62.
- Marcilla A, Catalá L, García-Quesada JC, Valdés FJ, Hernández MR. A review of thermochemical conversion of microalgae. *Renew Sustain Energy Rev* 2013;27:11–9.
- Azizi K, Keshavarz Moraveji M, Abedini Najafabadi H. A review on bio-fuel production from microalgal biomass by using pyrolysis method. *Renew Sustain Energy Rev* 2018;82:3046–59.
- Amin S. Review on biofuel oil and gas production processes from microalgae. *Energy Convers Manage* 2009;50(7):1834–40.
- Yang C, Li R, Zhang B, Qiu Q, Wang B, Yang H, et al. Pyrolysis of microalgae: a critical review. *Fuel Process Technol* 2019;186:53–72.
- Rowbotham J, Dyer P, Greenwell H, Theodorou M. Thermochemical processing of macroalgae: A late bloomer in the development of third-generation biofuels? *Biofuels* 2012;3(4):441–61.
- Lee XJ. Evaluation of cost effective adsorbent and biochar from Malaysia oil palm wastes: synthesis, characterisation and optimisation studies, in *Chemical and Environmental Engineering*. United Kingdom: University of Nottingham; 2018.
- Zhao B, Su Y, Liu D, Zhang H, Liu W, Cui G. SO₂/NO_x emissions and ash formation from algae biomass combustion: Process characteristics and mechanisms. *Energy* 2016;113:821–30.
- Sabil KM, Aziz MA, Lal B, Uemura Y. Effects of torrefaction on the physicochemical properties of oil palm empty fruit bunches, mesocarp fiber and kernel shell. *Biomass Bioenergy* 2013;56:351–60.
- Bruhn A, Dahl J, Nielsen HB, Nikolaisen L, Rasmussen MB, Markager S, et al. Bioenergy potential of *Ulva lactuca*: Biomass yield, methane production and combustion. *Bioresour Technol* 2011;102(3):2595–604.
- Choi HI, Lee JS, Choi JW, Shin YS, Sung YJ, Hong ME, et al. Performance and potential appraisal of various microalgae as direct combustion fuel. *Bioresour Technol* 2019;273:341–9.
- Molino A, Chianese S, Musmarra D. Biomass gasification technology: the state of the art overview. *Journal of Energy Chemistry* 2016;25(1):10–25.
- Samiran NA, Jaafar MNM, Ng J-H, Lam SS, Chong CT. Progress in biomass gasification technique – With focus on Malaysian palm biomass for syngas production. *Renew Sustain Energy Rev* 2016;62:1047–62.
- Duman G, Uddin MA, Yanik J. Hydrogen production from algal biomass via steam gasification. *Bioresour Technol* 2014;166:24–30.
- Guan Q, Wei C, Savage PEJPCCP. Kinetic model for supercritical water gasification of algae. 2012. 14(9): p. 3140-3147.
- Gan YY, Ong HC, Chen W-H, Sheen H-K, Chang J-S, Chong CT, et al. Microwave-assisted wet torrefaction of microalgae under various acids for coproduction of biochar and sugar. *J Cleaner Prod* 2020;253:119944.
- Bach Q-V, Kreiberg Ø. Upgrading biomass fuels via wet torrefaction: A review and comparison with dry torrefaction. *Renew Sustain Energy Rev* 2016;54:665–77.
- Uemura Y, Matsumoto R, Saadon S, Matsumura Y. A study on torrefaction of *Laminaria japonica*. *Fuel Process Technol* 2015;138:133–8.
- Chen W-H, Huang M-Y, Chang J-S, Chen C-Y. Thermal decomposition dynamics and severity of microalgae residues in torrefaction. *Bioresour Technol* 2014;169(Supplement C):258–64.
- Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: a review of subcritical water technologies. *Energy* 2011;36(5):2328–42.
- Huang H, Yuan X, Zeng G, Wang J, Li H, Zhou C, et al. Thermochemical liquefaction characteristics of microalgae in sub- and supercritical ethanol. *Fuel Process Technol* 2011;92(1):147–53.
- Gollakota ARK, Kishore N, Gu S. A review on hydrothermal liquefaction of biomass. *Renew Sustain Energy Rev* 2018;81:1378–92.
- Pourhosseini S, Norouzi O, Salimi P, Naderi HRJASC. and Engineering, Synthesis of a novel interconnected 3D pore network algal biochar constituting iron nanoparticles derived from a harmful marine biomass as high-performance asymmetric supercapacitor electrodes. 2018. 6(4): p. 4746-4758.
- Salimi P, Javadian S, Norouzi O, Gharibi HJES, Research P. Turning an environmental problem into an opportunity: potential use of biochar derived from a harmful marine biomass named *Cladophora glomerata* as anode electrode for Li-ion batteries. 2017. 24(36): p. 27974-27984.
- Onwudili JA, Lea-Langton AR, Ross AB, Williams PT. Catalytic hydrothermal gasification of algae for hydrogen production: Composition of reaction products and potential for nutrient recycling. *Bioresour Technol* 2013;127:72–80.
- Dhyani V, Bhaskar T. A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renewable Energy* 2018;129:695–716.
- Lee XJ, Lee LY, Hiew BYZ, Gan S, Thangalazhy-Gopakumar S, Kiat Ng H. Multistage optimizations of slow pyrolysis synthesis of biochar from palm oil sludge for adsorption of lead. *Bioresour Technol* 2017;245(Pt A):944–53.
- Chong CT, Mong GR, Ng J-H, Chong WWF, Ani FN, Lam SS, et al. Pyrolysis characteristics and kinetic studies of horse manure using thermogravimetric analysis. *Energy Convers Manage* 2019;180:1260–7.
- Han J, Li W, Liu D, Qin L, Chen W, Xing F. Pyrolysis characteristic and mechanism of waste tyre: A thermogravimetry-mass spectrometry analysis. *J Anal Appl Pyrol* 2018;129:1–5.
- Yanik J, Stahl R, Troeger N, Sinag A. Pyrolysis of algal biomass. *J Anal Appl Pyrol* 2013;103:134–41.

- [59] Lee XJ, Lee LY, Gan S, Thangalazhy-Gopakumar S, Ng HK. Biochar potential evaluation of palm oil wastes through slow pyrolysis: Thermochemical characterization and pyrolytic kinetic studies. *Bioresour Technol* 2017;236:155–63.
- [60] Liu S, Yu J, Bikane K, Chen T, Ma C, Wang B, et al. Rubber pyrolysis: Kinetic modeling and vulcanization effects. *Energy* 2018;155:215–25.
- [61] Uddin MN, Techato K, Taweekun J, Rahman MM, Rasul MG, Mahlia TMI, et al. An overview of recent developments in biomass pyrolysis technologies. *Energies* 2018;11(11).
- [62] Paerl HW, Otten TG, Kudela R. Mitigating the expansion of harmful algal blooms across the freshwater-to-marine continuum. *Environ Sci Technol* 2018;52(10):5519–29.
- [63] Maddi B, Viamajala S, Varanasi S. Comparative study of pyrolysis of algal biomass from natural lake blooms with lignocellulosic biomass. *Bioresour Technol* 2011;102(23):11018–26.
- [64] Bird MI, Wurster CM, de Paula Silva PH, Bass AM, de Nys R. Algal biochar production and properties. *Bioresour Technol* 2011;102(2):1886–91.
- [65] Zeng Y, Zhao B, Zhu L, Tong D, Hu C. Catalytic pyrolysis of natural algae from water blooms over nickel phosphide for high quality bio-oil production. *RSC Advances* 2013;3(27).
- [66] Gao L, Sun J, Xu W, Xiao G. Catalytic pyrolysis of natural algae over Mg-Al layered double oxides/ZSM-5 (MgAl-LDO/ZSM-5) for producing bio-oil with low nitrogen content. *Bioresour Technol* 2017;225:293–8.
- [67] Pittman JK, Dean AP, Osundeko O. The potential of sustainable algal biofuel production using wastewater resources. *Bioresour Technol* 2011;102(1):17–25.
- [68] Miao X, Wu Q, Yang C. Fast pyrolysis of microalgae to produce renewable fuels. *J Anal Appl Pyrol* 2004;71(2):855–63.
- [69] Sudhakar K, Mamat R, Samykano M, Azmi WH, Ishak FWF, Yusaf T. An overview of marine macroalgae as bioresource. *Renew Sustain Energy Rev* 2018;91:165–79.
- [70] Narala RR, Garg S, Sharma KK, Thomas-Hall SR, Deme M, Li Y, et al. Comparison of microalgae cultivation in photobioreactor, open raceway pond, and a two-stage hybrid system. *Front Energy Res* 2016;4.
- [71] Brennan L, Owende P. Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products. *Renew Sustain Energy Rev* 2010;14(2):557–77.
- [72] Chen CY, Yeh KL, Aisyah R, Lee DJ, Chang JS. Cultivation, photobioreactor design and harvesting of microalgae for biodiesel production: a critical review. *Bioresour Technol* 2011;102(1):71–81.
- [73] Hadiyanto H, Elmores S, Van Gerven T, Stankiewicz A. Hydrodynamic evaluations in high rate algae pond (HRAP) design. *Chem Eng J* 2013;217:231–9.
- [74] Slade R, Bauen A. Micro-algae cultivation for biofuels: Cost, energy balance, environmental impacts and future prospects. *Biomass Bioenergy* 2013;53:29–38.
- [75] Carvalho AP, Meireles LA, Malcata FX. Microalgal reactors: A review of enclosed system designs and performances. *Biotechnol Prog* 2006;22(6):1490–506.
- [76] Alcántara C, Posadas E, Guieysse B, Muñoz R. *Microalgae-based wastewater treatment*. Handbook of Marine Microalgae. United States of America: Elsevier Inc.; 2015. p. 439–55.
- [77] Goh BHH, Ong HC, Cheah MY, Chen W-H, Yu KL, Mahlia TMI. Sustainability of direct biodiesel synthesis from microalgae biomass: a critical review. *Renew Sustain Energy Rev* 2019;107:59–74.
- [78] Polat S, Ozogul Y. Biochemical composition of some red and brown macro algae from the Northeastern Mediterranean Sea. *Int J Food Sci Nutr* 2009;59(7–8):566–72.
- [79] Tiwari BK, Troy DJ. *Seaweed sustainability—food and nonfood applications, in Seaweed Sustainability*. 2015, Elsevier Inc.: United States of America. p. 1–6.
- [80] Bae YJ, Ryu C, Jeon JK, Park J, Suh DJ, Suh YW, et al. The characteristics of bio-oil produced from the pyrolysis of three marine macroalgae. *Bioresour Technol* 2011;102(3):3512–20.
- [81] Raheem A, Prinsen P, Vuppaladadiyam AK, Zhao M, Luque R. A review on sustainable microalgae based biofuel and bioenergy production: Recent developments. *J Cleaner Prod* 2018;181:42–59.
- [82] Buschmann AH, Camus C, Infante J, Neori A, Israel Á, Hernández-González MC, et al. Seaweed production: overview of the global state of exploitation, farming and emerging research activity. *Eur J Phycol* 2017;52(4):391–406.
- [83] Choi JH, Kim S-S, Kim J, Woo HC. Fast pyrolysis of fermentation residue derived from *Saccharina japonica* for a hybrid biological and thermal process. *Energy* 2019;170:239–49.
- [84] Abdullah B, Syed Muhammad SAFA, Shokravi Z, Ismail S, Kassim KA, Mahmood AN, Aziz MMA. Fourth generation biofuel: A review on risks and mitigation strategies. *Renew Sustain Energy Rev* 2019;107:37–50.
- [85] Borowitzka MA. Commercial production of microalgae: ponds, tanks, tubes and fermenters. *J Biotechnol* 1999;70(1):313–21.
- [86] Tredici MR, Rodolfi L, Biondi N, Bassi N, Sampietro G. Techno-economic analysis of microalgal biomass production in a 1-ha Green Wall Panel (GWP[®]) plant. *Algal Research* 2016;19:253–63.
- [87] Nautiyal P, Subramanian KA, Dastidar MG. Adsorptive removal of dye using biochar derived from residual algae after in-situ transesterification: Alternate use of waste of biodiesel industry. *J Environ Manage* 2016;182:187–97.
- [88] Pan P, Hu C, Yang W, Li Y, Dong L, Zhu L, et al. The direct pyrolysis and catalytic pyrolysis of *Nannochloropsis* sp. residue for renewable bio-oils. *Bioresour Technol* 2010;101(12):4593–9.
- [89] Mata TM, Martins AA, Caetano NS. Microalgae for biodiesel production and other applications: a review. *Renew Sustain Energy Rev* 2010;14(1):217–32.
- [90] Abinandan S, Subashchandrabose SR, Venkateswarlu K, Megharaj M. Nutrient removal and biomass production: advances in microalgal biotechnology for wastewater treatment. *Crit Rev Biotechnol* 2018;38(8):1244–60.
- [91] Bulgariu L, Gavrilescu M. Bioremediation of heavy metals by microalgae. *Handbook of Marine Microalgae*. United States of America: Elsevier Inc.; 2015. p. 457–69.
- [92] Roberts DA, Paul NA, Bird MI, de Nys R. Bioremediation for coal-fired power stations using macroalgae. *J Environ Manage* 2015;153:25–32.
- [93] Converti A, Casazza AA, Ortiz EY, Perego P, Del Borghi M. Effect of temperature and nitrogen concentration on the growth and lipid content of *Nannochloropsis oculata* and *Chlorella vulgaris* for biodiesel production. *Chem Eng Process Process Intensif* 2009;48(6):1146–51.
- [94] Aslam A, Thomas-Hall SR, Manzoor M, Jabeen F, Iqbal M, Uz Zaman Q, et al. Mixed microalgae consortia growth under higher concentration of CO₂ from un-filtered coal fired flue gas: Fatty acid profiling and biodiesel production. *J Photochem Photobiol B* 2018;179:126–33.
- [95] Sydney EB, Sturm W, de Carvalho JC, Thomaz-Soccol V, Larroche C, Pandey A, et al. Potential carbon dioxide fixation by industrially important microalgae. *Bioresour Technol* 2010;101(15):5892–6.
- [96] Eloka-Eboka AC, Inambao FL. Effects of CO₂ sequestration on lipid and biomass productivity in microalgal biomass production. *Appl Energy* 2017;195:1100–11.
- [97] Singh SP, Singh P. Effect of CO₂ concentration on algal growth: A review. *Renew Sustain Energy Rev* 2014;38:172–9.
- [98] Tang D, Han W, Li P, Miao X, Zhong J. CO₂ biofixation and fatty acid composition of *Scenedesmus obliquus* and *Chlorella pyrenoidosa* in response to different CO₂ levels. *Bioresour Technol* 2011;102(3):3071–6.
- [99] Chen WH, Lin BJ, Huang MY, Chang JS. Thermochemical conversion of microalgal biomass into biofuels: a review. *Bioresour Technol* 2015;184:314–27.
- [100] Smith AM, Ross AB. Production of bio-coal, bio-methane and fertilizer from seaweed via hydrothermal carbonisation. *Algal Research* 2016;16:1–11.
- [101] Keibelmann K, Hornung A, Karsten U, Griffiths G. Thermo-chemical behaviour and chemical product formation from Polar seaweeds during intermediate pyrolysis. *J Anal Appl Pyrol* 2013;104:131–8.
- [102] Verma P, Kumar M, Mishra G, Sahoo D. Multivariate analysis of fatty acid and biochemical constituents of seaweeds to characterize their potential as bioresource for biofuel and fine chemicals. *Bioresour Technol* 2017;226:132–44.
- [103] Huang F, Tahmasebi A, Maliutina K, Yu J. Formation of nitrogen-containing compounds during microwave pyrolysis of microalgae: Product distribution and reaction pathways. *Bioresour Technol* 2017;245(Pt A):1067–74.
- [104] Zainan NH, Srivatsa SC, Li F, Bhattacharya S. Quality of bio-oil from catalytic pyrolysis of microalgae *Chlorella vulgaris*. *Fuel* 2018;223:12–9.
- [105] Altenor S, Ncibi MC, Emmanuel E, Gaspard S. Textural characteristics, physico-chemical properties and adsorption efficiencies of Caribbean alga *Turbinaria turbinata* and its derived carbonaceous materials for water treatment application. *Biochem Eng J* 2012;67:35–44.
- [106] Parsa M, Jalilzadeh H, Pazoki M, Ghazemzadeh R, Abdul M. Hydrothermal liquefaction of *Gracilaria gracilis* and *Cladophora glomerata* macro-algae for bio-crude production. *Bioresour Technol* 2018;250:26–34.
- [107] Li B, Yang L, Wang C-Q, Zhang Q-P, Liu Q-C, Li Y-D, et al. Adsorption of Cd(II) from aqueous solutions by rape straw biochar derived from different modification processes. *Chemosphere* 2017;175(Supplement C):332–40.
- [108] Jena U, Das KC. Comparative Evaluation of Thermochemical Liquefaction and Pyrolysis for Bio-Oil Production from Microalgae. *Energy Fuels* 2011;25(11):5472–82.
- [109] Fang J, Zhan L, Ok YS, Gao B. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. *J Ind Eng Chem* 2018;57(Supplement C):15–21.
- [110] Maguyon MCC, Capareda SC. Evaluating the effects of temperature on pressurized pyrolysis of *Nannochloropsis oculata* based on products yields and characteristics. *Energy Convers Manage* 2013;76:764–73.
- [111] Maliutina K, Tahmasebi A, Yu J. Pressurized entrained-flow pyrolysis of microalgae: Enhanced production of hydrogen and nitrogen-containing compounds. *Bioresour Technol* 2018;256:160–9.
- [112] Shuping Z, Yulong W, Mingde Y, Kaleem I, Chun L, Tong J. Production and characterization of bio-oil from hydrothermal liquefaction of microalgae *Dunaliella tertiolecta* cake. *Energy* 2010;35(12):5406–11.
- [113] Anshah E, Wang L, Zhang B, Shahbazi A. Catalytic pyrolysis of raw and hydrothermally carbonized *Chlamydomonas debaryana* microalgae for denitrogenation and production of aromatic hydrocarbons. *Fuel* 2018;228:234–42.
- [114] Anand V, Gautam R, Vinu R. Non-catalytic and catalytic fast pyrolysis of *Schizochytrium limacinum* microalga. *Fuel* 2017;205:1–10.
- [115] Wang X, Sheng L, Yang X. Pyrolysis characteristics and pathways of protein, lipid and carbohydrate isolated from microalgae *Nannochloropsis* sp. *Bioresour Technol* 2017;229:119–25.
- [116] Thangalazhy-Gopakumar S, Adhikari S, Chattanathan SA, Gupta RB. Catalytic pyrolysis of green algae for hydrocarbon production using H⁺ZSM-5 catalyst. *Bioresour Technol* 2012;118:150–7.
- [117] Trivedi J, Aila M, Bangwal DP, Kaul S, Garg MO. Algae based biorefinery—How to make sense? *Renew Sustain Energy Rev* 2015;47:295–307.
- [118] Hong Y, Chen W, Luo X, Pang C, Lester E, Wu T. Microwave-enhanced pyrolysis of macroalgae and microalgae for syngas production. *Bioresour Technol* 2017;237:47–56.
- [119] Higasio YS, Shoji T. Heterocyclic compounds such as pyrroles, pyridines, pyroliidins, piperidines, indoles, imidazol and pyrazins. *Appl Catal A* 2001;221(1):197–207.
- [120] Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. *Energy Convers Manage* 2007;48(1):87–92.
- [121] Kan T, Strezov V, Evans TJ. Lignocellulosic biomass pyrolysis: a review of product properties and effects of pyrolysis parameters. *Renew Sustain Energy Rev* 2016;57:1126–40.

- [122] Dominguez A, Fernandez Y, Fidalgo B, Pis JJ, Menendez JA. Bio-syngas production with low concentrations of CO₂ and CH₄ from microwave-induced pyrolysis of wet and dried sewage sludge. *Chemosphere* 2008;70(3):397–403.
- [123] Macquarrie DJ, Clark JH, Fitzpatrick E. The microwave pyrolysis of biomass. *Biofuels*, *Bioprod Biorefin* 2012;6(5):549–60.
- [124] Yan F, Luo SY, Hu ZQ, Xiao B, Cheng G. Hydrogen-rich gas production by steam gasification of char from biomass fast pyrolysis in a fixed-bed reactor: influence of temperature and steam on hydrogen yield and syngas composition. *Bioresour Technol* 2010;101(14):5633–7.
- [125] Burhenne L, Messmer J, Aicher T, Laborie M-P. The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis. *J Anal Appl Pyrolysis* 2013;101:177–84.
- [126] Baloch HA, Nizamuddin S, Siddiqui MTH, Riaz S, Jatoti AS, Dumbre DK, et al. Recent advances in production and upgrading of bio-oil from biomass: A critical overview. *J Environ Chem Eng* 2018;6(4):5101–18.
- [127] Dong M, Lu J, Yao S, Li J, Li J, Zhong Z, et al. Application of LIBS for direct determination of volatile matter content in coal. *J Anal At Spectrom* 2011;26(11).
- [128] Yang C, Li R, Cui C, Liu S, Qiu Q, Ding Y, et al. Catalytic hydroprocessing of microalga-derived biofuels: a review. *Green Chem* 2016;18(13):3684–99.
- [129] Chaiwong K, Kiatsiriroat T, Vorayos N, Thararax C. Study of bio-oil and bio-char production from algae by slow pyrolysis. *Biomass Bioenergy* 2013;56:600–6.
- [130] Lee Y, Park J, Ryu C, Gang KS, Yang W, Park YK, et al. Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500 degrees C. *Bioresour Technol* 2013;148:196–201.
- [131] Liu X, Zhang Y, Li Z, Feng R, Zhang Y. Characterization of corn-cob-derived biochar and pyrolysis kinetics in comparison with corn stalk and sawdust. *Bioresour Technol* 2014;170:76–82.
- [132] He C, Giannis A, Wang J-Y. Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior. *Appl Energy* 2013;111:257–66.
- [133] Chanaka Udayanga WD, Veksha A, Giannis A, Lim TT. Pyrolysis derived char from municipal and industrial sludge: Impact of organic decomposition and inorganic accumulation on the fuel characteristics of char. *Waste Manag* 2019;83:131–41.
- [134] Peng Y, Hu J, Yang B, Lin X-P, Zhou X-F, Yang X-W, Liu Y. Chapter 5 - Chemical composition of seaweeds, in *Seaweed Sustainability*, B.K. Tiwari and D.J. Troy, Editors. 2015, Academic Press: San Diego. p. 79-124.
- [135] Cao L, Yu IKM, Cho DW, Wang D, Tsang DCW, Zhang S, et al. Microwave-assisted low-temperature hydrothermal treatment of red seaweed (*Gracilaria lemaneiformis*) for production of levulinic acid and algae hydrochar. *Bioresour Technol* 2019;273:251–8.
- [136] Ross AB, Jones JM, Kubacki ML, Bridgeman T. Classification of macroalgae as fuel and its thermochemical behaviour. *Bioresour Technol* 2008;99(14):6494–504.
- [137] Chen H, Zhou D, Luo G, Zhang S, Chen J. Macroalgae for biofuels production: Progress and perspectives. *Renew Sustain Energy Rev* 2015;47:427–37.
- [138] Butler E, Devlin G, Meier D, McDonnell K. A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renew Sustain Energy Rev* 2011;15(8):4171–86.
- [139] Ceylan S, Topcu Y. Pyrolysis kinetics of hazelnut husk using thermogravimetric analysis. *Bioresour Technol* 2014;156:182–8.
- [140] Ly HV, Kim S-S, Kim J, Choi JH, Woo HC. Effect of acid washing on pyrolysis of *Cladophora socialis* alga in microtubing reactor. *Energy Convers Manage* 2015;106:260–7.
- [141] Carpio RB, Zhang Y, Kuo C-T, Chen W-T, Schideman LC, de Leon RL. Characterization and thermal decomposition of demineralized wastewater algae biomass. *Algal Research* 2019:38.
- [142] Cao B, Wang S, Hu Y, Abomohra AE-F, Qian L, He Z, et al. Effect of washing with diluted acids on *Enteromorpha clathrata* pyrolysis products: Towards enhanced bio-oil from seaweeds. *Renewable Energy* 2019;138:29–38.
- [143] Al Chami Z, Amer N, Smets K, Yperman J, Carleer R, Dumontet S, et al. Evaluation of flash and slow pyrolysis applied on heavy metal contaminated *Sorghum bicolor* shoots resulting from phytoremediation. *Biomass Bioenergy* 2014;63:268–79.
- [144] Yu KL, Lau BF, Show PL, Ong HC, Ling TC, Chen WH, et al. Recent developments on algal biochar production and characterization. *Bioresour Technol* 2017;246:2–11.
- [145] Yaman S. Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Convers Manage* 2004;45(5):651–71.
- [146] Jung KW, Jeong TU, Kang HJ, Ahn KH. Characteristics of biochar derived from marine macroalgae and fabrication of granular biochar by entrapment in calcium-alginate beads for phosphate removal from aqueous solution. *Bioresour Technol* 2016;211:108–16.
- [147] Roberts DA, Paul NA, Dworjany SA, Bird MI, de Nys R. Biochar from commercially cultivated seaweed for soil amelioration. *Sci Rep* 2015;5:9665.
- [148] Park SH, Cho HJ, Ryu C, Park Y-K. Removal of copper(II) in aqueous solution using pyrolytic biochars derived from red macroalga *Porphyra tenera*. *J Ind Eng Chem* 2016;36:314–9.
- [149] Choi JH, Kim S-S, Suh DJ, Jang E-J, Min K-I, Woo HC. Characterization of the bio-oil and bio-char produced by fixed bed pyrolysis of the brown alga *Saccharina japonica*. *Korean J Chem Eng* 2016;33(9):2691–8.
- [150] Grierson S, Strezov V, Ellem G, McGregor R, Herberson J. Thermal characterisation of microalgae under slow pyrolysis conditions. *J Anal Appl Pyroly* 2009;85(1–2):118–23.
- [151] Grierson S, Strezov V, Shah P. Properties of oil and char derived from slow pyrolysis of *Tetraselmis chui*. *Bioresour Technol* 2011;102(17):8232–40.
- [152] Ahmed A, Abu Bakar MS, Azad AK, Sukri RS, Phusunti N. Intermediate pyrolysis of *Acacia cincinnata* and *Acacia holosericea* species for bio-oil and biochar production. *Energy Convers Manage* 2018;176:393–408.
- [153] Keibelmann K, Hornung A, Karsten U, Griffiths G. Intermediate pyrolysis and product identification by TGA and Py-GC/MS of green microalgae and their extracted protein and lipid components. *Biomass Bioenergy* 2013;49:38–48.
- [154] Mahmood ASN, Brammer JG, Hornung A, Steele A, Poulston S. The intermediate pyrolysis and catalytic steam reforming of Brewers spent grain. *J Anal Appl Pyroly* 2013;103:328–42.
- [155] Yang Y, Zhang Y, Omairey E, Cai J, Gu F, Bridgwater AV. Intermediate pyrolysis of organic fraction of municipal solid waste and rheological study of the pyrolysis oil for potential use as bio-bitumen. *J Cleaner Prod* 2018;187:390–9.
- [156] Trinh TN, Jensen PA, Dam-Johansen K, Knudsen NO, Sørensen HR, Hvilsted S. Comparison of Lignin, Macroalgae, Wood, and Straw Fast Pyrolysis. *Energy Fuels* 2013;27(3):1399–409.
- [157] Sharifzadeh M, Sadeqzadeh M, Guo M, Borhani TN, Murthy Konda NVSN, Garcia MC, et al. The multi-scale challenges of biomass fast pyrolysis and bio-oil upgrading: Review of the state of art and future research directions. *Prog Energy Combust Sci* 2019;71:1–80.
- [158] Ly HV, Kim S-S, Woo HC, Choi JH, Suh DJ, Kim J. Fast pyrolysis of macroalga *Saccharina japonica* in a bubbling fluidized-bed reactor for bio-oil production. *Energy* 2015;93:1436–46.
- [159] Kim SJ, Jung SH, Kim JS. Fast pyrolysis of palm kernel shells: influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds. *Bioresour Technol* 2010;101(23):9294–300.
- [160] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* 2012;38:68–94.
- [161] Ly HV, Kim S-S, Choi JH, Woo HC, Kim J. Fast pyrolysis of *Saccharina japonica* alga in a fixed-bed reactor for bio-oil production. *Energy Convers Manage* 2016;122:526–34.
- [162] Wang K, Brown RC, Homsy S, Martinez L, Sidhu SS. Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production. *Bioresour Technol* 2013;127:494–9.
- [163] Campanella A, Harold MP. Fast pyrolysis of microalgae in a falling solids reactor: Effects of process variables and zeolite catalysts. *Biomass Bioenergy* 2012;46:218–32.
- [164] Wang S, Wang Q, Jiang X, Han X, Ji H. Compositional analysis of bio-oil derived from pyrolysis of seaweed. *Energy Convers Manage* 2013;68:273–80.
- [165] Harman-Ware AE, Morgan T, Wilson M, Crocker M, Zhang J, Liu K, et al. Microalgae as a renewable fuel source: Fast pyrolysis of *Scenedesmus* sp. *Renewable Energy* 2013;60:625–32.
- [166] Gelin F, Gatellier JPLA, Damsté JSS, Metzger P, Derenne S, Largeau C, et al. Mechanisms of flash pyrolysis of ether lipids isolated from the green microalga *Botryococcus braunii* race A. *J Anal Appl Pyroly* 1993;27(2):155–68.
- [167] Gelin F, de Leeuw JW, Sinnighe Damsté JS, Derenne S, Largeau C, Metzger P. Scope and limitations of flash pyrolysis—gas chromatography/mass spectrometry as revealed by the thermal behaviour of high-molecular-weight lipids derived from the green microalga *Botryococcus braunii*. *J Anal Appl Pyroly* 1994;28(2):183–204.
- [168] Miandad R, Barakat MA, Aburiazaiza AS, Rehan M, Nizami AS. Catalytic pyrolysis of plastic waste: a review. *Process Saf Environ Prot* 2016;102:822–38.
- [169] Abu El-Rub Z, Bramer EA, Brem G. Review of Catalysts for Tar Elimination in Biomass Gasification Processes. *Ind Eng Chem Res* 2004;43(22):6911–9.
- [170] Kalogiannis KG, Stefanidis SD, Karakoulia SA, Triantafyllidis KS, Yiannoulakis H, Michailof C, et al. First pilot scale study of basic vs acidic catalysts in biomass pyrolysis: Deoxygenation mechanisms and catalyst deactivation. *Appl Catal B* 2018;238:346–57.
- [171] Iisa K, French RJ, Orton KA, Yung MM, Johnson DK, ten Dam J, et al. In Situ and ex Situ Catalytic Pyrolysis of Pine in a Bench-Scale Fluidized Bed Reactor System. *Energy Fuels* 2016;30(3):2144–57.
- [172] Babich IV, van der Hulst M, Lefferts L, Mouljin JA, O'Connor P, Seshan K. Catalytic pyrolysis of microalgae to high-quality liquid bio-fuels. *Biomass Bioenergy* 2011;35(7):3199–207.
- [173] Dong X, Chen Z, Xue S, Zhang J, Zhou J, Liu Y, et al. Catalytic pyrolysis of microalga *Chlorella pyrenoidosa* for production of ethylene, propylene and butene. *RSC Advances* 2013;3(48).
- [174] French R, Czernik S. Catalytic pyrolysis of biomass for biofuels production. *Fuel Process Technol* 2010;91(1):25–32.
- [175] Isahak WNRW, Hisham MWM, Yarmo MA, Yun Hin T-Y. A review on bio-oil production from biomass by using pyrolysis method. *Renew Sustain Energy Rev* 2012;16(8):5910–23.
- [176] Kalogiannis KG, Stefanidis SD, Lappas AA. Catalyst deactivation, ash accumulation and bio-oil deoxygenation during ex situ catalytic fast pyrolysis of biomass in a cascade thermal-catalytic reactor system. *Fuel Process Technol* 2019;186:99–109.
- [177] Dai L, Wang Y, Liu Y, Ruan R, Duan D, Zhao Y, et al. Catalytic fast pyrolysis of torrefied corn cob to aromatic hydrocarbons over Ni-modified hierarchical ZSM-5 catalyst. *Bioresour Technol* 2019;272:407–14.
- [178] Muñoz R, Gonzalez-Fernandez C. Microalgae-based biofuels and bioproducts: from feedstock cultivation to end-products. Woodhead Publishing; 2017.
- [179] Aysu T, Maroto-Valer MM, Sanna A. Ceria promoted deoxygenation and denitrogenation of *Thalassiosira weissflogii* and its model compounds by catalytic in-situ pyrolysis. *Bioresour Technol* 2016;208:140–8.
- [180] Taghavi S, Norouzi O, Tavasoli A, Di Maria F, Signoretto M, Menegazzo F, et al. Catalytic conversion of Venice lagoon brown marine algae for producing hydrogen-rich gas and valuable biochemical using algal biochar and Ni/SBA-15 catalyst. *Int J Hydrogen Energy* 2018;43(43):19918–29.
- [181] Norouzi O, Di Maria F. Catalytic Effect of Functional and Fe Composite Biochars on Biofuel and Biochemical Derived from the Pyrolysis of Green Marine Biomass. *Fermentation* 2018;4(4):96.
- [182] Sabegh MY, Norouzi O, Jafarian S, Khosh AG, Tavasoli A. Pyrolysis of marine

- biomass to produce bio-oil and its upgrading using a novel multi-metal catalyst prepared from the spent car catalytic converter. *Bioresour Technol* 2018;249:473–8.
- [183] Anand V, Sunjeev V, Vinu R. Catalytic fast pyrolysis of *Arthrospira platensis* (spirulina) algae using zeolites. *J Anal Appl Pyrol* 2016;118:298–307.
- [184] Lee HW, Jeon J-K, Park SH, Jeong K-E, Chae H-J, Park Y-K. Catalytic pyrolysis of *Laminaria japonica* over nanoporous catalysts using Py-GC/MS. *Nanoscale Res Lett* 2011;6(1):500.
- [185] Lee HW, Choi SJ, Park SH, Jeon J-K, Jung S-C, Kim SC, et al. Pyrolysis and co-pyrolysis of *Laminaria japonica* and polypropylene over mesoporous Al-SBA-15 catalyst. *Nanoscale Res Lett* 2014;9(1):376.
- [186] Aysu T, Ola O, Maroto-Valer MM, Sanna A. Effects of titania based catalysts on in-situ pyrolysis of *Pavlova* microalgae. *Fuel Process Technol* 2017;166:291–8.
- [187] Norouzi O, Tavasoli A, Jafarian S, Esmailpour S. Catalytic upgrading of bio-products derived from pyrolysis of red macroalgae *Gracilaria gracilis* with a promising novel micro/mesoporous catalyst. *Bioresour Technol* 2017;243:1–8.
- [188] Kubů M, Millini R, Žilková N. 10-ring Zeolites: Synthesis, characterization and catalytic applications. *Catal Today* 2019;324:3–14.
- [189] Shirazi L, Jamshidi E, Ghasemi MR. The effect of Si/Al ratio of ZSM-5 zeolite on its morphology, acidity and crystal size. *Cryst Res Technol* 2008;43(12):1300–6.
- [190] Chang Z, Duan P, Xu Y. Catalytic hydro-pyrolysis of microalgae: influence of operating variables on the formation and composition of bio-oil. *Bioresour Technol* 2015;184:349–54.
- [191] Ly HV, Choi JH, Woo HC, Kim S-S, Kim J. Upgrading bio-oil by catalytic fast pyrolysis of acid-washed *Saccharina japonica* alga in a fluidized-bed reactor. *Renewable Energy* 2019;133:11–22.
- [192] Norouzi O, Jafarian S, Safari F, Tavasoli A, Nejati B. Promotion of hydrogen-rich gas and phenolic-rich bio-oil production from green macroalgae *Cladophora glomerata* via pyrolysis over its bio-char. *Bioresour Technol* 2016;219:643–51.
- [193] Wang S, Cao B, Liu X, Xu L, Hu Y, Afonaa-Mensah S, et al. A comparative study on the quality of bio-oil derived from green macroalgae *Enteromorpha clathrata* over metal modified ZSM-5 catalysts. *Bioresour Technol* 2018;256:446–55.
- [194] Ma C, Geng J, Zhang D, Ning X. Non-catalytic and catalytic pyrolysis of *Ulva prolifera* macroalgae for production of quality bio-oil. *J Energy Inst* 2019.
- [195] Jafarian S, Tavasoli A. A comparative study on the quality of bioproducts derived from catalytic pyrolysis of green microalgae *Spirulina* (*Arthrospira*) *platensis* over transition metals supported on HMS-ZSM5 composite. *Int J Hydrogen Energy* 2018;43(43):19902–17.
- [196] Kawale HD, Kishore N. Production of hydrocarbons from a green algae (*Oscillatoria*) with exploration of its fuel characteristics over different reaction atmospheres. *Energy* 2019;178:344–55.
- [197] Rodriguez JA, Grinter DC, Liu Z, Palomino RM, Senanayake SD. Ceria-based model catalysts: fundamental studies on the importance of the metal-ceria interface in CO oxidation, the water-gas shift, CO₂ hydrogenation, and methane and alcohol reforming. *Chem Soc Rev* 2017;46(7):1824–41.
- [198] Gautam R, Vinu R. Non-catalytic fast pyrolysis and catalytic fast pyrolysis of *Nannochloropsis oculata* using Co-Mo/ γ -Al₂O₃ catalyst for valuable chemicals. *Algal Research* 2018;34:12–24.
- [199] Aysu T, Abd Rahman NA, Sanna A. Catalytic pyrolysis of *Tetraselmis* and *Isochrysis* microalgae by nickel ceria based catalysts for hydrocarbon production. *Energy* 2016;103:205–14.
- [200] Aysu T, Sanna A. *Nannochloropsis* algae pyrolysis with ceria-based catalysts for production of high-quality bio-oils. *Bioresour Technol* 2015;194:108–16.
- [201] Uzojejinwa BB, He X, Wang S, El-Fatah Abomohra A, Hu Y, Wang Q. Co-pyrolysis of biomass and waste plastics as a thermochemical conversion technology for high-grade biofuel production: Recent progress and future directions elsewhere worldwide. *Energy Convers Manage* 2018;163:468–92.
- [202] Abnisa F, Wan Daud WMA. A review on co-pyrolysis of biomass: an optional technique to obtain a high-grade pyrolysis oil. *Energy Convers Manage* 2014;87:71–85.
- [203] Hassan H, Lim JK, Hameed BH. Recent progress on biomass co-pyrolysis conversion into high-quality bio-oil. *Bioresour Technol* 2016;221:645–55.
- [204] Duan P, Jin B, Xu Y, Wang F. Co-pyrolysis of microalgae and waste rubber tire in supercritical ethanol. *Chem Eng J* 2015;269:262–71.
- [205] Xie Q, Addy M, Liu S, Zhang B, Cheng Y, Wan Y, et al. Fast microwave-assisted catalytic co-pyrolysis of microalgae and scum for bio-oil production. *Fuel* 2015;160:577–82.
- [206] Azizi K, Keshavarz Moraveji M, Abedini Najafabadi H. Simultaneous pyrolysis of microalgae *C. vulgaris*, wood and polymer: The effect of third component addition. *Bioresour Technol* 2018;247:66–72.
- [207] Wang S, Shang H, Abomohra AE-F, Wang Q. One-step conversion of microalgae to alcohols and esters through co-pyrolysis with biodiesel-derived glycerol. *Energy Convers Manage* 2019;198:111792.
- [208] Zhao B, Wang X, Yang X. Co-pyrolysis characteristics of microalgae *Isochrysis* and *Chlorella*: Kinetics, biocrude yield and interaction. *Bioresour Technol* 2015;198:332–9.
- [209] Chen L, Yu Z, Liang J, Liao Y, Ma X. Co-pyrolysis of *Chlorella vulgaris* and kitchen waste with different additives using TG-FTIR and Py-GC/MS. *Energy Convers Manage* 2018;177:582–91.
- [210] Wang S, Wang Q, Hu YM, Xu SN, He ZX, Ji HS. Study on the synergistic co-pyrolysis behaviors of mixed rice husk and two types of seaweed by a combined TG-FTIR technique. *J Anal Appl Pyrol* 2015;114:109–18.
- [211] Hua M-Y, Li B-X. Co-pyrolysis characteristics of the sugarcane bagasse and *Enteromorpha prolifera*. *Energy Convers Manage* 2016;120:238–46.
- [212] Uzojejinwa BB, He X, Wang S, Abomohra AE-F, Hu Y, He Z, et al. Co-pyrolysis of macroalgae and lignocellulosic biomass. *J Therm Anal Calorim* 2018.
- [213] Chen W, Li K, Xia M, Yang H, Chen Y, Chen X, et al. Catalytic deoxygenation co-pyrolysis of bamboo wastes and microalgae with biochar catalyst. *Energy* 2018;157:472–82.
- [214] Kositkanawuth K, Bhatt A, Sattler M, Dennis B. Renewable energy from waste: investigation of co-pyrolysis between sargassum macroalgae and polystyrene. *Energy Fuels* 2017;31(5):5088–96.
- [215] Tang Z, Chen W, Chen Y, Yang H, Chen H. Co-pyrolysis of microalgae and plastic: characteristics and interaction effects. *Bioresour Technol* 2019;274:145–52.
- [216] Wu Z, Yang W, Li Y, Yang B. Co-pyrolysis behavior of microalgae biomass and low-quality coal: products distributions, char-surface morphology, and synergistic effects. *Bioresour Technol* 2018;255:238–45.
- [217] Kirtania K, Bhattacharya S. Pyrolysis kinetics and reactivity of algae-coal blends. *Biomass Bioenergy* 2013;55:291–8.
- [218] Feroso J, Corbet T, Ferrara F, Pettinau A, Maggio E, Sanna A. Synergistic effects during the co-pyrolysis and co-gasification of high volatile bituminous coal with microalgae. *Energy Convers Manage* 2018;164:399–409.
- [219] Wang X, Zhao B, Yang X. Co-pyrolysis of microalgae and sewage sludge: Biocrude assessment and char yield prediction. *Energy Convers Manage* 2016;117:326–34.
- [220] Marker T, Roberts M, Linck M, Felix L, Ortiz-Toral P, Wangerow J, et al. Biomass to gasoline and diesel using integrated hydro-pyrolysis and hydroconversion. *Gas Technology Inst. United States of America*; 2013.
- [221] Yan W-H, Wang K, Duan P-G, Wang B, Wang F, Shi X-L, et al. Catalytic hydro-pyrolysis and co-hydro-pyrolysis of algae and used engine oil for the production of hydrocarbon-rich fuel. *Energy* 2017;133:1153–62.
- [222] Duan P, Bai X, Xu Y, Zhang A, Wang F, Zhang L, et al. Non-catalytic hydro-pyrolysis of microalgae to produce liquid biofuels. *Bioresour Technol* 2013;136:626–34.
- [223] Beneroso D, Bermudez JM, Arenillas A, Menendez JA. Microwave pyrolysis of microalgae for high syngas production. *Bioresour Technol* 2013;144:240–6.
- [224] Zhang X, Rajagopalan K, Lei H, Ruan R, Sharma BK. An overview of a novel concept in biomass pyrolysis: microwave irradiation. *Sustainable Energy Fuels* 2017;1(8):1664–99.
- [225] Zhang R, Li L, Tong D, Hu C. Microwave-enhanced pyrolysis of natural algae from water blooms. *Bioresour Technol* 2016;212:311–7.
- [226] Amin M, Chetpattananondh P, Ratanawilai S. Application of extracted marine *Chlorella* sp. residue for bio-oil production as the biomass feedstock and microwave absorber. *Energy Convers Manage* 2019;195:819–29.
- [227] Motasemi F, Afzal MT. A review on the microwave-assisted pyrolysis technique. *Renew Sustain Energy Rev* 2013;28:317–30.
- [228] Zhang Y, Chen P, Liu S, Peng P, Min M, Cheng Y, et al. Effects of feedstock characteristics on microwave-assisted pyrolysis - A review. *Bioresour Technol* 2017;230:143–51.
- [229] Yin C. Microwave-assisted pyrolysis of biomass for liquid biofuels production. *Bioresour Technol* 2012;120:273–84.
- [230] Du Z, Li Y, Wang X, Wan Y, Chen Q, Wang C, et al. Microwave-assisted pyrolysis of microalgae for biofuel production. *Bioresour Technol* 2011;102(7):4890–6.
- [231] Hu Z, Ma X, Chen C. A study on experimental characteristic of microwave-assisted pyrolysis of microalgae. *Bioresour Technol* 2012;107:487–93.
- [232] Budarin VL, Zhao Y, Gronnow MJ, Shuttleworth PS, Breeden SW, Macquarrie DJ, et al. Microwave-mediated pyrolysis of macro-algae. *Green Chem* 2011;13(9):2330–3.
- [233] Ferrera-Lorenzo N, Fuente E, Bermudez JM, Suarez-Ruiz I, Ruiz B. Conventional and microwave pyrolysis of a macroalgae waste from the Agar-Agar industry. Prospects for bio-fuel production. *Bioresour Technol* 2014;151:199–206.
- [234] Borges FC, Xie Q, Min M, Muniz LA, Farenzena M, Trierweiler JO, et al. Fast microwave-assisted pyrolysis of microalgae using microwave absorbent and HZSM-5 catalyst. *Bioresour Technol* 2014;166:518–26.
- [235] Van de Velden M, Baeyens J, Brems A, Janssens B, Dewil R. Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. *Renewable Energy* 2010;35(1):232–42.
- [236] Raveendran K, Ganesh A, Khilar KC. Pyrolysis characteristics of biomass and biomass components. *Fuel* 1996;75(8):987–98.
- [237] Bach QV, Chen WH. Pyrolysis characteristics and kinetics of microalgae via thermogravimetric analysis (TGA): A state-of-the-art review. *Bioresour Technol* 2017;246:88–100.
- [238] Saber M, Nakhshiniev B, Yoshikawa K. A review of production and upgrading of algal bio-oil. *Renew Sustain Energy Rev* 2016;58:918–30.
- [239] Bird MI, Wurster CM, De Paula Silva PH, Paul NA, De Nys R. Algal biochar: effects and applications. *GCB Bioenergy* 2012;4(1):61–9.
- [240] Choi J, Choi J-W, Suh DJ, Ha J-M, Hwang JW, Jung HW, et al. Production of brown algae pyrolysis oils for liquid biofuels depending on the chemical pre-treatment methods. *Energy Convers Manage* 2014;86:371–8.
- [241] Lin J, Ma R, Luo J, Sun S, Cui C, Fang L, et al. Microwave pyrolysis of food waste for high-quality syngas production: Positive effects of a CO₂ reaction atmosphere and insights into the intrinsic reaction mechanisms. *Energy Convers Manage* 2020;206.