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A state-of-the-art review on algae pyrolysis for bioenergy and biochar production

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Abstract

Algae, as a feedstock with minimum land footprint, is considered a promising biomass for sustainable fuels, chemicals, and materials. Unlike lignocellulosic biomass, algae consist mainly of lipids, carbohydrates, and proteins. This review focusses on the bio-oil and biochar co-products of algae-pyrolysis and presents the current state-of-the-art in the pyrolysis technologies and key applications of algal biochar. Algal biochar holds potential to be a cost-effective fertilizer, as it has high P, N and other nutrient contents. Beyond soil applications, algae-derived biochar has many other applications, such as wastewater-treatment, due to its porous structure and strong ion-exchange capacity. High specific capacitance and stability also make algal biochar a potential supercapacitor material. Furthermore, algal biochar can be great catalysts (or catalyst supports). This review sheds light on a wide range of algae-pyrolysis related topics, including advanced-pyrolysis techniques and the potential biochar applications in soil amendment, energy storage, catalysts, chemical industries, and wastewater-treatment plants.
1. Introduction

The increase in world population and the rapid expansion of industrialization have led to continuous growth in global energy consumption (Syvitski et al., 2020). In 2019, the global mean concentrations of CO$_2$, methane (CH$_4$) and nitrous oxide (N$_2$O) were 409.9 ppm, 1866.3 ppb and 332.1 ppb, which were 47.3%, 156%, and 23% higher than that in 1750, respectively (IPCC, 2021). The concentrations of these three greenhouse gases (GHGs) in the atmosphere are higher than at any point in the past 800,000 years (IPCC, 2021). Consequently, the earth’s temperature rose by 1 °C and is expected to increase by another 2.5-4 °C by the end of the 21st century under high emission scenarios (Klein et al., 2021). To address these issues, a range of renewable energy technologies has been developed and deployed, including bioenergy (Sekar et al., 2021; Röder et al., 2020; Mandley et al., 2020). In the EU, bioenergy accounts for 64% of the total renewable energy consumption, which is equivalent to approx. 5.6 EJ yr$^{-1}$ (Mandley et al., 2020). However, large-scale utilisation of bioenergy still faces a number of technical and non-technical barriers, such as low energy density (Nyoni et al., 2020), limiting economic transportation distance, poor storage stability (Hu et al., 2021), affecting biomass storage, and potential for land competition with food production and other uses (Yang et al., 2021a). The typical Energy Return on Investment (EROI) of biofuels is lower than 5, and much lower in some cases, which indicates that the energy consumption during production is relatively high compared to that of fossil fuels (Buchanan, 2019). Furthermore, inappropriate bioenergy utilization in low- and middle-income countries, such as inefficient production of charcoal for cooking, can have undesirable consequences, such as deforestation, soil degradation, and air pollution (Röder et al., 2020).

Conceptually, there are four generations of biofuel technologies, depending on the types of feedstocks used. The first generation of biofuels relies on sugars in edible food crops, such as
corn and vegetable oils. Extensive use of the first-generation biofuels can compete for land and
crops with food and feed uses and as a result increase food prices and put pressure on land use
(Rulli et al., 2016). Due to these limitations of first-generation biofuels, new technologies that
do not rely on readily available sugars and fats have been developed. These so-called second-
generation biofuels can utilize a wide range of lignocellulosic biomass, including agricultural
and forestry residues (straw, sawdust, etc.) as well as dedicated energy crops, such as jatropha,
miscanthus, or short-rotation willow, to produce ethanol, dimethyl ether, or Fischer Tropsch
synthesis fuel (Raud et al., 2019; Usmani et al., 2021). Although second-generation biofuels do
not require food crops and therefore are not in direct competition with food, they still require
land to produce biomass. The third-generation biofuels address this issue by using aquatic
biomass, such as microalgae or macroalgae as feedstock (Singh et al., 2011). High lipid content,
fast growth rate and low land demand make algae a promising third-generation energy crop
(Sekar et al., 2021). In the fourth-generation biofuels, genetically modified microorganisms
such as microalgae and fungi are used as feedstock. Previous studies indicated that the third
and fourth-generation biofuels are related to algae, so the development of biofuels and algae
research in the future have a similar direction (Bach et al., 2017; Abdullah et al., 2019).

There are several processes for the conversion of algae to biofuels, chemicals, and materials.
Fermentation can be used to convert lipids extracted from algae into biodiesel, and it can also
convert carbohydrate components into bioethanol (Debiagi et al., 2017). Algae can be
converted into methane by anaerobic digestion (Zhong et al., 2013). Bio-oil, biochar and
syngas can be produced through thermochemical conversion technologies such as pyrolysis,
torrefaction, and gasification (Parvez et al., 2019). Algal pyrolysis thermally decomposes algal
biomass into a variety of pyrolytic products such as bio-oil (e.g., aromatic hydrocarbons,
nitrogen-containing compounds, carboxylic acid, furans and ketones), syngas (e.g., CO and
H₂), and biochar (Lee et al., 2020; Hong et al., 2017). The pyrolysis process involves moisture
loss, decomposition of organic structures, and disintegration of solid residuals (Demirbas, 2009). Depending on the operating process design and conditions used (mainly temperature, heating rate and residence time), pyrolysis can be generally divided into slow, fast, and flash pyrolysis. Slow pyrolysis typically has a heating rate of 0.1-1 °C s\(^{-1}\) and residence time of several minutes or even hours, whereas fast pyrolysis has a heating rate of more than 100 °C s\(^{-1}\) and is typically carried out at the temperatures between 400 and 600 °C (Onay and Kockar, 2003; Bridgwater et al., 1999). In the flash pyrolysis, biomass undergo a higher heating rates of \(10^3–10^4 \text{ °C s}^{-1}\) for a very shorter retention time (<0.5 s) at temperatures of 800-1000 °C (Kan et al., 2016).

Biochar is the major product of slow pyrolysis due to the sufficient residence time, promoting char formation, while fast and flash pyrolysis yield more bio-oil (Demirbas, 2004; Bridgwater et al., 1999). Currently, two major applications of pyrolytic bio-oil are energy source and chemical production (Mandley et al., 2020; Chew et al., 2017). However, algal bio-oil produced by pyrolysis generally has a high viscosity, which means that it cannot be directly used in internal combustion engines. The oxygen content (10-30 wt%) of algal bio-oil is relatively lower than that obtained by pyrolysis of agricultural and forestry residues (about 45-50 wt%); however, it is still high compared to that of heavy petroleum fuel oil (about 1.0 wt%) (Saber et al., 2016). The high oxygen content can lead to low HHV of bio-oil, which is a huge barrier for it to become the fossil fuel alternative (Saber et al., 2016). Bio-refinery and pyrolysis technology updating can be conducted to upgrade the quality of bio-oil. Hence, this review focus on the latter, intending to provide the update of advanced pyrolysis technology in the recent years. The characteristics of different feedstocks can also significantly affect the bio-oil quality. Due to the aqueous growth environment, most of the algal biomass have high moisture content, leading to a high moisture content of the pyrolytic bio-oil, thereby affecting the quality of the bio-oil (Lee et al., 2020). In addition, the fatty acid and aldehyde contents of algal
biomass can cause corrosiveness and low chemical stability of bio-oil produced, which are common problems for bio-oil from all biomass types (Saber et al., 2016; Oasmaa, 2016). Although there is a huge gap waiting to be filled between ideas and commercialization, the researchers should realise that the basic advantage of algae as a feedstock is its fast growth rate (Dauta et al., 1990) and high yield (David et al., 2015). When used for biochar production, the high growth rate of algae allows for faster rate of atmospheric carbon removal and sequestration.

Since the second half of the 20th century, pyrolysis liquid products, such as biofuels have received a lot of attention due to the need to find alternatives to fossil fuels. But in the past decade, a new focus on algae-derived biochar has emerged as a potential contributor to the reduction of carbon content in the atmosphere, with the advantage of not requiring land to produce biomass. Compared to biochar derived from terrestrial biomass, algae-based biochar has distinct physical and chemical properties due to the difference in the biomass composition, often characterized by high mineral matter content and absence of lignin. Algae-derived biochar typically has higher cation exchange capacity, nitrogen content, and pH value compared to biochar from lignocellulosic biomass (Lee et al., 2020; Chen et al., 2020). Another advantage of algae as a feedstock for biochar is its fast growth rate ranging from 10 to 27 g/m² day (Dauta et al., 1990; Sekar et al., 2021; Bach and Chen, 2017; Lee et al., 2020) and high yield ranging from about 36% to 68% (Roberts et al., 2015; Bird et al., 2011), which directly impacts the rate at which biochar can sequester carbon (Bird et al., 2011).

Both the liquid and solid products of algae pyrolysis are important and need to be exploited hand in hand to maximise the environmental and economic benefits, and this paper therefore reviews the different technological options for co-production of algal bio-oil and biochar, as well as key applications of algal biochar. Only a better understanding of potential applications can make algal biochar play a more important role in mitigating climate change. At the same
time, understanding the different production technologies of algal bio-oil can make the production of algae biochar more efficient and economical, as highlighted in this review.

2. Chemical composition of algae

Algae can be the most extensive source of simple microorganisms and account for approximately half of photosynthesis activities on earth (Bach and Chen, 2017; Sirajunnisa and Surendhiran, 2016). Algae growth rate is extremely high compared to other biological materials, about 500-1500 times higher (Bach and Chen, 2017). Algae generally refer to autotrophic and embryo less plants capable of oxygen releasing and photosynthesis (Ferrera-Lorenzo et al., 2014). Algae can be divided into macroalgae (such as Kelp, *Porphyra, Undaria pinnatifida*, etc.) and microalgae (such as *Chlorella, Spirulina, Scenedesmus, Haematococcus pluvialis, Anabaena*, etc.) based on their cell sizes. It is worth mentioning that besides the main components of lipids, proteins, and carbohydrates, other important and valuable components, such as pigments, vitamins, antioxidants and fatty acids are present in algae and can be important co-products of algae processing, often with high value uses as food additives or in production of pharmaceuticals or cosmetics (Koyande et al., 2021). Algal carbohydrates are already proven to be the potential feedstocks for bioethanol production (Bach and Chen, 2017; Sirajunnisa and Surendhiran, 2016).

Lipids are natural macromolecular organic compounds widely present in biological tissues (Debiagi et al., 2017). The lipid content of algae typically ranges from 0.9 to 71.5 wt% depending on the algae species, growing conditions, seasons and geography factors (Lee et al., 2020). Microalgae like *Chlorella pyrenoidose* have a high lipid of content up to 71.5 wt% making them favorable feedstocks for lipid extraction and transesterification into biofuels (Lee et al., 2020). Macroalgae on the other hand, have a much lower lipid content, typically 0.9-4.35
wt% (Maddi et al., 2011), which makes them less desirable feedstock for direct bio-oil extraction. However, pyrolysis might be a more suitable thermal conversion method for macroalgae and extracted microalgae.

Carbohydrates are mainly formed in algal biomass in the form of polysaccharides and sugar monomers such as starch, cellulose, and glucose, similar to terrestrial plants (Lee et al., 2020). The carbohydrate content of microalgae ranges from 0.1 to 56.92 wt%, while that of macroalgae ranges from 12.43 to 47.7 wt%, as listed in Table 1. Mannitol, is usually regarded as the main photosynthetic product for algal biomass, can be utilized in the pharmaceutical industry and food (sweeteners) industry (Debiagi et al., 2017). Different carbohydrate structures exist in different algae species. For example, cellulose, carrageenan and agar exits in red algae; alginic acid, fucoidan, mannitol, and laminarin exist in brown algae; lipopolysaccharides and peptidoglycan exist in blue algae (Lee et al., 2020). As for the bio-oil and syngas production aspect, glucose and starch are desirable feedstock for bioethanol and H₂ production (Chew et al., 2017). In another research, Azizi et al. (2018) indicated that carbohydrates could also be converted into phenols and ketones during pyrolysis. Furans, aldehydes and ketones, phenols, and acids were formed during the co-pyrolysis of cellulose with Enteromorpha clathrata polysaccharides (ENP) and Sargassum fusiforme polysaccharides (SAP) (Cao et al., 2018).

Proteins are substances with certain spatial structures formed by twisting and folding polypeptide chains composed of amino acids through dehydration and condensation (Onwezen et al., 2021). As shown in Table 1, the typical protein content of microalgae is in the range between 10.8 and 65.2 wt%, while that of macroalgae is somewhat lower, between 7.9 and 42.11 wt%. The common chemical products produced from algal proteins are pyrroles and indoles for applications in pharmaceuticals, adhesives, and herbicides (Lee et al., 2020; Onwezen et al., 2021). In addition, the residual proteins after the oil extraction from algae can
also be treated as fertilizers or animal feeds. When used in pyrolysis, presence of proteins can lead to formation of nitrogen rich bio-oil, combustion of which would generate N-containing environmental pollutants, such as NO and NO\(_2\) (Debiagi et al., 2017). Thus, denitrification of algae-derived pyrolytic bio-oil is an important area of research (Tang et al., 2020; Hu et al., 2021). On the other hand, presence of nitrogen in the biochar resulting from algae pyrolysis can be beneficial when used in soil amendment and several other applications, as discussed later in this paper.

The typical moisture content of algae biomass is considerably higher than that of terrestrial biomass and can reach as high as over 95 wt% (see Table 1). This can cause poor bio-oil quality (Lee et al., 2020). Due to the high moisture content dewatering and drying is necessary before pyrolysis. The moisture content of algae before pyrolysis will also depend on any extraction steps preceding thermal conversion, as most water can be removed in these upstream stages. In any case, drying of algae is energy intensive. According to a report by Gan et al. (2018), reducing the moisture content by 10-15 wt% requires 3–5 MJ of energy. Therefore, integration of waste heat from the pyrolysis plant itself or heat from external renewable sources, such as solar thermal should be considered in future applications.

Volatile matter content (VM) and fixed carbon content (FC) are two parameters used to preliminarily assess whether biomass can be a suitable pyrolysis feedstock (Lee et al., 2020). VM is the combustible gas or vapor released during heating of biomass, and FC is the solid that remains after high temperature pyrolysis minus any ash. As shown in Table 1, the VM content of microalgae ranges from just under 60 wt% to over 90 wt%, while that of macroalgae is somewhat lower, typically between just under 50% and above 80%. The FC content typically has the opposite trend, with lower FC for microalgae (4.05-16.2 wt%), and higher for macroalgae (10.64-18.6 w%). The VM/FC ratio can be used to predict the biochar yield, with higher VM/FC resulting in lower biochar yield.
Due to the assimilation of inorganic elements (e.g., K, Na, Ca, Mg, Fe, Zn, Cu and Mn) from marine, wastewater and other aqueous environments used for algae cultivation the ash content of algae tends to be relatively high (Lee et al., 2020). The typical ash content of microalgae is in the range of 5.6-30.77 wt% and that of macroalgae 3.0-29.10 wt%, as shown in Table 1. The ash composition depends on the algae species and its environment (Singh et al. 2021). Different ash types can affect the production of bio-oil and biochar. For example, K can inhibit catalytic pyrolysis, and P can reduce the yield of bio-oil and biochar (Butler et al., 2011).

In addition, erosion of mechanical components, equipment fouling, and slagging can cause severe problems in thermochemical conversion of algae. Thus, various options of algae de-ashing, such as acid washing, may be necessary for some processes and products, although it can increase the cost of the algal bio-oil and biochar production. It is worth noting that algal biochar's high ash content can be beneficial in soil amendment, as well as enhancing the pseudo-capacitive performance, resulting in favorable electrochemical properties as algae-based electrodes for supercapacitors.

3. Current state-of-the-art of algal biochar

3.1. Properties of algal biochar

Notable features of biochar, such as high stability (Yaashikaa et al., 2020), abundant functional groups and nutrients (Janu et al., 2021), and high porosity and surface area (Leng et al., 2021), makes it suitable for a range of applications. As most of the volatiles in the feedstock can be removed during pyrolysis, the resulting biochar can be highly stable and recalcitrant to decomposition (Bach and Chen, 2017). As a result, biochar can be stored in soil for thousands of years; securely locking away carbon in solid form, in effect resulting in atmospheric carbon
removal and sequestration (Mašek et al., 2013). Another advantage of biochar is that its high inorganic content can provide nutrients for crop growth (Mašek et al., 2016; Roberts et al., 2015). In addition, the porous structure of biochar can increase the water retention of soil, thus improving the water use efficiency of plants and crops (Mašek et al., 2016; Edeh et al., 2021).

Algal biochar typically has a higher content of extractable inorganic nutrients (P, Ca, K and Mg) than lignocellulosic biochar, which can be beneficial to soils, and thereby to crop productivity (Bird et al., 2011; Michalak et al., 2019). During pyrolysis, the low volatilization temperature of N, S, and Cl as well as low melting temperature of Na and K contained in algae can present challenges related to corrosion and deposit formation (Mašek et al., 2016; Saber et al., 2016). The remaining minerals that were no volatilised during pyrolysis would be retained in the biochar, mainly within the ash fraction. As alluded to earlier, the mineral content and composition is species and environment dependent. When algae from heavy metal contaminated environments are used, these heavy metals present in the biochar can have harmful effect on plant and crop growth in different soil conditions. For example, excessive content of Fe, Zn, Cu, Mn, Cd, and Hg can cause toxic effect on plant growth (Lee et al., 2020). While some research has been published on the effects of pyrolysis conditions on the content of metals in algae biochar (Jung et al., 2016), there is yet insufficient understanding of how process conditions can be optimised to maximise retention and availability of desirable metals, such as K, P, Mg, etc. and minimise retention and availability of undesirable heavy metals, e.g., Hg, Cd. Further research in this area is therefore needed.

Surface area and porosity are important properties in most biochar applications. Relatively modest surface areas of algae biochar have been reported, when compared to terrestrial biochar, especially woody biomass. For example, Michalak et al. (2019) and Roberts et al. (2015) reported that Cladophora glomerata and Eucheuma pyrolysis yielded biochar with specific surface areas of about 20 m²g⁻¹ and 34.8 m²g⁻¹, while coconut shell biochar, wheat straw
biochar, and rice husk biochar had relatively high surface areas of around 155 m$^2$g$^{-1}$ (Batista et al., 2018; Zhao et al., 2019), 210 m$^2$g$^{-1}$ (Medynśka-Juraszek et al., 2020; Sun et al., 2014), and 170 m$^2$g$^{-1}$ (Paethanom and Yoshikawa, 2012; Tsai, et al., 2021), respectively. Although the surface area of raw algal biochar is on average not as large as that of biochar from other biomass, it can be improved by further pre- or post-treatment. Work by Zhou et al. (2018) indicated that KOH treated Kelp biochar had a high specific surface area of 507.177 m$^2$g$^{-1}$ and pore volume of 0.3797 cm$^3$g$^{-1}$. This high porosity could give a large number of adsorption sites, boosting pollutant decomposition in water treatment. Similarly, Rajapaksha et al. (2016) have investigated the benefits of steam activation on biochar characterises. It was found that the surface area of tea waste biochar rose from 342.2 to 575.1 m$^2$g$^{-1}$. In addition, the influence of water washing treatment on Ulva prolifera biochar was investigated (Yang et al., 2021b). The BET results showed that the surface area of obtained biochar increased from 13.46 to 257.41 m$^2$g$^{-1}$. This indicated that the reduction of ash and dissolved organic matter contents can promote the algal biochar’s surface area. Likewise, acid (H$_3$PO$_4$) washing can also promote the porosity of biochar (Zhao et al., 2017). The H$_3$PO$_4$-pretreated Pine tree sawdust biochar had a high specific surface area of 930 m$^2$ g$^{-1}$ and a total pore volume of 0.558 cm$^3$ g$^{-1}$, compared to 51.0 m$^2$ g$^{-1}$ and 0.046 cm$^3$ g$^{-1}$ in the untreated biochar. Regarding the factors affecting the surface area of algal biochar, Bird et al. (2011) and Ronsse et al. (2013) reported that higher pyrolysis temperature and lower ash content in algal biomass could lead to the higher surface area of algal biochar. Although some work of research studying surface area and porosity of algal biochar have been conducted, a comprehensive understanding of relationship between surface area, porosity and algal biochar applications remains underexplored.

3.2. Soil amendment
Application of seaweed directly onto fields has been traditionally done in many coastal areas. Since the Iron Age, Scotland has used seaweed to make fertilizer and feed (Billing et al., 2021). Seaweed as a staple item of diet has been used in China since prehistoric times. Aquaculture seaweed output in China accounts for almost 2/3 of global production, with an increase of 8.6-fold from 242,495 t in 1983 to 2,089,153 t in 2015 (United Nations Food and Agriculture Organization, 2014). Algal biochar can also be utilised in agriculture, horticulture or forestry as a soil amendment as most of the nutrients contained in algae is retained and indeed concentrated in the biochar. Roberts et al. (2015) reported that their seaweed biochar had high N (~2 wt%), P (2.6 g kg$^{-1}$), and K (~67 g kg$^{-1}$) contents and exchangeable cations (especially K content, with 298 cmol kg$^{-1}$). The high nutrient content makes seaweed biochar a unique ameliorant that could be applied to improve soil fertility. A similar research conducted by Katakula et al. (2020) proved that the high N (4.3 wt%), P (6.3 g kg$^{-1}$), and Ca (16.2 g kg$^{-1}$) content of *Laminaria pallida* biochar and high Mg (6.4 g kg$^{-1}$) and K (151 g kg$^{-1}$) content of *Gracilariopsis funicularis* biochar can provide a nutrient source in organic agriculture. Therefore, the utilisation of these algal biochar can reduce the demand for chemical fertilisers, lowering greenhouse gas emissions from fertiliser production. However, although algal biochar is considered a potential strategy for soil improvement, the practice of adding algal biochar to improve soil quality still faces several potential barriers. Boakye et al. (2016) indicated that kelp biochar had a high concentration of metals and ashes, which could cause toxic effect on plant growth. In addition, due to the aquatic growth environment of algae, algal biochar usually has a high exchangeable Na content, which could cause soil salinity (Roberts et al., 2015). In order to overcome these problems, especially contaminants, pre-treatment and post-treatment processes have been proposed that can ameliorate the issues. For example, Boakye et al. (2016) suggested pre-treatment processes, such as washing biochar, might reduce the level of toxicity. Roberts et al. (2015) indicated that blending mineral-rich seaweed biochar with C-rich
lignocellulosic biochar could reduce the Na content and increase the carbon content of biochar mixture, which results in unique soil ameliorants tailored to the needs of specific soil types. Moreover, work by Cole et al. (2017) proposed a method of composting algal biochar, algae biomass, and sugarcane bagasse, which can increase yield of corn by 15%. The possible reason can be inferred that algal biochar can absorb unstable nitrogen and phosphorus elements to prevent nutrient loss in the soil and reduce the Na content at the same time. The literature also suggested leaching can lower the Na content of algal biochar, which could suppress the soil salinity to some extent. Nevertheless, the existing pre- and post-treatment methods would easily increase the cost of final scenario. Further research is needed to develop sustainable and cost-effective methods to mitigate potential toxic effect of algal biochar’s metal and ash content.

3.3. Wastewater treatment

A wide range of organic and inorganic contaminants in wastewater can be removed using algal biochar as an adsorbent. There are four major mechanisms for inorganic ion (nutrients and heavy metals) removal when algal biochar acts as potential sorbent in wastewater treatment: surface complexation with functional groups, precipitation, electrostatic interactions, and ion exchange (Michalak et al., 2019; Jin et al. 2016; Son et al., 2018; Wang et al., 2016; Wang et al., 2020). As mentioned earlier, due to its high mineral content, algal biochar tends to have a high cation exchange capacity (CEC), making it suitable for removal of heavy metals. Michalak et al. (2019) observed a high capacity of macroalgae (Cladophora glomerata) biochar for heavy metal removal. The results showed that the removal efficiency for Cr$^{3+}$, Cu$^{2+}$ and Zn$^{2+}$ were 89.9%, 97.1% and 93.7% respectively. Meanwhile, the Ca$^{2+}$, Mg$^{2+}$ and Na$^+$ content in algal biochar were dramatically decreased. It can be inferred that the cation exchange
was the major mechanism for heavy metal removal when *Cladophora glomerata* biochar was used.

Surface complexation is another dominant mechanism for pollutant adsorption due to the abundant functional groups on algal biochar surface. Jin et al. (2016) observed a high $\text{Cu}^{2+}$ removal potential of an anaerobically digested algae-dairy-manure-derived biochar with high concentration of oxygen-containing functional groups like $-\text{COOH}$ and $-\text{OH}$. Similar work by Liu et al. (2021) also found that the functional groups of $\text{C}=\text{C}$, $\text{C}=\text{O}$, $\text{CH}_2$, and $\text{C}=\text{O}$ changed when the *Microcystis* (Blue algae) biochar interacted with $\text{Cd}$ (II). This indicated that $\text{Cd}$ (II) complexed with carboxyl or hydroxyl functional groups of the biochar surface. Among all adsorption mechanisms, precipitation can be the most efficient mechanism for removal of heavy metals (Son et al., 2018). However, algal biochar has relatively low abundance of $\text{PO}_4^{3-}$, $\text{CO}_3^{2-}$, and $\text{SiO}_3^{2-}$, resulting in low precipitation during adsorption. This can however be addressed during or after biochar production by different modification processes. Modification of biochar surface morphology is a novel method to increase electrostatic interaction during adsorption. Pyrolytic $\text{SiO}_2$-biochar nanocomposites were prepared from vermiculite-treated macroalgae by Wang et al. (2016). The researchers observed that the novel $\text{SiO}_2$-biochar had a high phosphate removal ability, which reduced the phosphate content from 50 mg L$^{-1}$ to 10 mg L$^{-1}$ within 12 h. The possible reason for this was the increased electrostatic interactions at $\text{SiO}_2$ site on the biochar surface. Another novel blue algae biochar composite impregnated with $\alpha$-$\text{Fe}_2\text{O}_3$ was synthesized by Wang et al. (2020). Experimental results showed maximum chelated nickel adsorption rate of 98.87% from Zn-Ni alloy electroplating wastewater. The pollutant ions were attracted to the algal biochar surface by electrostatic attraction when the pH was higher than 3.

Besides inorganic contaminants, algal biochar is also suitable for removal of organic contaminants. Earlier studies identified several key mechanisms, such as, hydrophobic
interaction, H-bonding/π-π interaction, polarity selectivity, partition and pore-filling effect, applicable in removal of organic pollutants (Cheng et al., 2020; Chabi et al., 2020; Hung et al., 2020; Zheng et al., 2017). In their study, Cheng et al. (2020) fabricated an enhanced macroalgal biochar by co-pyrolysis of Enteromorpha prolifera, ferric chloride, and zinc chloride to treat polycyclic aromatic hydrocarbons (PAH)-contaminated water. The highest PAH adsorption capacity was up to 90 mg g\(^{-1}\). The results showed that π-π interaction dominated the adsorption when PAH concentrations was low, and partition dominated when concentration was high, while pore-filling also played a role. Similarly, Chabi et al. (2020) identified the important role of π-π interaction in tetracycline removal from aqueous solution using Chlorella biochar.

Various modification options are available to enhance algal biochar’s performance in removal of organic contaminants. For example, Hung et al. (2020) produced red algae biochar modified with CaO/CaCO\(_3\) with enhanced performance in remediation of 4-nonylphenol (4-NP) from marine sediments. They found that calcium ions in biochar can improve removal of 4-NP under alkaline conditions. The adsorption mechanism was deemed to be associated mainly with the electrostatic attraction and hydrophobic interaction of 4-NP and oxygen-containing functional groups on the biochar surface. The modified CaO/CaCO\(_3\) on biochar surface increased the number of adsorption site and enhanced direct electron transfer. Although there has been research on use of algal biochar in wastewater treatment and on mechanisms involved in removal of different contaminants, concerted effort is needed on bringing this knowledge together to enable engineering of biochar with improved performance, both by matching feedstock and processing conditions as well as use of additives and modification processes.

3.4. Supercapacitor
With the increasing demand for electric mobility and other applications requiring energy storage, supercapacitors have received considerable attention due to their relatively higher power density, cyclic stability, rate capability and reversibility compared to lithium-ion batteries (Parsimehr and Ehsani, 2020; Singh et al. 2021; Pourhosseini et al., 2017; Wang et al., 2018). Their unique characteristics make supercapacitors a better choice for energy storage in specific areas, such as wind turbine systems, electric vehicles, cranes, and computers (Raymundo-Piñero et al., 2009; Yu et al., 2016). The electrochemical properties of algal biochar electrodes are determined by the feedstock and processing conditions used. As discussed in section 3.1, the surface area of algal biochar is typically relatively low, and as this is an important parameter for supercapacitor applications. Therefore, modifications are required to increase the specific surface area (SSA) and porosity as well as to introduce surface functional groups (Cheng et al., 2017). Table 2 shows examples of recent developments in supercapacitors derived from algal biochar.

The most common method for increasing the SSA of carbon materials, adjusting the pore structure, and enhancing surface functional groups are activation, metal oxides/hydroxides loading, heteroatom doping, and nanostructure composites (Cheng et al. 2017). Various physical and chemical modifications for biochar and their electrochemical behaviours in supercapacitors have been reviewed comprehensively by Norouzi et al. (2020). The main advantage of algal biochar over lignocellulosic biochar is that they would be self-activated and/or N-doped during the pyrolysis due to their higher nitrogen content and alkali and alkaline earth metals (AAEMs) content. This characteristic makes them more flexible to be modified in terms of physical and chemical structure. Pourhosseini et al. (2017) indicated the adjustable architecture of green macroalgae (Cladophora glomerata) via synthesizing 2D and 3D biochar functionalised with various functional groups. The electrochemical performance of these materials, as active materials in supercapacitors, was investigated. The novel KOH activated
3D algal biochar, showed a high specific capacitance of 376.7 F g⁻¹ at the current density of 1 A g⁻¹ with a high energy density of 42.4 Wh kg⁻¹. Comparatively, the specific capacitance of the control group (without activation) was 197.8 F g⁻¹ with the energy density of 22.25 Wh kg⁻¹. Furthermore, metal oxides/hydroxides loading of algal biochar can enhance the pseudo-capacitive performance of the electrode, owing to the increased redox activities. A high-performance asymmetric supercapacitor was prepared, which contained functional biochar (FBC) as anode electrodes and iron oxide/carbon composites (MBC and FCBC) as cathode electrodes in KCl electrolyte (Pourhosseini et al., 2018). MBC was derived from Cladophora glomerata with FeCl₃ and KOH activation. The metal oxide loaded supercapacitor showed a high energy density of 41.5 Wh kg⁻¹ with a power density of 900 W kg⁻¹.

Although pristine algal biochar is rich in N content, heteroatom elements doping is still a potential post-modification method to improve the pseudo-capacitive performance and electric conductivity. A high-performance N-doped macroalgae (Enteromorpha prolifera) derived biochar obtained by Ren et al. (2018) was utilized as an electrode for supercapacitor. The prepared biochar revealed a surface area of 2000 m² g⁻¹ with 1.4-2.9 at% N-loadings. The algal biochar showed a specific capacitance of up to 200 F g⁻¹ at current density of 1 A g⁻¹ with KOH activation at 700 °C.

In addition, nanostructure composites can enhance the mechanical properties and surface redox reactions. Raymundo-Piñero et al. (2011) developed a novel high-power supercapacitor produced by co-pyrolysis of seaweed and multi-walled carbon nanotubes (CNTs). This high-power supercapacitor showed relatively high electrochemical performance compared with pristine algal biochar. Owing to the blend with CNTs of high conductivity and the presence of opened mesopores, the cell resistance decreased significantly, which led to the increase of specific power. Moreover, the high porosity of this new type of algae biochar material increases
its elasticity when used as a capacitor so that it can be adapted to various working conditions and sizes to reduce mechanical damage.

In addition to chemical modification, it is beneficial to simultaneously enhance the sample’s pseudocapacitance by introducing pseudocapacitive materials into the biochar structure. To this end, Norouzi et al. (2021) even further modified the structure of Cladophora glomerata algal biochar by incorporating the cobalt nanoparticles into its 3D interconnected structure. This modified biochar was used to fabricate both symmetric and asymmetric type supercapacitors. The maximum specific capacitance of this state-of-the-art electrode was 445 F g\(^{-1}\) at the current density of 1 A g\(^{-1}\).

It should be noted that surface morphology and BET surface area also play a crucial role in the design and fabrication of supercapacitors. The novel algal biochar morphologies reported in recent years, including their \(S_{\text{BET}}\) and supercapacitive performance, are summarised in Table 3. As can be seen, spherical-shaped, olive-shaped, circular-shaped and nanofibrous structures are great examples of regular 2D porous structure which have been derived from Chlorella zofingiensii, C. glomerata, C. glomerata and, Cladophora respectively. In the past few years, 3D architecture has seen a growing interest for supercapacitors, as it provides improved surface area and long ion-transport pathways. There are presently few available literatures that apply 3D structure algal biochar in supercapacitors. As seen, the most popular and studied preparation method to create a 3D architecture is a simple basic activation using KOH. For example, Zeng et al. (2017) could successfully reach a 3D hierarchical porous architecture through KOH chemical activation by pyrolysis at 600 °C. The specific surface area and capacitance were 4425 m\(^2\) g\(^{-1}\) and 277 F g\(^{-1}\) (at the current density of 0.1 A g\(^{-1}\)). Wang et al. (2019) followed the same preparation procedure to synthesize a 3D structure from Nostoc flagelliform algae. The maximum specific capacitance was 283 F g\(^{-1}\) at 0.1 A g\(^{-1}\). The energy density of 3D algal biochar supercapacitors can be even further enhanced by introducing...
pseudocapacitive materials, such as hetero atoms, metal oxides, and conductive polymers. For example, as shown in Table 3, *C. glomerata* converted into a 3D composite of metal and biochar via integration of KOH activation and Co(NO$_3$)$_{0.6}$H$_2$O or FeSO$_4$·7H$_2$O catalyzed HTC (Pourhosseini et al., 2018).

In conclusion, various modification methods, such as chemical activation, physical activation, heteroatom doping, and biochar-nanostructure composites, have been developed to improve the properties of biochar-derived carbon materials, such as specific surface area, pore structure, morphology, and surface chemistry, to meet the needs for high-performance supercapacitors. However, the cost of these post-modification methods is still high. Thus, it is crucial to find a cost-effective method to improve the electrochemical performance of algal biochar-based supercapacitors. Worth noting, algae biomass has high K content; thus, it is possible that algae biochar does not need further activation to improve its properties significantly, which might be the benefit to reduce the cost and environmental impact.

4. Current state-of-the-art of algal bio-oil production

4.1. Pyrolysis for algal bio-oil production

Fast pyrolysis is typically used for optimal bio-oil production because the short residence time of volatiles in the reactor does not allow extensive secondary reactions of volatile matters that would reduce the yield of bio-oil and increase the yield of biochar (Lee et al., 2020; Mašek, 2016). However, due to the requirements of high temperature and heating rate and the low thermal conductivity of biomass, the feedstock needs to be introduced in form of fine particles, typically smaller than 2 mm (Mašek et al., 2016; Lee et al., 2020). Therefore, the physical pre-treatment of algal feedstock is important for fast pyrolysis.
As a liquid pyrolytic product, algal bio-oil has low sulphide content, which results in negligible SO\(_x\) emission after combustion. In addition, algal bio-oil has a relatively high nitrogen content owing to the high protein content which would cause NO\(_x\) emission (Kim et al. 2014; Wildschut et al., 2010). Therefore, a considerable denitrification treatment of algal bio-oil is necessary after fast pyrolysis. Furthermore, the high viscosity of algal bio-oil is another obstacle that needs to be overcome before it can be used as a drop-in fuel (Djandja et al., 2020). The viscosity problem is much more serious for hydrothermal bio-oil than pyrolytic bio-oil. Corrosivity is a common problem for all types of bio-oil. In algae bio-oil, high fatty acid and aldehyde contents are the main causes of corrosivity (Saber et al., 2016; Oasmaa, 2016). Therefore, further refining of algal bio-oil is necessary.

A number of research articles have discussed pyrolysis of algae for bio-oil production under different temperatures, heating rates, and residence times (Wang et al., 2013; Ly et al., 2016; Ly et al., 2015). For example, Wang et al. (2013) investigated the fast pyrolysis of microalgae *Chlorella vulgaris* in a fluidized bed reactor at 500 °C. Bio-oil yield was 53 wt% with a high nitrogen content of 12.8 wt%, while biochar and syngas yields were 31 wt% and 10 wt%, respectively. However, the obtained algal bio-oil had a low HHV of 24.57 MJ kg\(^{-1}\). On the other hand, in another study macroalgae *Saccharina japonica*-derived bio-oil produced in a fixed-bed reactor at 350 °C reached HHV of 33.36 MJ kg\(^{-1}\) (Ly et al., 2016). This illustrates the sensitivity of the bio-oil quality to the feedstock and process setup and conditions. Results of a number of recent studies on algal bio-oil production are summarised in Figure 2. Overall, there has been a wealth of research on algal bio-oil over the past decades, however simple fast pyrolysis proved to yield bio-oil of insufficient quality. Therefore, in this part of the review focuses on advanced pyrolysis technologies, such as microwave-assisted pyrolysis, co-pyrolysis and catalytic pyrolysis which have strong potential to overcome the shortcomings and yield better quality bio-oil.
As discussed in section 2, algae are complex and heterogeneous feedstock consisting of 6%–70% proteins, 2%–50% lipids, and 4%–64% carbohydrates. During pyrolysis, these constituents undergo four main physical and chemical reactions: dehydration at lower temperatures (<200 °C), devolatilization of carbohydrates and protein (200-500 °C), dissolution of lipid (350-550 °C), and decomposition of more heat-resistant components (550-800 °C) (Chen et al. 2020). Figure 1 shows a suggested mechanism for the conversion of algae into chemicals via pyrolysis. Several mechanisms have been reported in the literature and they are developed thanks to various analytical techniques such as Py-GCMS, LmPy-GC/MS, TGA, and TG-FTIR. These techniques provide us fundamental understanding of pyrolysis reactions through detecting key compounds and intermediates (Ross et al., 2009; Silva et al., 2016; Marcilla et al., 2009). As illustrated in Figure 1, carbohydrates in algae first undergo dehydration, decarboxylation, and decarbonylation reactions to produce intermediates such as ketones, aldehydes, acids, alcohols, furfurals, and anhydrosugars. Anhydrosugars have the highest selectivity and are mainly obtained through hydrolysis, fragmentation, and dehydration of polysaccharides and oligosaccharides. At the same time, proteins in algae decompose into N-heterocyclic compounds such as pyridines, indoles, and quinolines. These compounds are considered platform chemicals to produce valuable chemicals that are used in pharmaceutical industries. Chet et al. conducted research on the nitrogen transformation during pyrolysis of Enteromorpha prolifera, Nannochloropsis sp., and Spirulina platensis at the temperatures of 400, 500, and 600 °C. They detected pyridinic-N, pyrrolic-N, and nitrogen-based polycyclic compounds in the char (Chen et al., 2017). As Figure 1 shows, some of these compounds could transfer into the liquid portion and convert into either alkenes via deamination or carboxylic
acid amides and nitriles through amination of carboxylic acids. Nitrogen-based compounds in the bio-oil are considered great precursors for producing ammonia, long-chain nitriles, and aromatic hydrocarbons (Gautam and Vinu, 2020). For example, Wang et al. (2013) performed catalytic pyrolysis with HZSM-5 to convert *Chlorella vulgaris* into aromatics and ammonia. The amount of nitrogen (mol %) appearing as ammonia was 53% at the temperature of 800 °C. Recycled form of ammonia has potential application as fertilizer in macroalgae cultivation. Moreover, benzene, toluene, and xylene (BTX), showed the highest combined carbon yield of 15%. BTX compounds are essential for extracting and creating commercial products such as benzene and nylon (Wang and Brown, 2013).

Lipids are more resistant to thermal decomposition than carbohydrates and protein. Lipids mainly contain triglycerides, free fatty acids, and steroids. Triglycerides produce long-chain fatty acids by cutting acyl chains from the glycerol molecule through the hydrolysis process. Saturated fatty acids would be converted into ketones, aldehydes, acids, alcohols by decarboxylation during pyrolysis. However, unsaturated fatty acids generate carbon dioxide, carbon monoxide, and hydrocarbons. Finally, the intermediates produced by carbohydrate and lipid undergo further cracking and deoxygenation to produce linear and aromatic hydrocarbons.

Despite all these developments, algae bio-oil is not suitable for direct usage in engines or commercial production of valuable chemicals without further treatment. This is mainly due to the high acidity, high oxygen content, high viscosity, and low calorific value. There are however several advanced processing options that can considerably improve the yield of quality bio-oil suitable for use as a fuel or source of chemicals, as discussed below.

### 4.3. Microwave-assisted pyrolysis
Pyrolysis technology based on microwave heating has made a great progress in the past 10 years (Ferrera-Lorenzo et al., 2014; Du et al., 2011; Beneroso et al., 2013). Microwave radiation spans the electromagnetic spectrum frequency range between 0.3 to 300 GHz and wavelengths ranging from 1000 to 1mm (Yang et al., 2019). Microwave heating is achieved by resonantion of the frequency of the microwave radiation and that of the vibration of the polar molecules (mainly water) in the target sample, allowing the biomass to be uniformly heated from the inside (Lee et al., 2020). Microwave irradiation can accelerate thermochemical conversion processes in large-sized feedstock; therefore, fine feedstock grinding is not necessary for microwave-assisted pyrolysis, offering a potential benefit for scale-up of algal pyrolysis in the future (Yang et al., 2019; Lee et al., 2020). In addition, easy operation and selective heating are also desirable for commercialising and industrialising of algal pyrolysis (Ethaib et al., 2020). On the other hand, dielectric properties of biomass largely depend on moisture content (Antunes et al., 2018), and therefore low moisture content could cause low heating efficiency, whereas high moisture content can increase energy requirement and heating time.

Several published studies have discussed the differences between conventional pyrolysis and microwave-assisted pyrolysis. For example, Ferrera-Lorenzo et al. (2014) conducted a comparative study of the pyrolysis of macroalgae waste in a conventional furnace and in a microwave furnace. The results showed conventional pyrolytic bio-oil had more phenolic, pyrrole, and alkane chemicals, whereas microwave pyrolysis bio-oil contained more benzene and pyridine compounds, along with a significant number of light compounds. There is also a difference in the energy required for pyrolysis. Gronnow et al. (2013) showed that the energy required to produce 1 ton of biochar from conventional pyrolysis (2940 MJ t\textsuperscript{-1}) is approximately one-third that for microwave pyrolysis (11720 MJ t\textsuperscript{-1}) when efficiency of conversion of heat to electricity powering the microwave process is considered. However, when the pyrolysis
process is integrated into, the process can generate surplus heat or electricity due to the high energy content in the volatiles and gases. Microwave-assisted pyrolysis can offer an advantage over conventional pyrolysis as similar conversion can be achieved at lower temperatures (Mašek et al., 2013).

Therefore, another potential major advantage of microwave-assisted pyrolysis aimed at energy applications is the higher yield of pyrolysis gases. Beneroso et al. (2013) found that microwave-assisted pyrolysis gave rise to higher gas yield (57.2 wt%) compared to conventional pyrolysis (34.7 wt%) at 800 °C; whereas the liquid product yield decreased from 33.7 wt% to 15.4 wt%. This might be due to the secondary cracking of liquid products into incondensable gases during microwave heating. In a similar research, the macroalgae Porphyra was microwave-assisted pyrolyzed and had a highest syngas yield of 87.1 wt% at 700 °C (Hong et al., 2017). The obtained syngas had high HHV (18.2 MJ kg\(^{-1}\)) and comparable \(H_2+CO\) fraction (33.1-41.2 mol kg\(^{-1}\)) to that of conventional coal gasification processes. Furthermore, the addition of adsorbers and catalysts could further boost formation of gas products.

Microwave-assisted pyrolysis of Chlorella vulgaris using activated carbon, CaO, SiC and solid residue (Chlorella vulgaris biochar) as catalysts (Hu et al., 2012) showed that the gas yield had increased by 75.66%, 49.97%, 49.97%, and 25.83%, respectively.

Use of microwave adsorbers can also affect the quality and yield of bio-oil. Borges et al. (2014) conducted microwave-assisted pyrolysis of Chlorella and Nannochloropsis using HZSM-5 catalyst and microwave absorbent (SiC). The maximum bio-oil yields were 57 wt% and 59 wt%, respectively, which were both higher than previous microwave-assisted pyrolysis with no adsorbent and catalyst. As mentioned before, moisture content in the feedstock can affect the energy efficiency of microwave heating. Macroalgae are natural microwave absorbers because of their relatively high moisture content, whereas microalgae need to be blended with strong microwave absorbers such as activated carbon and biochar (Lee et al.,
Overall, microwave-assisted pyrolysis has a great promise in algae processing and good scale-up potential, although further research is still needed on the role of process conditions, adsorbents and catalysts on production of chemicals, fuels and biochar.

4.4. Co-pyrolysis

Co-pyrolysis is a potential strategy for improving bio-oil yield and quality by blending algae with another feedstock. Co-pyrolysis does not require additional special equipment or additives except for equipment for blending algae with another feedstock. Thus, it can be considered a lower cost method compared to other advanced processing options. By blending complementary biomass, it is possible to overcome some of the potential limitations of algae, such as high ash content or high moisture content.

A number of studies have investigated the chemical composition of bio-oil produced from co-pyrolysis of algae and other biomass. For example, Cao et al. (2018) studied the co-pyrolysis of cellulose with *Enteromorpha clathrata* and *Sargassum fusiforme*. They found that co-pyrolysis increased the content of furans, aldehydes, and ketones in bio-oil, while the contents of phenols, acids and N-containing compounds decreased dramatically. Similar observations of synergies in co-pyrolysis were made by Hua and Li (2016) in co-pyrolysis of sugarcane bagasse and *Enteromorpha prolifera*. Their results showed that the synergistic effects lowered the concentrations of acids, ketones, aldehydes, and phenolic compounds in bio-oil and increased the concentrations of hydrocarbons, alcohols, and esters.

Previous studies have found that the blending ratio can be a dominant factor affecting the bio-oil quality. For instance, Xu et al. (2019) claimed that when the amount of rice husk was raised in the mixture (*Enteromorpha* and rice husk), the distribution of furans and esters of bio-oil increased, while N-containing compounds and hydrocarbons decreased. Therefore,
understanding the optimal mixture ratio of algal co-pyrolysis is crucial for optimum bio-oil quality. Effective hydrogen index (EHI) can be used as an evaluation criterion for the quality of algae-mixed biomass in co-pyrolysis (Lee et al., 2020). The low EHI (<0.3) of algal biomass can inhibit the production of hydrocarbon-based compounds, so the chemicals with high EHI (~2), such as polyethylene, alcohol, and esters, are preferable in the blend. Co-pyrolysis of *Nannochloropsis sp.* and scum from wastewater treatment plant was conducted by Xie et al. (2015). The EHI value of *Nannochloropsis sp.* was 0.095 while that of scum was 1.59. When the EHI value of the feedstock-mixture was at 1.2 with the ratio of microalgae to scum was 1:2, the best aromatics concentration occurred in bio-oil. Similarly, the H/C ratio can also be used as an evaluation criterion, and a higher H/C ratio is preferred. In addition, many investigators have recently turned to co-pyrolysis of algae with non-biomass materials.

Research on co-pyrolysis of microalgae with low-density polyethylene (LDPE) showed that presence of LDPE promoted the formation of formic/acetic ester and long-chain alcohol, whereas it reduced O content from 45.5 wt% to 10.2 wt% in *Enteromorpha prolifera* (EP) bio-oil and N content from 19.5 wt% to 6.6 wt% in *Spirulina platensis* (SP) bio-oil (Tang et al., 2020). The bio-oil yield was significantly increased because the volatile content of LDPE can crack into liquid products. The co-pyrolysis of *Enteromorpha prolifera* with waste plastics (HDPE) was further conducted by Xu et al. (2020). The results indicated that the nitrogen-containing compounds, oxygenates and acids were sharply decreased in algal bio-oil while light hydrocarbons and aromatics contents were increased due to the high hydrogen content in HDPE. The study also proved the catalytic coking was inhibited and the formation of solid residues was reduced because of the synergetic effects when combining catalytic pyrolysis with co-pyrolysis.

Co-pyrolysis is an attractive alternative to simple pyrolysis, capable of generating higher bio-oil yield and better bio-oil quality owing to the synergistic effects. The mixture of algal
biomass with other feedstocks can increase the EHI values and decrease the N concentrations, resulting in desirable bio-oil quality with high HHV. On the other hand, choosing some expensive feedstocks as co-heating materials may improve the pyrolysis performance, but it will increase the cost and may affect the possibility for practical use of these products. Due to the limited literature, more types of co-pyrolysis materials and detailed kinetic analysis should be considered in future study.

4.5. Catalytic pyrolysis

To further improve the pyrolysis performance and the yield and quality of pyrolysis products, a large number of catalysts have been studied (Cao et al., 2018; Pan et al. 2010; Anand et al., 2016; Miandad et al., 2016). Catalytic pyrolysis has proven to be a promising thermal conversion option for bio-oil production with several advantages such as low energy input, high algal bio-oil quality, and low pyrolysis temperature (Miandad et al., 2016; Gao et al., 2017; Anand et al., 2016; Yuan et al., 2020). For example, catalytic pyrolysis can upgrade the algal bio-oil through deoxygenation and denitrification, where the oxygenates and N-containing compounds are converted into aromatic compounds and ammonia, respectively (Saber et al., 2016). In-situ and ex-situ pyrolysis are two main approaches to achieve the effective catalytic pyrolysis. In-situ catalytic cracking mixes the biomass and catalysts in the reactor, and this approach can be adopted directly in conventional pyrolyzer. The blended catalysts can be treated as heat carrier and catalyst. In-situ catalytic pyrolysis can inhibit the generation of tar, thereby increasing the production of bio-oil and pyrolysis gas, such as CO (Iisa et al., 2016). However, the weak deoxygenation reaction and the gradual loss of activity of the catalyst limit the performance of in-situ catalytic pyrolysis (Iisa et al., 2016). On the other hand, ex-situ catalytic pyrolysis utilises a dedicated catalytic reactor located downstream
of the pyrolyzer. Ex-situ catalytic pyrolysis has the advantages of being more controllable, catalyst is recyclable, and it avoids interference between feedstocks and catalysts (Kalogiannis et al., 2019). There is a wide range of potential catalysts that have been tested in in-situ and ex-situ catalytic pyrolysis. Zeolites are crystalline microporous aluminosilicates made up of SiO$_4$- and AlO$_4$-tetrahedra that share corners, which have been shown to be valuable in industrial catalysis (Miandad et al., 2016). Cao et al. (2018) have used ZSM-5 as a catalyst to study the catalytic effect on *Enteromorpha clathrata* and *Sargassum fusiforme* for enhanced production of upgraded algal bio-oil. The study pointed out that ZSM-5 can significantly reduce the production of acids and N-containing compounds during pyrolysis. The improved denitrification reactions in zeolite-based catalytic pyrolysis were also observed by other researchers. For example, Hu et al. (2021) stated that ZSM-5/MCM-41-catalysed pyrolysis had a lower content of N-containing compounds in algal bio-oil than bio-oil from conventional pyrolysis. This research also showed that ZSM-5 can be an effective catalyst for generation of aromatic compounds while MCM-41 can be used to promote formation of alcohols.

Another important application of catalysts is in bio-oil deoxygenation. In their research Pan et al. (2010) compared conventional pyrolysis and HZSM-5-based catalytic pyrolysis of *Nannochloropsis*. The results showed decrease in bio-oil oxygen concentration from 30.09 wt% to 19.53% due to the catalytic effect. HZSM-5 cab effectively reduce the oxygen content of bio-oils while increasing their heating value. In addition, Anand et al. (2016) tested catalytic fast pyrolysis of *Arthrospira platensis* using different zeolites (ZSM5, Zβ and ZY). The results showed that the use of high acidity ZY and Zβ catalysts promoted the synthesis of C2-C4 nitriles, whereas the use of ZY and Zβ catalysts resulted in the formation of cycloalkanes. Therefore, catalyst type selection is important for synthesis of valuable chemicals from algal biomass.
The acidic sites on the surface of zeolite-based catalysts are desired characteristics for promoting the deoxygenation process (Verdoliva et al., 2019). However, the resulting high acidity bio-oil is not desirable for large-scale production. Thus, metal-doped catalysts have gained great attention recently, to moderate the acidity in zeolites (Lee et al., 2020). Norouzi, O. et al. (2017) conducted catalytic pyrolysis of *Gracilaria gracilis* using Co-Mo supported zeolites. The catalysts considerably reduced acetic and formic acid concentrations from 9.56% to 8.12 wt%. Meanwhile, the concentrations of phenol and furfural dropped from 6.65 wt% and 6.98 wt% to 5.88 wt% and 5.49 wt%, respectively. Another study by Hao et al. (2021) proposed the catalytic effect of nickel-iron-layered double oxides (NiFe-LDO) on rice straw and ulva prolifera macroalgae mixture. The results showed that the catalytic pyrolysis inhibited the algal bio-oil yield because of coke formation; however, the 5% Ga/NiFe-LDO/AC catalyst can dramatically improve the algal bio-oil quality by increasing deoxygenation and aromatization reactions during pyrolysis. The study implied that the synthesized Ga/NiFe-LDO/AC can be a promising catalyst for algal bio-oil upgrading. In another previous research, Yuan et al. (2020) used Mg-Ce-ZSM-5 as a carrier to study the interaction between seaweed and catalyst during pyrolysis. The study had shown that MgO played an effective role in breaking chemical bonds and generating smaller molecular structures, resulting in a decrease in the bio-oil yield and an increase in biogas production. However, the addition of Mg-Ce changed the chemical structure of algae bio-oil, which means that the aromatization of ZSM-5 is enhanced, and more polycyclic aromatic hydrocarbons are produced. In addition, the catalyst ratio of 1:1 was found to produce the optimal hydrocarbons, about 89.35%.

To the best of our knowledge, the use of algal biochar as a catalyst was first proposed by (Norouzi, et al. 2016). In their recent studies, the catalytic behavior of biochar derived from *C. glomerata*, *G. gracilis*, and *Sargassum* was investigated in the pyrolysis process. These catalysts were proven to be a low-cost, efficient, renewable, and promising alternative to...
commercial catalysts. The results obtained from slow pyrolysis of macroalgae in the presence of algal biochar, silicon, and zeolite-based catalysts are summarized in Table 4. As can be seen, the catalytic behavior of algal biochar was, in some cases, comparable to conventional catalysts. Algal biochar owes the catalytic behavior to the alkali and alkaline earth metals (AAEM) in the ash. A simple mechanism proposed for the algal biochar with different AAEM compositions includes two reaction pathways. One is the formation of compounds containing C=O groups, such as acids, aldehydes, CO$_2$, etc. The other is the formation of compounds containing C-O-C groups, such as cellulose, levoglucosan, glucose, ethers, etc. AAEM act as a catalyst that favors the formation of compounds containing carbonyl groups and CO$_2$. Activated algal biochar can also be used as a great catalyst support for conventional active phases. Cobalt and iron active phases have a long history of importance in catalytic pyrolysis. In conclusion, exploring a cost-effective and reusable catalyst that can efficiently improve the algal bio-oil quality is highly desirable. Although the catalytic pyrolysis for algal bio-oil has been reviewed and analyzed in recent years, the relation between catalyst types (zeolite-based, metal-based and other novel catalysts) and the properties of algae-related pyrolytic products still needs more research. In addition, it is essential to consider crystalline structure, BET surface area, acidity and pore size when choosing the type of catalyst.

4. Future challenge and opportunities

This review highlighted that there are promising opportunities for integration of coproduction of algal biochar and bioenergy into algal biorefinery using pyrolysis, making it possible to achieve a net zero carbon balance or even become carbon negative. Such algal biochar-bioenergy system (ABBS) offers many intrinsic advantages, e.g., atmospheric carbon capture and storage, products for sustainable agriculture and environmental management, offering a cost-effective and environmentally friendly solution aligned with net-zero and
circular economy concepts. However, to turn this concept into a reality, considerable
development in a number of areas and aspects of the concept is needed, as alluded to in the
respective sections of the review. It is important to distinguish the different characteristics of
obtained algal biochar and bio-oil, compared to lignocellulosic counterparts, and implications
these have on their applications. Although research on algal bio-oil and algal biochar
production has made a significant progress in recent years on laboratory scale, there still
remains a huge gap between laboratory and industrial-scale deployment. Therefore, work on
scale-up of the processes involved is necessary to resolve technical and nontechnical challenges
throughout the whole chain, starting from algae production and harvesting. This needs to be
done hand in hand with comprehensive techno-economic analysis and lifecycle assessment of
algal bioenergy, biochar and related valuable byproducts (e.g., pharmaceuticals, animal feeds
and food additives) to identify the most suitable algal feedstock, processing technology and co-
product combinations and therefore aid future development and commercialisation.

5. Conclusions

Algae is a third-generation feedstock that can be converted into bioenergy, chemicals and
biochar through extraction and thermal conversion. This review highlights the key
opportunities and challenges of algal pyrolysis, and the applications of pyrolytic algal biochar,
taking advantage of its unique properties. Applications like soil amendment, wastewater
treatment, and supercapacitors are discussed. These applications vary depending on physical
and chemical properties of different biochar. As a possible fossil fuel alternative, algal
bioenergy is also reviewed. Microwave-assisted, catalytic, and co-pyrolysis are three important
advanced technology aiming to increase the bio-oil yield and improve the bio-oil quality
through denitrogenation and deoxygenation.
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CRediT authorship contribution statement

Jiacheng Sun: Conceptualization, Writing - original draft. Ondřej Mašek: Supervision, Writing - review & editing. Omid Norouzi: Writing - review & editing

References


### Tables

**Table 1. List of proximate analysis of common microalgae and macroalgae**

<table>
<thead>
<tr>
<th>Feedstocks</th>
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<th>Proximate analysis (wt%)</th>
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<tr>
<td></td>
<td>Li</td>
<td>Carbohy</td>
<td>Pr</td>
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<tr>
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**Macroalgae**

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<th>Side2</th>
<th>Side3</th>
<th>Side4</th>
<th>Side5</th>
<th>Side6</th>
<th>Side7</th>
<th>Side8</th>
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<td>Uzoejirwa et al.</td>
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<td></td>
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<td>8.56</td>
<td>(2019)</td>
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<td>1</td>
<td>9</td>
<td>4.6</td>
<td>1</td>
<td>8.0</td>
<td>79.9 (2017)</td>
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<tr>
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<th>Algae &amp; Fucoid</th>
<th>Iron</th>
<th>Algae &amp; Fucoid</th>
<th>Algae &amp; Fucoid</th>
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<td>1</td>
<td>Taghavi et al.</td>
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<td>-</td>
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<td>84.5</td>
<td>1</td>
<td>Michalak et al.</td>
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<td>50.3</td>
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<td>Liu et al. (2018)</td>
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<td>71.7</td>
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<td>Liu et al. (2018)</td>
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<td>94</td>
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<td>32.61</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>Verma et al. (2017)</td>
</tr>
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<td>Dictyopteris australis</td>
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<td>33.12</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>Verma et al. (2017)</td>
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<td>33.61</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>Verma et al. (2017)</td>
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<td>33.93</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>Verma et al. (2017)</td>
</tr>
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<td>Portieria hornemannii</td>
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<td>27.30</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>Verma et al. (2017)</td>
</tr>
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<td>Halymenia floresii</td>
<td>-</td>
<td>-</td>
<td>95.0</td>
<td>-</td>
<td>0</td>
<td>Polat et al. (2008)</td>
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Table 2. The recent developments on supercapacitors derived from algal biochar

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<tr>
<th>Biochar type</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Specific capacitance (F g⁻¹)</th>
<th>Current density (A g⁻¹)</th>
<th>Energy density (Wh kg⁻¹)</th>
<th>Cycle stability (%)</th>
<th>References</th>
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<tr>
<td><em>Chlorella vulgaris</em></td>
<td>3516</td>
<td>142</td>
<td>1</td>
<td>8.9</td>
<td>22</td>
<td>Han et al. (2019)</td>
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<td>Algal Species</td>
<td>Biomass (mg/d)</td>
<td>Ash (g/d)</td>
<td>CH (g/d)</td>
<td>O (g/d)</td>
<td>N (%)</td>
<td>Protein (%)</td>
</tr>
<tr>
<td>------------------------</td>
<td>---------------</td>
<td>-----------</td>
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<td>---------</td>
<td>-------</td>
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<tr>
<td>Chlorella</td>
<td>1337.9</td>
<td>353</td>
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<td>10</td>
<td>92.00</td>
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<tr>
<td>Nannochloropsis salina</td>
<td>1784</td>
<td>347</td>
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<td>83.00</td>
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<tr>
<td>Cladophora</td>
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<td>376.7</td>
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<td>42.4</td>
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<td>99.20</td>
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<tr>
<td>Cladophora glomerata</td>
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<td>427.3</td>
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<td>41.5</td>
<td>10</td>
<td>93.10</td>
</tr>
<tr>
<td>Kelp</td>
<td>4425</td>
<td>277</td>
<td>0.1</td>
<td>8</td>
<td>20</td>
<td>92.00</td>
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<tr>
<td>Turbinaria conoides</td>
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<td>416</td>
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<td>52</td>
<td>50</td>
<td>85.30</td>
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<td>Ulva fasciata</td>
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<td>46.1</td>
<td>50</td>
<td>97.50</td>
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<td>Undaria pinnatifida</td>
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<td>425</td>
<td>0.1</td>
<td>42</td>
<td>10</td>
<td>94.00</td>
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**Note:** Biomass values are in mg/d, ash and CH are in mg/d, O is in mg/d, N is in %, and protein is in %.
Table 3. Preparation method, morphology, and supercapacitor performance of algal biochar

<table>
<thead>
<tr>
<th>Algae</th>
<th>Preparation method</th>
<th>Morphology</th>
<th>Surf area (m² g⁻¹)</th>
<th>Specific capacitance (F g⁻¹)</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>S. Platensis</td>
<td>Integration of HTC (180 °C, 24h) and KOH chemical activation (pyrolysis at 650-700 °C)</td>
<td>Hierarchical</td>
<td>~18</td>
<td>170-200 F g⁻¹</td>
<td>Sevilla et al. (2014)</td>
</tr>
<tr>
<td>Kelp</td>
<td>NH₃ chemical activation (pyrolysis at 700 °C)</td>
<td>3D interconnected</td>
<td>10 m² g⁻¹</td>
<td>440 F g⁻¹ at 0.5 A g⁻¹</td>
<td>Li et al. (2015)</td>
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<tr>
<td>Kelp</td>
<td>KOH chemical activation (pyrolysis at 600 °C)</td>
<td>3D hierarchical</td>
<td>442 m² g⁻¹</td>
<td>277 F g⁻¹ at 0.1 A g⁻¹</td>
<td>Zeng et al. (2017)</td>
</tr>
<tr>
<td>Algae Species</td>
<td>Activation Method</td>
<td>Structural Characteristic</td>
<td>Current Density (A g(^{-1}))</td>
<td>Specific Capacitance (F g(^{-1}))</td>
<td>Reference</td>
</tr>
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<tr>
<td>Nanochloropsis salina</td>
<td>Co(OH)(_2) chemical activation (pyrolysis at 550 °C)</td>
<td>Circular-shaped structure</td>
<td>0.2</td>
<td>347</td>
<td>Zhou et al. (2017)</td>
</tr>
<tr>
<td>Chlorella zofingiensis</td>
<td>KOH chemical activation (pyrolysis at 600 °C)</td>
<td>Spherical structure</td>
<td>7.9</td>
<td>353</td>
<td>Zhu et al. (2018)</td>
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<tr>
<td>Nostoc flagelliform</td>
<td>KOH/HF chemical activation (pyrolysis at 600-900 °C)</td>
<td>3D porous active carbon</td>
<td>6</td>
<td>283</td>
<td>Wang et al. (2019)</td>
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<tr>
<td>C. glomerata</td>
<td>slow pyrolysis (900 °C) and activated through a novel activation process with nitric acid</td>
<td>2D olive-shaped structure</td>
<td>354</td>
<td>376.7</td>
<td>Pourhossein et al. (2017)</td>
</tr>
<tr>
<td>C. glomerata</td>
<td>A suspension of algae and FeCl(_3) was centrifuged, and the solid residue was pyrolyzed at the temperature of 700 °C for 4 h</td>
<td>A mixture of cubic and olive-shaped structure</td>
<td>475</td>
<td>299.3</td>
<td>Pourhossein et al. (2018)</td>
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<tr>
<td>C. glomerata</td>
<td>KOH was centrifuged, and the solid residue was pyrolyzed at the temperature of 700 °C for 2 h</td>
<td>Circular-shaped structure</td>
<td>670</td>
<td>332.2</td>
<td>Pourhossein et al. (2018)</td>
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<tr>
<td>C. glomerata</td>
<td>Integration of KOH and FeSO(_4)·7H(_2)O catalysed HTC</td>
<td>3D interconnected structure</td>
<td>957</td>
<td>427.3</td>
<td>Pourhossein et al. (2018)</td>
</tr>
<tr>
<td>C. glomerata</td>
<td>Integration of KOH and Co(NO(_3)(_3))·0.6H(_2)O catalysed HTC</td>
<td>3D interconnected structure</td>
<td>605</td>
<td>445</td>
<td>Norouzi et al. (2021)</td>
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Table 4. Recent progress in presenting algal biochar as a catalyst in the slow pyrolysis process

<table>
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<tr>
<th>Macroalgae</th>
<th>C. glomerata (Norouzi and Di Maria, 2018)</th>
<th>Sargassum (Taghavi et al., 2018)</th>
<th>G. gracilis (Norouzi et al., 2017)</th>
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<td>Algal biochar</td>
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<td>Iron composite</td>
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<td>algal biochar</td>
<td>multi metal</td>
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<td>biochar</td>
<td>silica</td>
<td>biochar</td>
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<tr>
<td>Optimum</td>
<td>500</td>
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<td>700</td>
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| temperature (°C) |                                  | 500                             | 700                               | 500
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<td>(wt.%)</td>
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<td><strong>Acid yield</strong></td>
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<td>11.47</td>
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<td>15.38</td>
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<td>(%)</td>
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<td><strong>Phenol yield</strong></td>
<td>8.50</td>
<td>31.54</td>
<td>11.80</td>
<td>2.39</td>
<td>4.27</td>
<td>15.04</td>
<td>5.95</td>
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<tr>
<td>(%)</td>
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<td><strong>H₂ yield</strong></td>
<td>8.85</td>
<td>4.81</td>
<td>7.99</td>
<td>1.23</td>
<td>8.54</td>
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<td>(mmol/g feedstock)</td>
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<td><strong>CO₂ yield</strong></td>
<td>11.25</td>
<td>3.40</td>
<td>6.30</td>
<td>2.94</td>
<td>6.90</td>
<td>5.61</td>
<td>4.07</td>
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<td>(mmol/g feedstock)</td>
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<td><strong>CO yield</strong></td>
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<td>1.63</td>
<td>5.02</td>
<td>1.25</td>
<td>4.89</td>
<td>2.29</td>
<td>1.97</td>
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<td>(mmol/g feedstock)</td>
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<tr>
<td><strong>CH₄ yield</strong></td>
<td>0.80</td>
<td>3.33</td>
<td>1.84</td>
<td>0.74</td>
<td>5.50</td>
<td>2.23</td>
<td>3.58</td>
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<td>(mmol/g feedstock)</td>
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**Highlights**

- Chemical components and characteristics of microalgae and macroalgae are discussed
- Algal biochar uses in soil, wastewater treatment, and supercapacitors are discussed
- Overview of bio-oil production by conventional and advanced pyrolysis is provided