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Review

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

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1 A state-of-the-art review on algae pyrolysis for bioenergy

2 and biochar production

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24 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.

49 1. Introduction

50

51 The increase in world population and the rapid expansion of industrialization have led to 52 continuous growth in global energy consumption (Syvitski et al., 2020). In 2019, the global 53 mean concentrations of CO₂, methane (CH₄) and nitrous oxide (N₂O) were 409.9 ppm, 1866.3 54 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 55 56 are higher than at any point in the past 800,000 years (IPCC, 2021). Consequently, the earth's temperature rosed by 1 °C and is expected to increase by another 2.5-4 °C by the end of the 21st 57 58 century under high emission scenarios (Klein et al., 2021). To address these issues, a range of 59 renewable energy technologies has been developed and deployed, including bioenergy (Sekar 60 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 61 62 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 63 64 transportation distance, poor storage stability (Hu et al., 2021), affecting biomass storage, and 65 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 66 67 some cases, which indicates that the energy consumption during production is relatively high 68 compared to that of fossil fuels (Buchanan, 2019). Furthermore, inappropriate bioenergy 69 utilization in low- and middle-income countries, such as inefficient production of charcoal for 70 cooking, can have undesirable consequences, such as deforestation, soil degradation, and air 71 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

74 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 75 76 (Rulli et al., 2016). Due to these limitations of first-generation biofuels, new technologies that 77 do not rely on readily available sugars and fats have been developed. These so-called secondgeneration biofuels can utilize a wide range of lignocellulosic biomass, including agricultural 78 79 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 80 synthesis fuel (Raud et al., 2019; Usmani et al., 2021). Although second-generation biofuels do 81 82 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 83 84 biomass, such as microalgae or macroalgae as feedstock (Singh et al., 2011). High lipid content, 85 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 86 such as microalgae and fungi are used as feedstock. Previous studies indicated that the third 87 88 and fourth-generation biofuels are related to algae, so the development of biofuels and algae 89 research in the future have a similar direction (Bach et al., 2017; Abdullah et al., 2019).

90 There are several processes for the conversion of algae to biofuels, chemicals, and materials. 91 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 92 93 converted into methane by anaerobic digestion (Zhong et al., 2013). Bio-oil, biochar and 94 syngas can be produced through thermochemical conversion technologies such as pyrolysis, 95 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, 96 97 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 98

99 loss, decomposition of organic structures, and disintegration of solid residuals (Demirbas, 100 2009). Depending on the operating process design and conditions used (mainly temperature, 101 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 102 103 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, 104 2003; Bridgwater et al., 1999). In the flash pyrolysis, biomass undergo a higher heating rates 105 of 10^3 – 10^4 °C s⁻¹ for a very shorter retention time (<0.5 s) at temperatures of 800-1000 °C 106 107 (Kan et al., 2016).

108 Biochar is the major product of slow pyrolysis due to the sufficient residence time, 109 promoting char formation, while fast and flash pyrolysis yield more bio-oil (Demirbas, 2004; 110 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-111 oil produced by pyrolysis generally has a high viscosity, which means that it cannot be directly 112 113 used in internal combustion engines. The oxygen content (10-30 wt%) of algal bio-oil is 114 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%) 115 116 (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 117 technology updating can be conducted to upgrade the quality of bio-oil. Hence, this review 118 119 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 120 121 quality. Due to the aqueous growth environment, most of the algal biomass have high moisture 122 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 123

124 125 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 126 127 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 128 129 high growth rate of algae allows for faster rate of atmospheric carbon removal and 130 sequestration.

Since the second half of the 20th century, pyrolysis liquid products, such as biofuels have 131 132 received a lot of attention due to the need to find alternatives to fossil fuels. But in the past 133 decade, a new focus on algae-derived biochar has emerged as a potential contributor to the 134 reduction of carbon content in the atmosphere, with the advantage of not requiring land to 135 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, 136 137 often characterized by high mineral matter content and absence of lignin. Algae-derived 138 biochar typically has higher cation exchange capacity, nitrogen content, and pH value 139 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 140 141 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 142 143 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 144 145 hand in hand to maximise the environmental and economic benefits, and this paper therefore 146 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 147 can make algal biochar play a more important role in mitigating climate change. At the same 148

time, understanding the different production technologies of algal bio-oil can make theproduction of algae biochar more efficient and economical, as highlighted in this review.

151

152 2. Chemical composition of algae

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Algae can be the most extensive source of simple microorganisms and account for 154 approximately half of photosynthesis activities on earth (Bach and Chen, 2017; Sirajunnisa and 155 156 Surendhiran, 2016). Algae growth rate is extremely high compared to other biological materials, 157 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., 158 159 2014). Algae can be divided into macroalgae (such as Kelp, Porphyra, Undaria pinnatifida, 160 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 161 162 components of lipids, proteins, and carbohydrates, other important and valuable components, 163 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 164 production of pharmaceuticals or cosmetics (Koyande et al., 2021). Algal carbohydrates are 165 already proven to be the potential feedstocks for bioethanol production (Bach and Chen, 2017; 166 Sirajunnisa and Surendhiran, 2016). 167

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.

177 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). 178 179 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 180 as the main photosynthetic product for algal biomass, can be utilized in the pharmaceutical 181 182 industry and food (sweeteners) industry (Debiagi et al., 2017). Different carbohydrate 183 structures exist in different algae species. For example, cellulose, carrageenan and agar exits 184 in red algae; alginic acid, fucoidan, mannitol, and laminarin exist in brown algae; 185 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 186 production (Chew et al., 2017). In another research, Azizi et al. (2018) indicated that 187 188 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 189 with Enteromorpha clathrata polysaccharides (ENP) and Sargassum fusiforme 190 191 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

199 also be treated as fertilizers or animal feeds. When used in pyrolysis, presence of proteins can 200 lead to formation of nitrogen rich bio-oil, combustion of which would generate N-containing 201 environmental pollutants, such as NO and NO₂ (Debiagi et al., 2017). Thus, denitrification of 202 algae-derived pyrolytic bio-oil is an important area of research (Tang et al., 2020; Hu et al., 203 2021). On the other hand, presence of nitrogen in the biochar resulting from algae pyrolysis 204 can be beneficial when used in soil amendment and several other applications, as discussed 205 later in this paper.

206 The typical moisture content of algae biomass is considerably higher than that of terrestrial 207 biomass and can reach as high as over 95 wt% (see Table 1). This can cause poor bio-oil quality 208 (Lee et al., 2020). Due to the high moisture content dewatering and drying is necessary before 209 pyrolysis. The moisture content of algae before pyrolysis will also depend on any extraction 210 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), 211 212 reducing the moisture content by 10-15wt% requires 3–5 MJ of energy. Therefore, integration 213 of waste heat from the pyrolysis plant itself or heat from external renewable sources, such as 214 solar thermal should be considered in future applications.

Volatile matter content (VM) and fixed carbon content (FC) are two parameters used to 215 216 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 217 218 that remains after high temperature pyrolysis minus any ash. As shown in Table 1, the VM 219 content of microalgae ranges from just under 60 wt% to over 90 wt%, while that of macroalgae 220 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 221 macroalgae (10.64-18.6 w%). The VM/FC ratio can be used to predict the biochar yield, with 222 223 higher VM/FC resulting in lower biochar yield.

224 Due to the assimilation of inorganic elements (e.g., K, Na, Ca, Mg, Fe, Zn, Cu and Mn) 225 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 226 227 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. 228 229 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). 230 231 In addition, erosion of mechanical components, equipment fouling, and slagging can cause 232 severe problems in thermochemical conversion of algae. Thus, various options of algae de-233 ashing, such as acid washing, may be necessary for some processes and products, although it 234 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 235 pseudo-capacitive performance, resulting in favorable electrochemical properties as algae-236 based electrodes for supercapacitors. 237

- 238
- 239 3. Current state-of-the-art of algal biochar
- 240
- 241 3.1. Properties of algal biochar
- 242

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

249 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., 250 251 2015). In addition, the porous structure of biochar can increase the water retention of soil, thus 252 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 253 254 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 255 temperature of N, S, and Cl as well as low melting temperature of Na and K contained in algae 256 257 can present challenges related to corrosion and deposit formation (Mašek et al., 2016; Saber et 258 al., 2016). The remaining minerals that were no volatilised during pyrolysis would be retained 259 in the biochar, mainly within the ash fraction. As alluded to earlier, the mineral content and composition is species and environment dependant. When algae from heavy metal 260 contaminated environments are used, these heavy metals present in the biochar can have 261 harmful effect on plant and crop growth in different soil conditions. For example, excessive 262 263 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 264 of metals in algae biochar (Jung et al., 2016), there is yet insufficient understanding of how 265 266 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, 267 268 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

274	biochar, and rice husk biochar had relatively high surface areas of around 155 m^2g^{-1} (Batista et
275	al., 2018; Zhao et al., 2019), 210 m ² g ⁻¹ (Medynśka-Juraszek et al., 2020; Sun et al., 2014), and
276	170 m ² g ⁻¹ (Paethanom and Yoshikawa, 2012; Tsai, et al., 2021), respectively. Although the
277	surface area of raw algal biochar is on average not as large as that of biochar from other biomass,
278	it can be improved by further pre- or post-treatment. Work by Zhou et al. (2018) indicated that
279	KOH treated Kelp biochar had a high specific surface area of 507.177 m ² g ⁻¹ and pore volume
280	of 0.3797 cm ³ g ⁻¹ . This high porosity could give a large number of adsorption sites, boosting
281	pollutant decomposition in water treatment. Similarly, Rajapaksha et al. (2016) have
282	investigated the benefits of steam activation on biochar characterises. It was found that the
283	surface area of tea waste biochar rose from 342.2 to 575.1 m ² g ⁻¹ . In addition, the influence of
284	water washing treatment on Ulva prolifera biochar was investigated (Yang et al., 2021b). The
285	BET results showed that the surface area of obtained biochar increased from 13.46 to 257.41
286	m ² g ⁻¹ . This indicated that the reduction of ash and dissolved organic matter contents can
287	promote the algal biochar's surface area. Likewise, acid (H ₃ PO ₄) washing can also promote the
288	porosity of biochar (Zhao et al., 2017). The H ₃ PO ₄ -pretreated Pine tree sawdust biochar had a
289	high specific surface area of 930 m ² g ⁻¹ and a total pore volume of 0.558 cm ³ g ⁻¹ , compared to
290	51.0 m^2 g ⁻¹ and 0.046 cm ³ g ⁻¹ in the untreated biochar. Regarding the factors affecting the
291	surface area of algal biochar, Bird et al. (2011) and Ronsse et al. (2013) reported that higher
292	pyrolysis temperature and lower ash content in algal biomass could lead to the higher surface
293	area of algal biochar. Although some work of research studying surface area and porosity of
294	algal biochar have been conducted, a comprehensive understanding of relationship between
295	surface area, porosity and algal biochar applications remains underexplored.

296

297 3.2. Soil amendment

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299 Application of seaweed directly onto fields has been traditionally done in many coastal 300 areas. Since the Iron Age, Scotland has used seaweed to make fertilizer and feed (Billing et al., 301 2021). Seaweed as a staple item of diet has been used in China since prehistoric times. 302 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 303 304 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 305 306 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 307 308 (especially K content, with 298 cmol kg⁻¹). The high nutrient content makes seaweed biochar 309 a unique ameliorant that could be applied to improve soil fertility. A similar research conducted 310 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 311 Gracilariopsis funicularis biochar can provide a nutrient source in organic agriculture. 312 Therefore, the utilisation of these algal biochar can reduce the demand for chemical fertilisers, 313 lowering greenhouse gas emissions from fertiliser production. However, although algal biochar 314 is considered a potential strategy for soil improvement, the practice of adding algal biochar to 315 316 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 317 318 plant growth. In addition, due to the aquatic growth environment of algae, algal biochar usually 319 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 320 321 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. 322 Roberts et al. (2015) indicated that blending mineral-rich seaweed biochar with C-rich 323

324 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. 325 Moreover, work by Cole et al. (2017) proposed a method of composting algal biochar, algae 326 327 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 328 329 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 330 salinity to some extent. Nevertheless, the existing pre- and post-treatment methods would 331 easily increase the cost of final scenario. Further research is needed to develop sustainable and 332 cost-effective methods to mitigate potential toxic effect of algal biochar's metal and ash content. 333 334

- 335 3.3. Wastewater treatment
- 336

A wide range of organic and inorganic contaminants in wastewater can be removed using 337 algal biochar as an adsorbent. There are four major mechanisms for inorganic ion (nutrients 338 339 and heavy metals) removal when algal biochar acts as potential sorbent in wastewater treatment: 340 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 341 al., 2020). As mentioned earlier, due to its high mineral content, algal biochar tends to have a 342 high cation exchange capacity (CEC), making it suitable for removal of heavy metals. 343 Michalak et al. (2019) observed a high capacity of macroalgae (*Cladophora glomerata*) 344 biochar for heavy metal removal. The results showed that the removal efficiency for Cr³⁺, Cu²⁺ 345 and Zn²⁺ were 89.9%, 97.1% and 93.7% respectively. Meanwhile, the Ca²⁺, Mg²⁺ and Na⁺ 346 content in algal biochar were dramatically decreased. It can be inferred that the cation exchange 347

348 was the major mechanism for heavy metal removal when *Cladophora glomerata* biochar was349 used.

350 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 Cu²⁺ 351 removal potential of an anaerobically digested algae-dairy-manure-derived biochar with high 352 353 concentration of oxygen-containing functional groups like -COOH and -OH. Similar work by Liu et al. (2021) also found that the functional groups of C=C, C=O, CH₂, and C-O changed 354 when the Microcystic (Blue algae) biochar interacted with Cd (II). This indicated that Cd (II) 355 356 complexed with carboxyl or hydroxyl functional groups of the biochar surface. Among all 357 adsorption mechanisms, precipitation can be the most efficient mechanism for removal of 358 heavy metals (Son et al., 2018). However, algal biochar has relatively low abundance of PO_4^{3-} , CO_3^{2-} , and SiO_3^{2-} , resulting in low precipitation during adsorption. This can however be 359 addressed during or after biochar production by different modification processes. Modification 360 of biochar surface morphology is a novel method to increase electrostatic interaction during 361 362 adsorption. Pyrolytic SiO₂-biochar nanocomposites were prepared from vermiculite-treated macroalgae by Wang et al. (2016). The researchers observed that the novel SiO₂-biochar had a 363 high phosphate removal ability, which reduced the phosphate content from 50 mg L⁻¹ to 10 mg 364 365 L⁻¹ within 12 h. The possible reason for this was the increased electrostatic interactions at SiO₂ site on the biochar surface. Another novel blue algae biochar composite impregnated with α -366 367 Fe2O3 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 368 pollutant ions were attracted to the algal biochar surface by electrostatic attraction when the 369 370 pH was higher than 3.

371 Besides inorganic contaminants, algal biochar is also suitable for removal of organic 372 contaminants. Earlier studies identified several key mechanisms, such as, hydrophobic

applicable in removal of organic pollutants (Cheng et al., 2020; Chabi et al., 2020; Hung et al., 374 2020; Zheng et al., 2017). In their study, Cheng et al. (2020) fabricated an enhanced macroalgal 375 376 biochar by co-pyrolysis of *Enteromorpha prolifera*, ferric chloride, and zinc chloride to treat polycyclic aromatic hydrocarbons (PAH)-contaminated water. The highest PAH adsorption 377 capacity was up to 90 mg g⁻¹. The results showed that π - π interaction dominated the adsorption 378 when PAH concentrations was low, and partition dominated when concentration was high, 379 while pore-filling also played a role. Similarly, Chabi et al. (2020) identified the important role 380 381 of π - π interaction in tetracycline removal from aqueous solution using *Chlorella* biochar.

382 Various modification options are available to enhance algal biochar's performance in 383 removal of organic contaminants. For example, Hung et al. (2020) produced red algae biochar modified with CaO/CaCO₃ with enhanced performance in remediation of 4-nonylphenol (4-384 NP) from marine sediments. They found that calcium ions in biochar can improve removal of 385 4-NP under alkaline conditions. The adsorption mechanism was deemed to be associated 386 387 mainly with the electrostatic attraction and hydrophobic interaction of 4-NP and oxygencontaining functional groups on the biochar surface. The modified CaO/CaCO₃ on biochar 388 surface increased the number of adsorption site and enhanced direct electron transfer. Although 389 390 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 391 392 knowledge together to enable engineering of biochar with improved performance, both by 393 matching feedstock and processing conditions as well as use of additives and modification 394 processes.

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396 3.4. Supercapacitor

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With the increasing demand for electric mobility and other applications requiring energy 398 399 storage, supercapacitors have received considerable attention due to their relatively higher 400 power density, cyclic stability, rate capability and reversibility compared to lithium-ion 401 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 402 403 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 404 biochar electrodes are determined by the feedstock and processing conditions used. As 405 406 discussed in section 3.1, the surface area of algal biochar is typically relatively low, and as this 407 is an important parameter for supercapacitor applications. Therefore, modifications are 408 required to increase the specific surface area (SSA) and porosity as well as to introduce surface 409 functional groups (Cheng et al., 2017). Table 2 shows examples of recent developments in 410 supercapacitors derived from algal biochar.

The most common method for increasing the SSA of carbon materials, adjusting the pore 411 412 structure, and enhancing surface functional groups are activation, metal oxides/hydroxides 413 loading, heteroatom doping, and nanostructure composites (Cheng et al. 2017). Various physical and chemical modifications for biochar and their electrochemical behaviours in 414 415 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 416 417 and/or N-doped during the pyrolysis due to their higher nitrogen content and alkali and alkaline 418 earth metals (AAEMs) content. This characteristic makes them more flexible to be modified in 419 terms of physical and chemical structure. Pourhosseini et al. (2017) indicated the adjustable 420 architecture of green macroalgae (*Cladophora glomerata*) via synthesizing 2D and 3D biochar 421 functionalised with various functional groups. The electrochemical performance of these materials, as active materials in supercapacitors, was investigated. The novel KOH activated 422

3D algal biochar, showed a high specific capacitance of 376.7 F g⁻¹ at the current density of 1 423 A g⁻¹ with a high energy density of 42.4 Whkg⁻¹. Comparatively, the specific capacitance of 424 the control group (without activation) was 197.8 F g⁻¹ with the energy density of 22.25 Whkg⁻ 425 426 ¹. Furthermore, metal oxides/hydroxides loading of algal biochar can enhance the pseudocapacitive performance of the electrode, owing to the increased redox activities. A high-427 428 performance asymmetric supercapacitor was prepared, which contained functional biochar (FBC) as anode electrodes and iron oxide/carbon composites (MBC and FCBC) as cathode 429 electrodes in KCl electrolyte (Pourhosseini et al., 2018). MBC was derived from Cladophora 430 431 glomerata with FeCl₃ and KOH activation. The metal oxide loaded supercapacitor showed a 432 high energy density of 41.5 W hkg⁻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 highpower 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 conditionsand sizes to reduce mechanical damage.

In addition to chemical modification, it is beneficial to simultaneously enhance the sample's pesocapacitance 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 456 457 the design and fabrication of supercapacitors. The novel algal biochar morphologies reported 458 in recent years, including their S_{BET} and supercapacitive performance, are summarised in Table 3. As can be seen, spherical-shaped, olive-shaped, circular-shaped and nanofibrous structures 459 460 are great examples of regular 2D porous structure which have been derived from Chlorella 461 zofingiensi, 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 462 area and long ion-transport pathways. There are presently few available literatures that apply 463 464 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 465 466 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 467 capacitance were 4425 m² g⁻¹ and 277 F g⁻¹ (at the current density of 0.1 A g⁻¹). Wang et al. 468 (2019) followed the same preparation procedure to synthesize a 3D structure from *Nostoc* 469 *flagelliform* algae. The maximum specific capacitance was 283 F g⁻¹ at 0.1 A g⁻¹. The energy 470 density of 3D algal biochar supercapacitors can be even further enhanced by introducing 471

472 pseudocapacitive materials, such as hetero toms, metal oxides, and conductive polymers. For 473 example, as shown in Table 3, *C. glomerata* converted into a 3D composite of metal and 474 biochar via integration of KOH activation and Co(NO₃) $0.6H_2O$ or FeSO₄·7H₂O catalyzed HTC 475 (Pourhosseini et al., 2018).

In conclusion, various modification methods, such as chemical activation, physical 476 477 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 478 479 structure, morphology, and surface chemistry, to meet the needs for high-performance 480 supercapacitors. However, the cost of these post-modification methods is still high. Thus, it is 481 crucial to find a cost-effective method to improve the electrochemical performance of algal 482 biochar-based supercapacitors. Worth noting, algae biomass has high K content; thus, it is 483 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. 484

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

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488 4.1. Pyrolysis for algal bio-oil production

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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 pretreatment of algal feedstock is important for fast pyrolysis.

497 As a liquid pyrolytic product, algal bio-oil has low sulphide content, which results in 498 negligible SO_x emission after combustion. In addition, algal bio-oil has a relatively high 499 nitrogen content owing to the high protein content which would cause NO_x emission (Kim et 500 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 501 502 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 503 bio-oil. Corrosivity is a common problem for all types of bio-oil. In algae bio-oil, high fatty 504 505 acid and aldehyde contents are the main causes of corrosivity (Saber et al., 2016; Oasmaa, 506 2016). Therefore, further refining of algal bio-oil is necessary.

507 A number of research articles have discussed pyrolysis of algae for bio-oil production under 508 different temperatures, heating rates, and residence times (Wang et al., 2013; Ly et al., 2016; 509 Ly et al., 2015). For example, Wang et al. (2013) investigated the fast pyrolysis of microalgae 510 Chlorella vulgaris in a fluidized bed reactor at 500 °C. Bio-oil yield was 53 wt% with a high 511 nitrogen content of 12.8 wt%, while biochar and syngas yields were 31 wt% and 10 wt%, 512 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 513 514 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 515 516 of a number of recent studies on algal bio-oil production are summarised in Figure 2. Overall, 517 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 518 519 focuses on advanced pyrolysis technologies, such as microwave-assisted pyrolysis, co-520 pyrolysis and catalytic pyrolysis which have strong potential to overcome the shortcomings and yield better quality bio-oil. 521

523 4.2. Reaction pathways in thermochemical conversion of algae into chemicals

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As discussed in section 2, algae are complex and heterogeneous feedstock consisting of 525 526 6%-70% proteins, 2%-50% lipids, and 4%-64% carbohydrates. During pyrolysis, these 527 constituents undergo four main physical and chemical reactions: dehydration at lower 528 temperatures (<200 °C), devolatilization of carbohydrates and protein (200-500 °C), 529 dissolution of lipid (350-550 °C), and decomposition of more heat-resistant components (550-530 800 °C) (Chen et al. 2020). Figure 1 shows a suggested mechanism for the conversion of algae 531 into chemicals via pyrolysis. Several mechanisms have been reported in the literature and they 532 are developed thanks to various analytical techniques such as Py-GCMS, LmPy-GC/MS, TGA, 533 and TG-FTIR. These techniques provide us fundamental understanding of pyrolysis reactions though detecting key compounds and intermediates (Ross et al., 2009; Silva et al., 2016; 534 Marcilla et al., 2009). As illustrated in Figure 1, carbohydrates in algae first undergo 535 536 dehydration, decarboxylation, and decarbonylation reactions to produce intermediates such as 537 ketones, aldehydes, acids, alcohols, furfurals, and anhydrosugars. Anhydrosugars have the 538 highest selectivity and are mainly obtained through hydrolysis, fragmentation, and dehydration 539 of polysaccharides and oligosaccharides. At the same time, proteins in algae decompose into 540 N-heterocyclic compounds such as pyridines, indoles, and quinolines. These compounds are 541 considered platform chemicals to produce valuable chemicals that are used in pharmaceutical 542 industries. Chet et al. conducted research on the nitrogen transformation during pyrolysis of Enteromorpha prolifera, Nannochloropsis sp., and Spirulina platensis at the temperatures of 543 544 400, 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 545 transfer into the liquid portion and convert into either alkenes via deamination or carboxylic 546

547 acid amides and nitriles through amination of carboxylic acids. Nitrogen-based compounds in 548 the bio-oil are considered great precursors for producing ammonia, long-chain nitriles, and 549 aromatic hydrocarbons (Gautam and Vinu, 2020). For example, Wang et al. (2013) performed 550 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. 551 552 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 553 554 15%. BTX compounds are essential for extracting and creating commercial products such as

benzene and nylon (Wang and Brown, 2013).

556 Lipids are more resistant to thermal decomposition than carbohydrates and protein. Lipids 557 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. 558 Saturated fatty acids would be converted into ketones, aldehydes, acids, alcohols by 559 decarboxylation during pyrolysis. However, unsaturated fatty acids generate carbon dioxide, 560 561 carbon monoxide, and hydrocarbons. Finally, the intermediates produced by carbohydrate and lipid undergo further cracking and deoxygenation to produce linear and aromatic hydrocarbons. 562 Despite all these developments, algae bio-oil is not suitable for direct usage in engines or 563 564 commercial production of valuable chemicals without further treatment. This is mainly due to 565 the high acidity, high oxygen content, high viscosity, and low calorific value. There are 566 however several advanced processing options that can considerably improve the yield of 567 quality bio-oil suitable for use as a fuel or source of chemicals, as discussed below.

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569 4.3. Microwave-assisted pyrolysis

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Pyrolysis technology based on microwave heating has made a great progress in the past 10 571 years (Ferrera-Lorenzo et al., 2014; Du et al., 2011; Beneroso et al., 2013). Microwave 572 573 radiation spans the electromagnetic spectrum frequency range between 0.3 to 300 GHz and 574 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 575 576 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 577 578 conversion processes in large-sized feedstock; therefore, fine feedstock grinding is not 579 necessary for microwave-assisted pyrolysis, offering a potential benefit for scale-up of algal 580 pyrolysis in the future (Yang et al., 2019; Lee et al., 2020). In addition, easy operation and 581 selective heating are also desirable for commercialising and industrialising of algal pyrolysis 582 (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 583 heating efficiency, whereas high moisture content can increase energy requirement and heating 584 585 time.

Several published studies have discussed the differences between conventional pyrolysis 586 and microwave-assisted pyrolysis. For example, Ferrera-Lorenzo et al. (2014) conducted a 587 588 comparative study of the pyrolysis of macroalgae waste in a conventional furnace and in a 589 microwave furnace. The results showed conventional pyrolytic bio-oil had more phenolic, 590 pyrrole, and alkane chemicals, whereas microwave pyrolysis bio-oil contained more benzene 591 and pyridine compounds, along with a significant number of light compounds. There is also a 592 difference in the energy required for pyrolysis. Gronnow et al. (2013) showed that the energy 593 required to produce 1 ton of biochar from conventional pyrolysis (2940 MJ t⁻¹) is approximately 594 one-third that for microwave pyrolysis (11720 MJ t⁻¹) when efficiency of conversion of heat to 595 electricity powering the microwave process is considered. However, when the pyrolysis

596 process is integrated into, the process can generate surplus heat or electricity due to the high 597 energy content in the volatiles and gases. Microwave-assisted pyrolysis can offer an advantage 598 over conventional pyrolysis as similar conversion can be achieved at lower temperatures 599 (Mašek et al., 2013).

Therefore, another potential major advantage of microwave-assisted pyrolysis aimed at 600 601 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 602 conventional pyrolysis (34.7 wt%) at 800 °C; whereas the liquid product yield decreased from 603 604 33.7 wt% to 15.4 wt%. This might be due to the secondary cracking of liquid products into 605 incondensable gases during microwave heating. In a similar research, the macroalgae Porphyra 606 was microwave-assisted pyrolyzed and had a highest syngas yield of 87.1 wt% at 700 °C (Hong 607 et al., 2017). The obtained syngas had high HHV (18.2 MJ kg⁻¹) and comparable H₂+CO 608 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. 609 610 Microwave-assisted pyrolysis of *Chlorella vulgaris* using activated carbon, CaO, SiC and solid 611 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. 612

613 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 614 615 HZSM-5 catalyst and microwave absorbent (SiC). The maximum bio-oil yields were 57 wt% 616 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 617 618 affect the energy efficiency of microwave heating. Macroalgae are natural microwave 619 absorbers because of their relatively high moisture content, whereas microalgae need to be 620 blended with strong microwave absorbers such as activated carbon and biochar (Lee et al.,

621 2020). Overall, microwave-assisted pyrolysis has a great promise in algae processing and good
622 scale-up potential, although further research is still needed on the role of process conditions,
623 adsorbents and catalysts on production of chemicals, fuels and biochar.

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625 4.4. Co-pyrolysis

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627 Co-pyrolysis is a potential strategy for improving bio-oil yield and quality by blending 628 algae with another feedstock. Co-pyrolysis does not require additional special equipment or 629 additives except for equipment for blending algae with another feedstock. Thus, it can be 630 considered a lower cost method compared to other advanced processing options. By blending 631 complementary biomass, it is possible to overcome some of the potential limitations of algae, 632 such as high ash content or high moisture content.

A number of studies have investigated the chemical composition of bio-oil produced from 633 co-pyrolysis of algae and other biomass. For example, Cao et al. (2018) studied the co-634 pyrolysis of cellulose with Enteromorpha clathrata and Sargassum fusiforme. They found that 635 636 co-pyrolysis increased the content of furans, aldehydes, and ketones in bio-oil, while the 637 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 638 sugarcane bagasse and Enteromorpha prolifera. Their results showed that the synergistic 639 640 effects lowered the concentrations of acids, ketones, aldehydes, and phenolic compounds in 641 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 biooil increased, while N-containing compounds and hydrocarbons decreased. Therefore,

646 understanding the optimal mixture ratio of algal co-pyrolysis is crucial for optimum bio-oil 647 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 648 649 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 650 651 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 652 653 the EHI value of the feedstock-mixture was at 1.2 with the ratio of microalgae to scum was 654 1:2, the best aromatics concentration occurred in bio-oil. Similarly, the H/C ratio can also be 655 used as an evaluation criterion, and a higher H/C ratio is preferred. In addition, many 656 investigators have recently turned to co-pyrolysis of algae with non-biomass materials. Research on co-pyrosis of microalgae with low-density polyethylene (LDPE) showed that 657 presence of LDPE promoted the formation of formic/acetic ester and long-chain alcohol, 658 whereas it reduced O content from 45.5 wt% to 10.2 wt% in Enteromorpha prolifera (EP) bio-659 oil and N content from 19.5 wt% to 6.6 wt% in Spirrulina platensis (SP) bio-oil (Tang et al., 660 2020). The bio-oil yield was significantly increased because the volatile content of LDPE can 661 crack into liquid products. The co-pyrolysis of *Enteromorpha prolifera* with waste plastics 662 663 (HDPE) was further conducted by Xu et al. (2020). The results indicated that the nitrogencontaining compounds, oxygenates and acids were sharply decreased in algal bio-oil while 664 665 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 666 residues was reduced because of the synergetic effects when combining catalytic pyrolysis with 667 668 co-pyrolysis.

669 Co-pyrolysis is an attractive alternative to simple pyrolysis, capable of generating higher 670 bio-oil yield and better bio-oil quality owing to the synergistic effects. The mixture of algal

674 will increase the cost and may affect the possibility for practical use of these products. Due to

675 the limited literature, more types of co-pyrolysis materials and detailed kinetic analysis should

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678 4.5. Catalytic pyrolysis

be considered in future study.

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To further improve the pyrolysis performance and the yield and quality of pyrolysis 680 681 products, a large number of catalysts have been studied (Cao et al., 2018; Pan et al. 2010; 682 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 683 input, high algal bio-oil quality, and low pyrolysis temperature (Miandad et al., 2016; Gao et 684 al., 2017; Anand et al., 2016; Yuan et al., 2020). For example, catalytic pyrolysis can upgrade 685 686 the algal bio-oil through deoxygenation and denitrification, where the oxygenates and N-687 containing compounds are converted into aromatic compounds and ammonia, respectively 688 (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 689 690 reactor, and this approach can be adopted directly in conventional pyrolyzer. The blended 691 catalysts can be treated as heat carrier and catalyst. In-situ catalytic pyrolysis can inhibit the 692 generation of tar, thereby increasing the production of bio-oil and pyrolysis gas, such as CO 693 (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 694 other hand, ex-situ catalytic pyrolysis utilises a dedicated catalytic reactor located downstream 695

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).

699 There is a wide range of potential catalysts that have been tested in in-situ and ex-situ 700 catalytic pyrolysis. Zeolites are crystalline microporous aluminosilicates made up of SiO₄- and 701 AlO₄-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 702 703 effect on Enteromorpha clathrata and Sargassum fusiforme for enhanced production of 704 upgraded algal bio-oil. The study pointed out that ZSM-5 can significantly reduce the 705 production of acids and N-containing compounds during pyrolysis. The improved 706 denitrification reactions in zeolite-based catalytic pyrolysis were also observed by other 707 researchers. For example, Hu et al. (2021) stated that ZSM-5/MCM-41-catalysed pyrolysis had 708 a lower content of N-containing compounds in algal bio-oil than bio-oil from conventional 709 pyrolysis. This research also showed that ZSM-5 can be an effective catalyst for generation of 710 aromatic compounds while MCM-41 can be used to promote formation of alcohols.

711 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 712 713 Nannochloropsis. The results showed decrease in bio-oil oxygen concentration from 30.09 wt% 714 to 19.53% due to the catalytic effect. HZSM-5 cab effectively reduce the oxygen content of 715 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 716 showed that the use of high acidity ZY and Z\beta catalysts promoted the synthesis of C2-C4 717 718 nitriles, whereas the use of ZY and Z β catalysts resulted in the formation of cycloalkanes. 719 Therefore, catalyst type selection is important for synthesis of valuable chemicals from algal 720 biomass.

721 The acidic sites on the surface of zeolite-based catalysts are desired characteristics for 722 promoting the deoxygenation process (Verdoliva et al., 2019). However, the resulting high 723 acidity bio-oil is not desirable for large-scale production. Thus, metal-doped catalysts have 724 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 725 726 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% 727 and 6.98 wt% to 5.88 wt% and 5.49 wt%, respectively. Another study by Hao et al. (2021) 728 729 proposed the catalytic effect of nickel-iron-layered double oxides (NiFe-LDO) on rice straw 730 and ulva prolifera macroalgae mixture. The results showed that the catalytic pyrolysis inhibited 731 the algal bio-oil yield because of coke formation; however, the 5% Ga/NiFe-LDO/AC catalyst 732 can dramatically improve the algal bio-oil quality by increasing deoxygenation and aromatization reactions during pyrolysis. The study implied that the synthesized Ga/NiFe-733 LDO/AC can be a promising catalyst for algal bio-oil upgrading. In another previous research, 734 735 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 736 breaking chemical bonds and generating smaller molecular structures, resulting in a decrease 737 738 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-5 739 740 is enhanced, and more polycyclic aromatic hydrocarbons are produced. In addition, the catalyst 741 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

746 commercial catalysts. The results obtained from slow pyrolysis of macroalgae in the presence 747 of algal biochar, silicon, and zeolite-based catalysts are summarized in Table 4. As can be seen, 748 the catalytic behavior of algal biochar was, in some cases, comparable to conventional catalysts. 749 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 750 751 compositions includes two reaction pathways. One is the formation of compounds containing C=O groups, such as acids, aldehydes, CO₂, etc. The other is the formation of compounds 752 753 containing C-O-C groups, such as cellulose, levoglucosan, glucose, ethers, etc. AAEM act as 754 a catalyst that favors the formation of compounds containing carbonyl groups and CO₂. 755 Activated algal biochar can also be used as a great catalyst support for conventional active 756 phases. Cobalt and iron active phases have a long history of importance in catalytic pyrolysis. 757 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 758 759 been reviewed and analyzed in recent years, the relation between catalyst types (zeolite-based, 760 metal-based and other novel catalysts) and the properties of algae-related pyrolytic products 761 still needs more research. In addition, it is essential to consider crystalline structure, BET 762 surface area, acidity and pore size when choosing the type of catalyst.

763

764 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

771	circular economy concepts. However, to turn this concept into a reality, considerable
772	development in a number of areas and aspects of the concept is needed, as alluded to in the
773	respective sections of the review. It is important to distinguish the different characteristics of
774	obtained algal biochar and bio-oil, compared to lignocellulosic counterparts, and implications
775	these have on their applications. Although research on algal bio-oil and algal biochar
776	production has made a significant progress in recent years on laboratory scale, there still
777	remains a huge gap between laboratory and industrial-scale deployment. Therefore, work on
778	scale-up of the processes involved is necessary to resolve technical and nontechnical challenges
779	throughout the whole chain, starting from algae production and harvesting. This needs to be
780	done hand in hand with comprehensive techno-economic analysis and lifecycle assessment of
781	algal bioenergy, biochar and related valuable byproducts (e.g., pharmaceuticals, animal feeds
782	and food additives) to identify the most suitable algal feedstock, processing technology and co-
783	product combinations and therefore aid future development and commercialisation.

784

785 5. Conclusions

786 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 787 opportunities and challenges of algal pyrolysis, and the applications of pyrolytic algal biochar, 788 789 taking advantage of its unique properties. Applications like soil amendment, wastewater 790 treatment, and supercapacitors are discussed. These applications vary depending on physical 791 and chemical properties of different biochar. As a possible fossil fuel alternative, algal 792 bioenergy is also reviewed. Microwave-assisted, catalytic, and co-pyrolysis are three important 793 advanced technology aiming to increase the bio-oil yield and improve the bio-oil quality 794 through denitrogenation and deoxygenation.

795

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805	
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1261	Tables

 Table 1.list of proximate analysis of common microalgae and macroalgae

Feedstocks	Chemical compositions (wt%)			Proximate an	alysis (wt%)	References	
	Li	Carbohy	Pr	Moi	Vol	Fi	A	
	pid	drate	otein	sture	atile	xed	sh	
					Matter	Carbon		
Microalgae								
Spirulina platensis	1	10.71	6	7.62	81.1	5.	6.	Tang et al. (2020)
	0.30		5.20		3	08	17	
Nannochloropsis sp.	3	18.67	4	4.23	79.2	1	6.	Tang et al. (2020)
	0.00		0.80		1	0.26	30	
Enteromorpha	1.	49.31	1	7.02	58.1	4.	3	Tang et al. (2020)
Prolifera	10		1.80		6	05	0.77	
Scenedesmus	-	-	-	12.1	75.2	7.	5.	Nyoni et al.
						1	6	(2020)
Spirulina	2.	23.4	5	6.7	73.5	1	6.	Hong et al.
	9		7.8			3.2	6	(2017)
Chlorella	5.	26.1	5	8.0	70.7	1	6.	Hong et al. 2017)
	4		5.6			5.2	1	
Chlorella sp.	-	-	-	7.28	81.1	-	1	Borges et al.
					5		1.57	(2014)
Nannochloropsis	-	-	-	3.21	90.7	-	6.	Borges et al.
					7		08	(2014)
Chlorella vulgaris	2	22.18	4	5.6	70.4	1	7.	Nejati et al.
	4.57		5.45			6.2	8	(2020)
Spirulina platensis	-	-	-	9.88	72.3	9.	1	Nautiyal et al.
					2	92	1.32	(2016)
Dunaliella tertiolecta	2.	21.69	6	-	-	-	-	Shuping et al.,
	87		1.32					2010)

		Jou	rnal Pr	e-proofs				
Chlorella spp.	2	15–16.5	-	6.2	-	-	2	Rizzo et al.
	9.6						1.6	(2013)
Chlorella vulgaris	1	12.4	5	4.4	67.2	1	1	López-González
	3.5		8.1			2.4	5.9	et al. (2014)
Scenedesmus	2	25.2	4	2.9	67.9	9.	1	López-González
almeriensis	4.6		4.2			7	9.4	et al. (2014)
Nannochloropsis	2	25.1	4	3.5	79.8	1	6.	López-González
gaditana	6.3		0.5			0.2	4	et al. (2014)
Chlorella	7	0.2	2	6.1	94.3	-	5.	Gai et al. (2013)
pyrenoidosa	1.5		2.5				7	
Spirulina platensis	6	4.8	1	6.8	90.4	-	9.	Gai et al. (2013)
	4.7		9.3				6	
Chlorella	1.	24.07	6	5.78	66.5	1	5.	Hu et al., (2015)
pyrenoidosa	83		2.42		1	5.98	95	
Cyanobacteria	5.	21.49	6	9.59	70.1	1	6.	Hu et al. (2015)
	48		0.28		3	0.14	14	
Chlorella vulgaris	1	56.92	2		74.5	1	9.	Bach et al. (2017)
ESP-31	4.83		2.5		9	6.39	02	
Scenedesmus obliquus	4.	13.41	3	5.13	70	5.	2	Chen et al. (2014)
	66		0.38			29	4.71	
Macroalgae								
Enteromorpha	4.	20.21	4	4.86	55.9	1	2	Xu et al. (2020)
prolifera	31		2.06		0	0.69	8.56	()
Enteromorpha	-	<u> </u>		6.80	53.9	1	2	Uzoeiinwa et al.
nrolifera				0.00	5	0.69	- 8 56	(2019)
Enteromorpha	<u> </u>	-	_	6.80	53.9	1	2	(2019) Xu et al. (2019)
				0.000	5	0.69	8.56	114 Co an (2013)
Enteromorpha	-	-	_	10.1	57.9	1	2	Xu et al. (2019)
clathrate				3	9	0.73	1.15	()
Pornhvra	1	47 7	3	93	70.8	1	3	Hong et al
1 or prijru	5		57	2.5	,0.0	69	0	(2017)
Native Laminaria	1	46.6	1	8.0	79 9	1	9	Kostas et al
digitata	0	10.0	2.9	0.0	, , , ,	3.1	9	(2019)
Laminaria dioitata	0	41.4		-	74.0	1	1	Kostas et al
Lummur tu utgitutu	Q.	71.7	4 1		77.0	86	21	(2019)
	,		7.1			0.0	4.1	(2017)

		Jou	ırnal Pre	e-proofs				
Sargassum	-	-	-	12.0	46.3	1	2	Taghavi et al.
				0	1	4.57	7.12	(2018)
Cladophora	-	-	-	6.1	84.5		1	Michalak et al.
glomerata							9.7	(2019)
Sargassum	-	-	-	2.41	50.3	1	2	Liu et al. (2018)
					2	8.17	9.10	
Enteromorpha	-	-	-	7.61	71.7	1	8.	Liu et al. (2018)
					1	2.35	94	
Ulva lactuca	1.	32.61	1	-	-	-	-	Verma et al.
	45		2.17					(2017)
Dictyopteris australis	1.	33.12	9.	-	-	-	-	Verma et al.
	34		70					(2017)
Porphyra spp.	2.	33.61	1	-	-	-	-	Verma et al.
	39		2.12					(2017)
Caulerpa vervelansis	3.	12.80	9.	-	-	-	-	Verma et al.
	69		03					(2017)
Turbinaria spp.	2.	33.93	1		-	-	-	Verma et al.
	87		3.83					(2017)
Portieria	1.	27.30	8.	-	-	-	-	Verma et al.
hornemannii	75		40					(2017)
Halymenia floresii	-	-	-	95.0	-	-	0.	Polat et al. (2008)
							96	



 Chlorella vulgaris
 3516
 142
 1
 8.9
 22
 91.5
 Han et al.

00 (2019)

			Journa	al Pre-p	roofs			
	Chlorella	1337.9	353	1	20	10	92	Zhu et al.
						000		(2018)
	Nannochloropsis	1784	347	0.2	26.1	50	83	Zhou et al.
salii	na					00		(2017)
	Cladophora	354	376.7	1	42.4	50	99.2	Pourhosseini
glor	merata					00		et al. (2017)
	Ascophyllum	1493	207.3	0.5	-	25	92.3	Perez-Salcedo
nod	losum					00		et al. (2020)
	Enteromorpha	2000	200	1	7	10	96	Ren et al.
prol	lifera					000		(2018)
	Cladophora	957	427.3	1	41.5	10	93.1	Pourhosseini
glor	meta					000		et al. (2018)
	Kelp	4425	277	0.1	8	20	92	Zeng et al.
						000		(2017)
	Turbinaria conoides	173.8	416	1	52	50	85.3	Divya and
						00		Rajalakshmi (2020)
	Ulva fasciata	376.82	332	0.5	46.1	50	97.5	Chaudhary et
						00		al. (2019)
	Undaria pinnatifida	3270	425	0.1	42	10	94	Kang et al.
						000		(2015)



Algae	Preparation method	Morphology	Surf	Specific	References	
			ace area	capacitance (F g ⁻¹)		
			(m ² g ⁻¹)			
S. Platensis	Integration of HTC (180 °C,	Hierarchical	~18	170-200 F g ⁻¹	Sevilla et al.	
	24h) and KOH chemical	porous	00-2200	at 0.1 A g ⁻¹	(2014)	
	activation (pyrolysis at 650-		m² g ⁻¹			
	700 °C)					
Kelp	NH3 chemical activation	3D	>10	440 F g ⁻¹ at	Li et al.	
	(pyrolysis at 700 °C)	interconnected	$00 \text{ m}^2 \text{ g}^{-1}$	0.5 A g ⁻¹	(2015)	
		structure				
Kelp	KOH chemical activation	3D	442	277 F g ⁻¹ at	Zeng et al.	
	(pyrolysis at 600 °C)	hierarchical	5 m² g ⁻¹	0.1 A g ⁻¹	(2017)	

porous

architecture

Nanochloropsis	Co(OH) ₂ chemical	Circular-	178	347 F g ⁻¹ at	Zhou et al.	
salina	activation (pyrolysis at 550 °C)	shaped structure 4		0.2 A g ⁻¹	(2017)	
Chlorella	KOH chemical activation	Spherical	133	353 F g ⁻¹ at 1	Zhu et al.	
zofingiensis	(pyrolysis at 600 °C)	structure	7.9	A g ⁻¹	(2018)	
Nostoc	KOH/HF chemical	3D porous	279	283 F g ⁻¹ at	Wang et al.	
flagelliform	activation (pyrolysis at 600-	active carbon	6	0.1 A g ⁻¹	(2019)	
	900 °C)					
C. glomerata	slow pyrolysis (900 °C) and	2D olive-	354	376.7 F g ⁻¹ at	Pourhossein	
	activated through a novel	shaped structure		the current	i et al. (2017)	
	activation process with nitric			density of 1Ag ⁻¹		
	acid					
C. glomerata	A suspension of algae and	A mixture of	475	299.3 F g ⁻¹ at	Pourhossein	
	\ensuremath{FeCl}_3 was centrifuged, and the	cubic and olive		the current	i et al. (2018)	
	solid residue was pyrolyzed at	shaped structure		density of 1Ag ⁻¹		
	the temperature of 700 °C for 4					
	h					
C. glomerata	A suspension of algae and	Circular-	670	332.2 F g ⁻¹ at	Pourhossein	
	KOH was centrifuged, and the	shaped structure		the current	i et al. (2018)	
	solid residue was pyrolyzed at			density of 1Ag ⁻¹		
	the temperature of 700 °C for 2					
	h					
C. glomerata	Integration of KOH	3D	957	427.3 F g ⁻¹ at	Pourhossein	
	activation and $FeSO_4 \cdot 7H_2O$	interconnected		the current	i et al. (2018)	
	catalysed HTC	structure		density of 1Ag ⁻¹		
C. glomerata	Integration of KOH	3D	605	445 F g ⁻¹ at	Norouzi et	
	activation and $Co(NO_3)0.6H_2O$	interconnected		the current	al. (2021)	
	catalysed HTC	structure		density of 1Ag ⁻¹		

1.1		Journal Pre-proofs		
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1344		Table 4. Recent progress in presenting algal biochar as a c	atalyst in the slow pyrolysis proc	ess
	Macroalgae	C. glomerata (Norouzi and Di Maria, 2018)	Sargassum (Taghavi et al.,	G.
	samples		2018)	gracilis
				(Norouzi et
				al., 2017)

Catalyst	Algal	Functional	Iron	Multi	Mesoporous	Algal	Zeolite
	biochar	algal biochar	composite	metal	silica	biochar	
			algal	catalysts			
			biochar				
Optimum	500	500	500	500	700	700	500
temperature (°C)							

	Journal Pre-proofs								
	Bio-oil	yield	39	45	43	29	41	41	42
	(wt.%)								
	Acid	yield	28.55	21.20	11.47	20.12	4.80	15.38	22.12
	(%)								
	Phenol	yield	8.50	31.54	11.80	2.39	4.27	15.04	5.95
	(%)								
	H ₂	yield	8.85	4.81	7.99	1.23	8.54	3.00	6.08
	(mmol/g								
1	feedstock)								
	CO₂	yield	11.25	3.40	6.30	2.94	6.90	5.61	4.07
	(mmol/g								
1	feedstock)		2.02	1.02	F 02	1.25	1.00	2.20	1.07
	(mmol/g	yiela	2.82	1.63	5.02	1.25	4.89	2.29	1.97
•	(mmor/g								
_	CH	vield	0.80	3.33	1.84	0.74	5.50	2.23	3.58
	(mmol/g	yield	0.00				0.00	2.20	0.00
f	feedstock)								
45					· · ·				
46									
47	[15	1]							
48	High	lights							
49									
50	-	Chemic	al compo	nents and cha	racteristic	s of microa	algae and m	acroalgae are d	iscussed
51									
52	-	Algal b	iochar use	es in soil, was	tewater tre	eatment, ar	nd supercapa	acitors are disc	ussed
53									
54	-	Overvie	ew of bio-	oil production	n by conve	entional an	d advanced	pyrolysis is pro	ovided
55					-				

[152]

1356

Journal Pression