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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**

25

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

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49 1. Introduction

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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
55 (IPCC, 2021). The concentrations of these three greenhouse gases (GHGs) in the atmosphere
56 are higher than at any point in the past 800,000 years (IPCC, 2021). Consequently, the earth's
57 temperature rose by 1 °C and is expected to increase by another 2.5-4 °C by the end of the 21st
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%
61 of the total renewable energy consumption, which is equivalent to approx. 5.6 EJ yr⁻¹ (Mandley
62 et al., 2020). However, large-scale utilisation of bioenergy still faces a number of technical and
63 non-technical barriers, such as low energy density (Nyoni et al., 2020), limiting economic
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
66 typical Energy Return on Investment (EROI) of biofuels is lower than 5, and much lower in
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).

72 Conceptually, there are four generations of biofuel technologies, depending on the types of
73 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
75 crops with food and feed uses and as a result increase food prices and put pressure on land use
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 second-
78 generation biofuels can utilize a wide range of lignocellulosic biomass, including agricultural
79 and forestry residues (straw, sawdust, etc.) as well as dedicated energy crops, such as jatropha,
80 miscanthus, or short-rotation willow, to produce ethanol, dimethyl ether, or Fischer Tropsch
81 synthesis fuel (Raud et al., 2019; Usmani et al., 2021). Although second-generation biofuels do
82 not require food crops and therefore are not in direct competition with food, they still require
83 land to produce biomass. The third-generation biofuels address this issue by using aquatic
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
86 (Sekar et al., 2021). In the fourth-generation biofuels, genetically modified microorganisms
87 such as microalgae and fungi are used as feedstock. Previous studies indicated that the third
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
92 convert carbohydrate components into bioethanol (Debiagi et al., 2017). Algae can be
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
96 biomass into a variety of pyrolytic products such as bio-oil (e.g., aromatic hydrocarbons,
97 nitrogen-containing compounds, carboxylic acid, furans and ketones), syngas (e.g., CO and
98 H₂), and biochar (Lee et al., 2020; Hong et al., 2017). The pyrolysis process involves moisture

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
102 pyrolysis. Slow pyrolysis typically has a heating rate of $0.1-1\text{ }^{\circ}\text{C s}^{-1}$ and residence time of
103 several minutes or even hours, whereas fast pyrolysis has a heating rate of more than $100\text{ }^{\circ}\text{C}$
104 s^{-1} and is typically carried out at the temperatures between 400 and $600\text{ }^{\circ}\text{C}$ (Onay and Kockar,
105 2003; Bridgwater et al., 1999). In the flash pyrolysis, biomass undergo a higher heating rates
106 of $10^3-10^4\text{ }^{\circ}\text{C s}^{-1}$ for a very shorter retention time ($<0.5\text{ s}$) at temperatures of $800-1000\text{ }^{\circ}\text{C}$
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
111 source and chemical production (Mandley et al., 2020; Chew et al., 2017). However, algal bio-
112 oil produced by pyrolysis generally has a high viscosity, which means that it cannot be directly
113 used in internal combustion engines. The oxygen content ($10-30\text{ wt}\%$) of algal bio-oil is
114 relatively lower than that obtained by pyrolysis of agricultural and forestry residues (about $45-$
115 $50\text{ wt}\%$); however, it is still high compared to that of heavy petroleum fuel oil (about $1.0\text{ wt}\%$)
116 (Saber et al., 2016). The high oxygen content can lead to low HHV of bio-oil, which is a huge
117 barrier for it to become the fossil fuel alternative (Saber et al., 2016). Bio-refinery and pyrolysis
118 technology updating can be conducted to upgrade the quality of bio-oil. Hence, this review
119 focus on the latter, intending to provide the update of advanced pyrolysis technology in the
120 recent years. The characteristics of different feedstocks can also significantly affect the bio-oil
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
123 of the bio-oil (Lee et al., 2020). In addition, the fatty acid and aldehyde contents of algal

124 biomass can cause corrosiveness and low chemical stability of bio-oil produced, which are
125 common problems for bio-oil from all biomass types (Saber et al., 2016; Oasmaa, 2016).
126 Although there is a huge gap waiting to be filled between ideas and commercialization, the
127 researchers should realise that the basic advantage of algae as a feedstock is its fast growth rate
128 (Dauta et al., 1990) and high yield (David et al., 2015). When used for biochar production, the
129 high growth rate of algae allows for faster rate of atmospheric carbon removal and
130 sequestration.

131 Since the second half of the 20th century, pyrolysis liquid products, such as biofuels have
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
136 has distinct physical and chemical properties due to the difference in the biomass composition,
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
140 advantage of algae as a feedstock for biochar is its fast growth rate ranging from 10 to 27 g/m²
141 day (Dauta et al., 1990; Sekar et al., 2021; Bach and Chen, 2017; Lee et al., 2020) and high
142 yield ranging from about 36% to 68% (Roberts et al., 2015; Bird et al., 2011), which directly
143 impacts the rate at which biochar can sequester carbon (Bird et al., 2011).

144 Both the liquid and solid products of algae pyrolysis are important and need to be exploited
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
147 well as key applications of algal biochar. Only a better understanding of potential applications
148 can make algal biochar play a more important role in mitigating climate change. At the same

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

151

152 2. Chemical composition of algae

153

154 Algae can be the most extensive source of simple microorganisms and account for
155 approximately half of photosynthesis activities on earth (Bach and Chen, 2017; Sirajunnisa and
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
158 embryo less plants capable of oxygen releasing and photosynthesis (Ferrera-Lorenzo et al.,
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*,
161 *Anabaena*, etc.) based on their cell sizes. It is worth mentioning that besides the main
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
164 important co-products of algae processing, often with high value uses as food additives or in
165 production of pharmaceuticals or cosmetics (Koyande et al., 2021). Algal carbohydrates are
166 already proven to be the potential feedstocks for bioethanol production (Bach and Chen, 2017;
167 Sirajunnisa and Surendhiran, 2016).

168 Lipids are natural macromolecular organic compounds widely present in biological tissues
169 (Debiagi et al., 2017). The lipid content of algae typically ranges from 0.9 to 71.5 wt%
170 depending on the algae species, growing conditions, seasons and geography factors (Lee et al.,
171 2020). Microalgae like *Chlorella pyrenoidose* have a high lipid of content up to 71.5 wt%
172 making them favorable feedstocks for lipid extraction and transesterification into biofuels (Lee
173 et al., 2020). Macroalgae on the other hand, have a much lower lipid content, typically 0.9-4.35

174 wt% (Maddi et al., 2011), which makes them less desirable feedstock for direct bio-oil
175 extraction. However, pyrolysis might be a more suitable thermal conversion method for
176 macroalgae and extracted microalgae.

177 Carbohydrates are mainly formed in algal biomass in the form of polysaccharides and sugar
178 monomers such as starch, cellulose, and glucose, similar to terrestrial plants (Lee et al., 2020).
179 The carbohydrate content of microalgae ranges from 0.1 to 56.92 wt%, while that of
180 macroalgae ranges from 12.43 to 47.7 wt%, as listed in Table 1. Mannitol, is usually regarded
181 as the main photosynthetic product for algal biomass, can be utilized in the pharmaceutical
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 exists
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
186 and syngas production aspect, glucose and starch are desirable feedstock for bioethanol and H₂
187 production (Chew et al., 2017). In another research, Azizi et al. (2018) indicated that
188 carbohydrates could also be converted into phenols and ketones during pyrolysis. Furans,
189 aldehydes and ketones, phenols, and acids were formed during the co-pyrolysis of cellulose
190 with *Enteromorpha clathrata* polysaccharides (ENP) and *Sargassum fusiforme*
191 polysaccharides (SAP) (Cao et al., 2018).

192 Proteins are substances with certain spatial structures formed by twisting and folding
193 polypeptide chains composed of amino acids through dehydration and condensation (Onwezen
194 et al., 2021). As shown in Table 1, the typical protein content of microalgae is in the range
195 between 10.8 and 65.2 wt%, while that of macroalgae is somewhat lower, between 7.9 and
196 42.11 wt%. The common chemical products produced from algal proteins are pyrroles and
197 indoles for applications in pharmaceuticals, adhesives, and herbicides (Lee et al., 2020;
198 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.
211 In any case, drying of algae is energy intensive. According to a report by Gan et al. (2018),
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.

215 Volatile matter content (VM) and fixed carbon content (FC) are two parameters used to
216 preliminarily assess whether biomass can be a suitable pyrolysis feedstock (Lee et al., 2020).
217 VM is the combustible gas or vapor released during heating of biomass, and FC is the solid
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
221 has the opposite trend, with lower FC for microalgae (4.05-16.2 wt%), and higher for
222 macroalgae (10.64-18.6 w%). The VM/FC ratio can be used to predict the biochar yield, with
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
226 content of algae tends to be relatively high (Lee et al., 2020). The typical ash content of
227 microalgae is in the range of 5.6-30.77 wt% and that of macroalgae 3.0-29.10 wt%, as shown
228 in Table 1. The ash composition depends on the algae species and its environment (Singh et al.
229 2021). Different ash types can affect the production of bio-oil and biochar. For example, K can
230 inhibit catalytic pyrolysis, and P can reduce the yield of bio-oil and biochar (Butler et al., 2011).
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
235 biochar's high ash content can be beneficial in soil amendment, as well as enhancing the
236 pseudo-capacitive performance, resulting in favorable electrochemical properties as algae-
237 based electrodes for supercapacitors.

238

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

240

241 3.1. Properties of algal biochar

242

243 Notable features of biochar, such as high stability (Yaashikaa et al., 2020), abundant
244 functional groups and nutrients (Janu et al., 2021), and high porosity and surface area (Leng et
245 al., 2021), makes it suitable for a range of applications. As most of the volatiles in the feedstock
246 can be removed during pyrolysis, the resulting biochar can be highly stable and recalcitrant to
247 decomposition (Bach and Chen, 2017). As a result, biochar can be stored in soil for thousands
248 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
250 inorganic content can provide nutrients for crop growth (Mašek et al., 2016; Roberts et al.,
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).

253 Algal biochar typically has a higher content of extractable inorganic nutrients (P, Ca, K and
254 Mg) than lignocellulosic biochar, which can be beneficial to soils, and thereby to crop
255 productivity (Bird et al., 2011; Michalak et al., 2019). During pyrolysis, the low volatilization
256 temperature of N, S, and Cl as well as low melting temperature of Na and K contained in algae
257 can present challenges related to corrosion and deposit formation (Mašek et al., 2016; Saber et
258 al., 2016). The remaining minerals that were not volatilised during pyrolysis would be retained
259 in the biochar, mainly within the ash fraction. As alluded to earlier, the mineral content and
260 composition is species and environment dependant. When algae from heavy metal
261 contaminated environments are used, these heavy metals present in the biochar can have
262 harmful effect on plant and crop growth in different soil conditions. For example, excessive
263 content of Fe, Zn, Cu, Mn, Cd, and Hg can cause toxic effect on plant growth (Lee et al., 2020).
264 While some research has been published on the effects of pyrolysis conditions on the content
265 of metals in algae biochar (Jung et al., 2016), there is yet insufficient understanding of how
266 process conditions can be optimised to maximise retention and availability of desirable metals,
267 such as K, P, Mg, etc. and minimise retention and availability of undesirable heavy metals,
268 e.g., Hg, Cd. Further research in this area is therefore needed.

269 Surface area and porosity are important properties in most biochar applications. Relatively
270 modest surface areas of algae biochar have been reported, when compared to terrestrial biochar,
271 especially woody biomass. For example, Michalak et al. (2019) and Roberts et al. (2015)
272 reported that *Cladophora glomerata* and *Eucheuma* pyrolysis yielded biochar with specific
273 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 $155 \text{ m}^2\text{g}^{-1}$ (Batista et
275 al., 2018; Zhao et al., 2019), $210 \text{ m}^2\text{g}^{-1}$ (Medynska-Juraszek et al., 2020; Sun et al., 2014), and
276 $170 \text{ m}^2\text{g}^{-1}$ (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 $507.177 \text{ m}^2\text{g}^{-1}$ and pore volume
280 of $0.3797 \text{ cm}^3\text{g}^{-1}$. 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 $575.1 \text{ m}^2\text{g}^{-1}$. 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^2g^{-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_3PO_4) washing can also promote the
288 porosity of biochar (Zhao et al., 2017). The H_3PO_4 -pretreated Pine tree sawdust biochar had a
289 high specific surface area of $930 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $0.558 \text{ cm}^3 \text{ g}^{-1}$, compared to
290 $51.0 \text{ m}^2 \text{ g}^{-1}$ and $0.046 \text{ cm}^3 \text{ g}^{-1}$ 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

298

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
303 increase of 8.6-fold from 242,495 t in 1983 to 2,089,153 t in 2015 (United Nations Food and
304 Agriculture Organization, 2014). Algal biochar can also be utilised in agriculture, horticulture
305 or forestry as a soil amendment as most of the nutrients contained in algae is retained and
306 indeed concentrated in the biochar. Roberts et al. (2015) reported that their seaweed biochar
307 had high N (~2 wt%), P (2.6 g kg⁻¹), and K (~67 g kg⁻¹) contents and exchangeable cations
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)
311 content of *Laminaria pallida* biochar and high Mg (6.4 g kg⁻¹) and K (151 g kg⁻¹) content of
312 *Gracilariopsis funicularis* biochar can provide a nutrient source in organic agriculture.
313 Therefore, the utilisation of these algal biochar can reduce the demand for chemical fertilisers,
314 lowering greenhouse gas emissions from fertiliser production. However, although algal biochar
315 is considered a potential strategy for soil improvement, the practice of adding algal biochar to
316 improve soil quality still faces several potential barriers. Boakye et al. (2016) indicated that
317 Kelp biochar had a high concentration of metals and ashes, which could cause toxic effect on
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
320 order to overcome these problems, especially contaminants, pre-treatment and post-treatment
321 processes have been proposed that can ameliorate the issues. For example, Boakye et al. (2016)
322 suggested pre-treatment processes, such as washing biochar, might reduce the level of toxicity.
323 Roberts et al. (2015) indicated that blending mineral-rich seaweed biochar with C-rich

324 lignocellulosic biochar could reduce the Na content and increase the carbon content of biochar
325 mixture, which results in unique soil ameliorants tailored to the needs of specific soil types.
326 Moreover, work by Cole et al. (2017) proposed a method of composting algal biochar, algae
327 biomass, and sugarcane bagasse, which can increase yield of corn by 15%. The possible reason
328 can be inferred that algal biochar can absorb unstable nitrogen and phosphorus elements to
329 prevent nutrient loss in the soil and reduce the Na content at the same time. The literature also
330 suggested leaching can lower the Na content of algal biochar, which could suppress the soil
331 salinity to some extent. Nevertheless, the existing pre- and post-treatment methods would
332 easily increase the cost of final scenario. Further research is needed to develop sustainable and
333 cost-effective methods to mitigate potential toxic effect of algal biochar's metal and ash content.

334

335 3.3. Wastewater treatment

336

337 A wide range of organic and inorganic contaminants in wastewater can be removed using
338 algal biochar as an adsorbent. There are four major mechanisms for inorganic ion (nutrients
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
341 exchange (Michalak et al., 2019; Jin et al. 2016; Son et al., 2018; Wang et al., 2016; Wang et
342 al., 2020). As mentioned earlier, due to its high mineral content, algal biochar tends to have a
343 high cation exchange capacity (CEC), making it suitable for removal of heavy metals.
344 Michalak et al. (2019) observed a high capacity of macroalgae (*Cladophora glomerata*)
345 biochar for heavy metal removal. The results showed that the removal efficiency for Cr^{3+} , Cu^{2+}
346 and Zn^{2+} were 89.9%, 97.1% and 93.7% respectively. Meanwhile, the Ca^{2+} , Mg^{2+} and Na^{+}
347 content in algal biochar were dramatically decreased. It can be inferred that the cation exchange

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

350 Surface complexation is another dominant mechanism for pollutant adsorption due to the
351 abundant functional groups on algal biochar surface. Jin et al. (2016) observed a high Cu^{2+}
352 removal potential of an anaerobically digested algae-dairy-manure-derived biochar with high
353 concentration of oxygen-containing functional groups like $-\text{COOH}$ and $-\text{OH}$. Similar work by
354 Liu et al. (2021) also found that the functional groups of $\text{C}=\text{C}$, $\text{C}=\text{O}$, CH_2 , and $\text{C}-\text{O}$ changed
355 when the *Microcystic* (Blue algae) biochar interacted with Cd (II). This indicated that Cd (II)
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-} ,
359 CO_3^{2-} , and SiO_3^{2-} , resulting in low precipitation during adsorption. This can however be
360 addressed during or after biochar production by different modification processes. Modification
361 of biochar surface morphology is a novel method to increase electrostatic interaction during
362 adsorption. Pyrolytic SiO_2 -biochar nanocomposites were prepared from vermiculite-treated
363 macroalgae by Wang et al. (2016). The researchers observed that the novel SiO_2 -biochar had a
364 high phosphate removal ability, which reduced the phosphate content from 50 mg L^{-1} to 10 mg
365 L^{-1} within 12 h. The possible reason for this was the increased electrostatic interactions at SiO_2
366 site on the biochar surface. Another novel blue algae biochar composite impregnated with α -
367 Fe_2O_3 was synthesized by Wang et al. (2020). Experimental results showed maximum
368 chelated nickel adsorption rate of 98.87% from Zn-Ni alloy electroplating wastewater. The
369 pollutant ions were attracted to the algal biochar surface by electrostatic attraction when the
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

373 interaction, H-bonding/ π - π interaction, polarity selectivity, partition and pore-filling effect,
374 applicable in removal of organic pollutants (Cheng et al., 2020; Chabi et al., 2020; Hung et al.,
375 2020; Zheng et al., 2017). In their study, Cheng et al. (2020) fabricated an enhanced macroalgal
376 biochar by co-pyrolysis of *Enteromorpha prolifera*, ferric chloride, and zinc chloride to treat
377 polycyclic aromatic hydrocarbons (PAH)-contaminated water. The highest PAH adsorption
378 capacity was up to 90 mg g⁻¹. The results showed that π - π interaction dominated the adsorption
379 when PAH concentrations was low, and partition dominated when concentration was high,
380 while pore-filling also played a role. Similarly, Chabi et al. (2020) identified the important role
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
384 modified with CaO/CaCO₃ with enhanced performance in remediation of 4-nonylphenol (4-
385 NP) from marine sediments. They found that calcium ions in biochar can improve removal of
386 4-NP under alkaline conditions. The adsorption mechanism was deemed to be associated
387 mainly with the electrostatic attraction and hydrophobic interaction of 4-NP and oxygen-
388 containing functional groups on the biochar surface. The modified CaO/CaCO₃ on biochar
389 surface increased the number of adsorption site and enhanced direct electron transfer. Although
390 there has been research on use of algal biochar in wastewater treatment and on mechanisms
391 involved in removal of different contaminants, concerted effort is needed on bringing this
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.

395

396 3.4. Supercapacitor

397

398 With the increasing demand for electric mobility and other applications requiring energy
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
402 al., 2018). Their unique characteristics make supercapacitors a better choice for energy storage
403 in specific areas, such as wind turbine systems, electric vehicles, cranes, and computers
404 (Raymundo-Piñero et al., 2009; Yu et al., 2016). The electrochemical properties of algal
405 biochar electrodes are determined by the feedstock and processing conditions used. As
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.

411 The most common method for increasing the SSA of carbon materials, adjusting the pore
412 structure, and enhancing surface functional groups are activation, metal oxides/hydroxides
413 loading, heteroatom doping, and nanostructure composites (Cheng et al. 2017). Various
414 physical and chemical modifications for biochar and their electrochemical behaviours in
415 supercapacitors have been reviewed comprehensively by Norouzi et al. (2020). The main
416 advantage of algal biochar over lignocellulosic biochar is that they would be self-activated
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
422 materials, as active materials in supercapacitors, was investigated. The novel KOH activated

423 3D algal biochar, showed a high specific capacitance of 376.7 F g^{-1} at the current density of 1
424 A g^{-1} with a high energy density of 42.4 Whkg^{-1} . Comparatively, the specific capacitance of
425 the control group (without activation) was 197.8 F g^{-1} with the energy density of 22.25 Whkg^{-1} .
426 Furthermore, metal oxides/hydroxides loading of algal biochar can enhance the pseudo-
427 capacitive performance of the electrode, owing to the increased redox activities. A high-
428 performance asymmetric supercapacitor was prepared, which contained functional biochar
429 (FBC) as anode electrodes and iron oxide/carbon composites (MBC and FCBC) as cathode
430 electrodes in KCl electrolyte (Pourhosseini et al., 2018). MBC was derived from *Cladophora*
431 *glomerata* with FeCl_3 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} .

433 Although pristine algal biochar is rich in N content, heteroatom elements doping is still a
434 potential post-modification method to improve the pseudo-capacitive performance and electric
435 conductivity. A high-performance N-doped macroalgae (*Enteromorpha prolifera*) derived
436 biochar obtained by Ren et al. (2018) was utilized as an electrode for supercapacitor. The
437 prepared biochar revealed a surface area of $2000 \text{ m}^2 \text{ g}^{-1}$ with 1.4-2.9 at% N-loadings. The algal
438 biochar showed a specific capacitance of up to 200 F g^{-1} at current density of 1 A g^{-1} with KOH
439 activation at $700 \text{ }^\circ\text{C}$.

440 In addition, nanostructure composites can enhance the mechanical properties and surface
441 redox reactions. Raymundo-Piñero et al. (2011) developed a novel high-power supercapacitor
442 produced by co-pyrolysis of seaweed and multi-walled carbon nanotubes (CNTs). This high-
443 power supercapacitor showed relatively high electrochemical performance compared with
444 pristine algal biochar. Owing to the blend with CNTs of high conductivity and the presence of
445 opened mesopores, the cell resistance decreased significantly, which led to the increase of
446 specific power. Moreover, the high porosity of this new type of algae biochar material increases

447 its elasticity when used as a capacitor so that it can be adapted to various working conditions
448 and sizes to reduce mechanical damage.

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

456 It should be noted that surface morphology and BET surface area also play a crucial role in
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
459 3. As can be seen, spherical-shaped, olive-shaped, circular-shaped and nanofibrous structures
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,
462 3D architecture has seen a growing interest for supercapacitors, as it provides improved surface
463 area and long ion-transport pathways. There are presently few available literatures that apply
464 3D structure algal biochar in supercapacitors. As seen, the most popular and studied
465 preparation method to create a 3D architecture is a simple basic activation using KOH. For
466 example, Zeng et al. (2017) could successfully reach a 3D hierarchical porous architecture
467 through KOH chemical activation by pyrolysis at $600 \text{ }^\circ\text{C}$. The specific surface area and
468 capacitance were $4425 \text{ m}^2 \text{ g}^{-1}$ and 277 F g^{-1} (at the current density of 0.1 A g^{-1}). Wang et al.
469 (2019) followed the same preparation procedure to synthesize a 3D structure from *Nostoc*
470 *flagelliform* algae. The maximum specific capacitance was 283 F g^{-1} at 0.1 A g^{-1} . The energy
471 density of 3D algal biochar supercapacitors can be even further enhanced by introducing

472 pseudocapacitive materials, such as hetero atoms, 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 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ catalyzed HTC
475 (Pourhosseini et al., 2018).

476 In conclusion, various modification methods, such as chemical activation, physical
477 activation, heteroatom doping, and biochar-nanostructure composites, have been developed to
478 improve the properties of biochar-derived carbon materials, such as specific surface area, pore
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
484 significantly, which might be the benefit to reduce the cost and environmental impact.

485

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

487

488 4.1. Pyrolysis for algal bio-oil production

489

490 Fast pyrolysis is typically used for optimal bio-oil production because the short residence
491 time of volatiles in the reactor does not allow extensive secondary reactions of volatile matters
492 that would reduce the yield of bio-oil and increase the yield of biochar (Lee et al., 2020; Mašek,
493 2016). However, due to the requirements of high temperature and heating rate and the low
494 thermal conductivity of biomass, the feedstock needs to be introduced in form of fine particles,
495 typically smaller than 2 mm (Mašek et al., 2016; Lee et al., 2020). Therefore, the physical pre-
496 treatment 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
501 bio-oil is necessary after fast pyrolysis. Furthermore, the high viscosity of algal bio-oil is
502 another obstacle that needs to be overcome before it can be used as a drop-in fuel (Djandja et
503 al., 2020). The viscosity problem is much more serious for hydrothermal bio-oil than pyrolytic
504 bio-oil. Corrosivity is a common problem for all types of bio-oil. In algae bio-oil, high fatty
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
513 other hand, in another study macroalgae *Saccharina japonica*-derived bio-oil produced in a
514 fixed-bed reactor at 350 °C reached HHV of 33.36 MJ kg⁻¹ (Ly et al., 2016). This illustrates
515 the sensitivity of the bio-oil quality to the feedstock and process setup and conditions. Results
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
518 pyrolysis proved to yield bio-oil of insufficient quality. Therefore, in this part of the review
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
521 and yield better quality bio-oil.

522

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

524

525 As discussed in section 2, algae are complex and heterogeneous feedstock consisting of
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
534 though detecting key compounds and intermediates (Ross et al., 2009; Silva et al., 2016;
535 Marcilla et al., 2009). As illustrated in Figure 1, carbohydrates in algae first undergo
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
543 *Enteromorpha prolifera*, *Nannochloropsis* sp., and *Spirulina platensis* at the temperatures of
544 400, 500, and 600 °C. They detected pyridinic-N, pyrrolic-N, and nitrogen-based polycyclic
545 compounds in the char (Chen et al., 2017). As Figure 1 shows, some of these compounds could
546 transfer into the liquid portion and convert into either alkenes via deamination or carboxylic

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.
551 The amount of nitrogen (mol %) appearing as ammonia was 53% at the temperature of 800 °C.
552 Recycled form of ammonia has potential application as fertilizer in macroalgae cultivation.
553 Moreover, benzene, toluene, and xylene (BTX), showed the highest combined carbon yield of
554 15%. BTX compounds are essential for extracting and creating commercial products such as
555 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
558 fatty acids by cutting acyl chains from the glycerol molecule through the hydrolysis process.
559 Saturated fatty acids would be converted into ketones, aldehydes, acids, alcohols by
560 decarboxylation during pyrolysis. However, unsaturated fatty acids generate carbon dioxide,
561 carbon monoxide, and hydrocarbons. Finally, the intermediates produced by carbohydrate and
562 lipid undergo further cracking and deoxygenation to produce linear and aromatic hydrocarbons.

563 Despite all these developments, algae bio-oil is not suitable for direct usage in engines or
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.

568

569 4.3. Microwave-assisted pyrolysis

570

571 Pyrolysis technology based on microwave heating has made a great progress in the past 10
572 years (Ferrera-Lorenzo et al., 2014; Du et al., 2011; Beneroso et al., 2013). Microwave
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
575 by resonant of the frequency of the microwave radiation and that of the vibration of the
576 polar molecules (mainly water) in the target sample, allowing the biomass to be uniformly
577 heated from the inside (Lee et al., 2020). Microwave irradiation can accelerate thermochemical
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
583 moisture content (Antunes et al., 2018), and therefore low moisture content could cause low
584 heating efficiency, whereas high moisture content can increase energy requirement and heating
585 time.

586 Several published studies have discussed the differences between conventional pyrolysis
587 and microwave-assisted pyrolysis. For example, Ferrera-Lorenzo et al. (2014) conducted a
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).

600 Therefore, another potential major advantage of microwave-assisted pyrolysis aimed at
601 energy applications is the higher yield of pyrolysis gases. Beneroso et al. (2013) found that
602 microwave-assisted pyrolysis gave rise to higher gas yield (57.2 wt%) compared to
603 conventional pyrolysis (34.7 wt%) at 800 °C; whereas the liquid product yield decreased from
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,
609 the addition of adsorbents and catalysts could further boost formation of gas products.
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
612 increased by 75.66%, 49.97%, 49.97%, and 25.83%, respectively.

613 Use of microwave adsorbents can also affect the quality and yield of bio-oil. Borges et al.
614 (2014) conducted microwave-assisted pyrolysis of *Chlorella* and *Nannochloropsis* using
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
617 with no adsorbent and catalyst. As mentioned before, moisture content in the feedstock can
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.

624

625 4.4. Co-pyrolysis

626

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.

633 A number of studies have investigated the chemical composition of bio-oil produced from
634 co-pyrolysis of algae and other biomass. For example, Cao et al. (2018) studied the co-
635 pyrolysis of cellulose with *Enteromorpha clathrata* and *Sargassum fusiforme*. They found that
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
638 observations of synergies in co-pyrolysis were made by Hua and Li (2016) in co-pyrolysis of
639 sugarcane bagasse and *Enteromorpha prolifera*. Their results showed that the synergistic
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.

642 Previous studies have found that the blending ratio can be a dominant factor affecting the
643 bio-oil quality. For instance, Xu et al. (2019) claimed that when the amount of rice husk was
644 raised in the mixture (*Enteromorpha* and rice husk), the distribution of furans and esters of bio-
645 oil 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
648 of algae-mixed biomass in co-pyrolysis (Lee et al., 2020). The low EHI (<0.3) of algal biomass
649 can inhibit the production of hydrocarbon-based compounds, so the chemicals with high EHI
650 (~2), such as polyethylene, alcohol, and esters, are preferable in the blend. Co-pyrolysis of
651 *Nannochloropsis sp.* and scum from wastewater treatment plant was conducted by Xie et al.
652 (2015). The EHI value of *Nannochloropsis sp.* was 0.095 while that of scum was 1.59. When
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.
657 Research on co-pyrolysis of microalgae with low-density polyethylene (LDPE) showed that
658 presence of LDPE promoted the formation of formic/acetic ester and long-chain alcohol,
659 whereas it reduced O content from 45.5 wt% to 10.2 wt% in *Enteromorpha prolifera* (EP) bio-
660 oil and N content from 19.5 wt% to 6.6 wt% in *Spirulina platensis* (SP) bio-oil (Tang et al.,
661 2020). The bio-oil yield was significantly increased because the volatile content of LDPE can
662 crack into liquid products. The co-pyrolysis of *Enteromorpha prolifera* with waste plastics
663 (HDPE) was further conducted by Xu et al. (2020). The results indicated that the nitrogen-
664 containing compounds, oxygenates and acids were sharply decreased in algal bio-oil while
665 light hydrocarbons and aromatics contents were increased due to the high hydrogen content in
666 HDPE. The study also proved the catalytic coking was inhibited and the formation of solid
667 residues was reduced because of the synergetic effects when combining catalytic pyrolysis with
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

671 biomass with other feedstocks can increase the EHI values and decrease the N concentrations,
672 resulting in desirable bio-oil quality with high HHV. On the other hand, choosing some
673 expensive feedstocks as co-heating materials may improve the pyrolysis performance, but it
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
676 be considered in future study.

677

678 4.5. Catalytic pyrolysis

679

680 To further improve the pyrolysis performance and the yield and quality of pyrolysis
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
683 thermal conversion option for bio-oil production with several advantages such as low energy
684 input, high algal bio-oil quality, and low pyrolysis temperature (Miandad et al., 2016; Gao et
685 al., 2017; Anand et al., 2016; Yuan et al., 2020). For example, catalytic pyrolysis can upgrade
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
689 effective catalytic pyrolysis. In-situ catalytic cracking mixes the biomass and catalysts in the
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
694 of the catalyst limit the performance of in-situ catalytic pyrolysis (Iisa et al., 2016). On the
695 other hand, ex-situ catalytic pyrolysis utilises a dedicated catalytic reactor located downstream

696 of the pyrolyzer. Ex-situ catalytic pyrolysis has the advantages of being more controllable,
697 catalyst is recyclable, and it avoids interference between feedstocks and catalysts (Kalogiannis
698 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 SiO_4 - and
701 AlO_4 -tetrahedra that share corners, which have been shown to be valuable in industrial catalysis
702 (Miandad et al., 2016). Cao et al. (2018) have used ZSM-5 as a catalyst to study the catalytic
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
712 et al. (2010) compared conventional pyrolysis and HZSM-5-based catalytic pyrolysis of
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 can effectively reduce the oxygen content of
715 bio-oils while increasing their heating value. In addition, Anand et al. (2016) tested catalytic
716 fast pyrolysis of *Arthrospira platensis* using different zeolites (ZSM5, $Z\beta$ and ZY). The results
717 showed that the use of high acidity ZY and $Z\beta$ catalysts promoted the synthesis of C2-C4
718 nitriles, whereas the use of ZY and $Z\beta$ 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,
725 O. et al. (2017) conducted catalytic pyrolysis of *Gracilaria gracilis* using Co-Mo supported
726 zeolites. The catalysts considerably reduced acetic and formic acid concentrations from 9.56%
727 to 8.12 wt%. Meanwhile, the concentrations of phenol and furfural dropped from 6.65 wt%
728 and 6.98 wt% to 5.88 wt% and 5.49 wt%, respectively. Another study by Hao et al. (2021)
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
733 aromatization reactions during pyrolysis. The study implied that the synthesized Ga/NiFe-
734 LDO/AC can be a promising catalyst for algal bio-oil upgrading. In another previous research,
735 Yuan et al. (2020) used Mg-Ce-ZSM-5 as a carrier to study the interaction between seaweed
736 and catalyst during pyrolysis. The study had shown that MgO played an effective role in
737 breaking chemical bonds and generating smaller molecular structures, resulting in a decrease
738 in the bio-oil yield and an increase in biogas production. However, the addition of Mg-Ce
739 changed the chemical structure of algae bio-oil, which means that the aromatization of ZSM-5
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%.

742 To the best of our knowledge, the use of algal biochar as a catalyst was first proposed by
743 (Norouzi, et al. 2016). In their recent studies, the catalytic behavior of biochar derived from *C.*
744 *glomerata*, *G. gracilis*, and *Sargassum* was investigated in the pyrolysis process. These
745 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
750 the ash. A simple mechanism proposed for the algal biochar with different AAEM
751 compositions includes two reaction pathways. One is the formation of compounds containing
752 C=O groups, such as acids, aldehydes, CO₂, etc. The other is the formation of compounds
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
758 algal bio-oil quality is highly desirable. Although the catalytic pyrolysis for algal bio-oil has
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

765 This review highlighted that there are promising opportunities for integration of
766 coproduction of algal biochar and bioenergy into algal biorefinery using pyrolysis, making it
767 possible to achieve a net zero carbon balance or even become carbon negative. Such algal
768 biochar-bioenergy system (ABBS) offers many intrinsic advantages, e.g., atmospheric carbon
769 capture and storage, products for sustainable agriculture and environmental management,
770 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
787 biochar through extraction and thermal conversion. This review highlights the key
788 opportunities and challenges of algal pyrolysis, and the applications of pyrolytic algal biochar,
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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800

801 CRediT authorship contribution statement

802

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

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806 References

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1261 **Tables**

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

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

<i>Chlorella spp.</i>	2	15–16.5	-	6.2	-	-	2	Rizzo et al.
	9.6						1.6	(2013)
<i>Chlorella vulgaris</i>	1	12.4	5	4.4	67.2	1	1	López-González
	3.5		8.1			2.4	5.9	et al. (2014)
<i>Scenedesmus</i>	2	25.2	4	2.9	67.9	9.	1	López-González
<i>almeriensis</i>	4.6		4.2			7	9.4	et al. (2014)
<i>Nannochloropsis</i>	2	25.1	4	3.5	79.8	1	6.	López-González
<i>gaditana</i>	6.3		0.5			0.2	4	et al. (2014)
<i>Chlorella</i>	7	0.2	2	6.1	94.3	-	5.	Gai et al. (2013)
<i>pyrenoidosa</i>	1.5		2.5				7	
<i>Spirulina platensis</i>	6	4.8	1	6.8	90.4	-	9.	Gai et al. (2013)
	4.7		9.3				6	
<i>Chlorella</i>	1.	24.07	6	5.78	66.5	1	5.	Hu et al., (2015)
<i>pyrenoidosa</i>	83		2.42		1	5.98	95	
<i>Cyanobacteria</i>	5.	21.49	6	9.59	70.1	1	6.	Hu et al. (2015)
	48		0.28		3	0.14	14	
<i>Chlorella vulgaris</i>	1	56.92	2		74.5	1	9.	Bach et al. (2017)
<i>ESP-31</i>	4.83		2.5		9	6.39	02	
<i>Scenedesmus obliquus</i>	4.	13.41	3	5.13	70	5.	2	Chen et al. (2014)
	66		0.38			29	4.71	
Macroalgae								
<i>Enteromorpha</i>	4.	20.21	4	4.86	55.9	1	2	Xu et al. (2020)
<i>prolifera</i>	31		2.06		0	0.69	8.56	
<i>Enteromorpha</i>	-	-	-	6.80	53.9	1	2	Uzoejinwa et al.
<i>prolifera</i>					5	0.69	8.56	(2019)
<i>Enteromorpha</i>	-	-	-	6.80	53.9	1	2	Xu et al. (2019)
					5	0.69	8.56	
<i>Enteromorpha</i>	-	-	-	10.1	57.9	1	2	Xu et al. (2019)
<i>clathrate</i>				3	9	0.73	1.15	
<i>Porphyra</i>	1.	47.7	3	9.3	70.8	1	3.	Hong et al.
	5		5.7			6.9	0	(2017)
<i>Native Laminaria</i>	1.	46.6	1	8.0	79.9	1	9.	Kostas et al.
<i>digitata</i>	0		2.9			3.1	9	(2019)
<i>Laminaria digitata</i>	0.	41.4	1	-	74.0	1	1	Kostas et al.
	9		4.1			8.6	2.1	(2019)

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

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Table 2. The recent developments on supercapacitors derived from algal biochar

Biochar type	Specific surface area (m ² g ⁻¹)	Specific capacitance (F g ⁻¹)	Current density (A g ⁻¹)	Energy density (W h kg ⁻¹)	Cycle stability	Cycle stability percent (%)	References
<i>Chlorella vulgaris</i>	3516	142	1	8.9	2200	91.5	Han et al. (2019)

<i>Chlorella</i>	1337.9	353	1	20	10	92	Zhu et al. (2018)
<i>Nannochloropsis salina</i>	1784	347	0.2	26.1	50	83	Zhou et al. (2017)
<i>Cladophora glomerata</i>	354	376.7	1	42.4	50	99.2	Pourhosseini et al. (2017)
<i>Ascophyllum nodosum</i>	1493	207.3	0.5	-	25	92.3	Perez-Salcedo et al. (2020)
<i>Enteromorpha prolifera</i>	2000	200	1	7	10	96	Ren et al. (2018)
<i>Cladophora glometa</i>	957	427.3	1	41.5	10	93.1	Pourhosseini et al. (2018)
<i>Kelp</i>	4425	277	0.1	8	20	92	Zeng et al. (2017)
<i>Turbinaria conoides</i>	173.8	416	1	52	50	85.3	Divya and Rajalakshmi (2020)
<i>Ulva fasciata</i>	376.82	332	0.5	46.1	50	97.5	Chaudhary et al. (2019)
<i>Undaria pinnatifida</i>	3270	425	0.1	42	10	94	Kang et al. (2015)

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Table 3. Preparation method, morphology, and supercapacitor performance of algal biochar

Algae	Preparation method	Morphology	Surface area ($\text{m}^2 \text{g}^{-1}$)	Specific capacitance (F g^{-1})	References
S. Platensis	Integration of HTC (180 °C, 24h) and KOH chemical activation (pyrolysis at 650-700 °C)	Hierarchical porous	~1800-2200 $\text{m}^2 \text{g}^{-1}$	170-200 F g^{-1} at 0.1 A g^{-1}	Sevilla et al. (2014)
Kelp	NH_3 chemical activation (pyrolysis at 700 °C)	3D interconnected structure	>1000 $\text{m}^2 \text{g}^{-1}$	440 F g^{-1} at 0.5 A g^{-1}	Li et al. (2015)
Kelp	KOH chemical activation (pyrolysis at 600 °C)	3D hierarchical	4425 $\text{m}^2 \text{g}^{-1}$	277 F g^{-1} at 0.1 A g^{-1}	Zeng et al. (2017)

			porous architecture				
Nanochloropsis salina	Co(OH) ₂	chemical activation (pyrolysis at 550 °C)	Circular-shaped structure	4	178	347 F g ⁻¹ at 0.2 A g ⁻¹	Zhou et al. (2017)
Chlorella zofingiensis	KOH	chemical activation (pyrolysis at 600 °C)	Spherical structure	7.9	133	353 F g ⁻¹ at 1 A g ⁻¹	Zhu et al. (2018)
Nostoc flagelliform	KOH/HF	chemical activation (pyrolysis at 600-900 °C)	3D porous active carbon	6	279	283 F g ⁻¹ at 0.1 A g ⁻¹	Wang et al. (2019)
C. glomerata		slow pyrolysis (900 °C) and activated through a novel activation process with nitric acid	2D olive-shaped structure		354	376.7 F g ⁻¹ at the current density of 1Ag ⁻¹	Pourhossein i et al. (2017)
C. glomerata		A suspension of algae and FeCl ₃ was centrifuged, and the solid residue was pyrolyzed at the temperature of 700 °C for 4 h	A mixture of cubic and olive shaped structure		475	299.3 F g ⁻¹ at the current density of 1Ag ⁻¹	Pourhossein i et al. (2018)
C. glomerata		A suspension of algae and KOH was centrifuged, and the solid residue was pyrolyzed at the temperature of 700 °C for 2 h	Circular-shaped structure		670	332.2 F g ⁻¹ at the current density of 1Ag ⁻¹	Pourhossein i et al. (2018)
C. glomerata		Integration of KOH activation and FeSO ₄ ·7H ₂ O catalysed HTC	3D interconnected structure		957	427.3 F g ⁻¹ at the current density of 1Ag ⁻¹	Pourhossein i et al. (2018)
C. glomerata		Integration of KOH activation and Co(NO ₃) _{0.6} H ₂ O catalysed HTC	3D interconnected structure		605	445 F g ⁻¹ at the current density of 1Ag ⁻¹	Norouzi et al. (2021)

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Table 4. Recent progress in presenting algal biochar as a catalyst in the slow pyrolysis process

Macroalgae samples	C. glomerata (Norouzi and Di Maria, 2018)				Sargassum (Taghavi et al., 2018)		G. gracilis (Norouzi et al., 2017)
Catalyst	Algal biochar	Functional algal biochar	Iron composite algal biochar	Multi metal catalysts	Mesoporous silica	Algal biochar	Zeolite
Optimum temperature (°C)	500	500	500	500	700	700	500

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 feedstock)							
CO ₂ yield	11.25	3.40	6.30	2.94	6.90	5.61	4.07
(mmol/g feedstock)							
CO yield	2.82	1.63	5.02	1.25	4.89	2.29	1.97
(mmol/g feedstock)							
CH ₄ yield	0.80	3.33	1.84	0.74	5.50	2.23	3.58
(mmol/g feedstock)							

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1348 **Highlights**

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1350 - Chemical components and characteristics of microalgae and macroalgae are discussed

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1352 - Algal biochar uses in soil, wastewater treatment, and supercapacitors are discussed

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1354 - Overview of bio-oil production by conventional and advanced pyrolysis is provided

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Journal Pre-proofs