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Review

Recent developments on algal biochar production and characterization

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GRAPHICAL ABSTRACT

ABSTRACT

Algal biomass is known as a promising sustainable feedstock for the production of biofuels and other valuable products. However, since last decade, massive amount of interests have turned to converting algal biomass into biochar. Due to their high nutrient content and ion-exchange capacity, algal biochars can be used as soil amendment for agriculture purposes or adsorbents in wastewater treatment for the removal of organic or inorganic pollutants. This review describes the conventional (e.g., slow and microwave-assisted pyrolysis) and newly developed (e.g., hydrothermal carbonization and torrefaction) methods used for the synthesis of algal-based biochars. The characterization of algal biochar and a comparison between algal biochar with biochar produced from other feedstocks are also presented. This review aims to provide updated information on the development of algal biochar in terms of the production methods and the characterization of its physical and chemical properties to justify and to expand their potential applications.

1. Introduction

Renewable energy such as biomass is receiving more attention on its applicability for sustainable supply to the environment (Al-Hamamri et al., 2017). Algal biomass is considered as a promising feedstock due to its wide distribution, rapid growth and high CO₂ fixation efficiency (Chen et al., 2015b; Roberts et al., 2015a). Growing algal biomass is a distinctive way to sequester atmospheric carbon dioxide to minimize greenhouse effect (Gronnow et al., 2013). A potential improvement on conversion of biomass to biochar through thermochemical processes...
such as pyrolysis, hydrothermal carbonization or torrefaction is commendable for further utilizing the algal biomass in the context of biorefinery. Upgrading of current thermochemical processes is important to enhance the economic feasibility of biochar production process with a faster rate, higher yield, and better quality for applications (e.g., higher value applications of biochars other than as fertilizer, such as adsorbent for environmental pollutant uptake or bio-materials for medical applications).

Biochar is a carbon-rich product of biomass produced by thermal decomposition under limited oxygen (O$_2$) supply at a relatively low temperature (Alhashemi and Aktas, 2017; Chang et al., 2015). The conversion of wet algal biomass into algal char can occur at a relatively moderate thermal condition in a short time under batch processing conditions (Heilmann et al., 2010). The composition of biochar varies with the types of feedstock. For example, microalgal biochar consists of large aggregates with irregular porosity. These features vary from the structure of lignocellulose biochar produced after thermal decomposition treatment (Torri et al., 2011). Algal biochar has lower surface area and carbon content, but higher cation exchange capacity compared to lignocellulose biochar. The higher pH properties of algal biochar can balance acidified soils, while the higher nutrient content of nitrogen, ash and inorganic elements are beneficial for soil amendment in agriculture (Koltowski et al., 2017; Sun et al., 2017).

In addition to soil amendment utilization, biochar can also be used as a bio-adsorbent in water treatment to remediate organic/inorganic contaminants due to its abundance of organic functional groups and inorganic minerals (Awad et al., 2017; Johansson et al., 2016). However, selection of cheap raw bio-materials with better properties and easy preparation steps of bio-adsorbent still present major challenges for the application of biochar in the conventional wastewater treatment (Inyang et al., 2016). Microalgae have been studied extensively as a potential biosorbent for the removal of organic and inorganic pollutants due to their biosorption capacity attributed by a large amount of functional groups (Guo et al., 2016; Zeraatkar et al., 2016). Those specific functional groups on microalgal biochar lead to some special physico-chemical properties that could enhance its adsorption efficiency for organic contaminants (Zheng et al., 2017). The biorefinery model of microalgae that can produce valuable biofuels and biochar simultaneously making it an interesting approach for future research and development. Therefore, this review aims to provide the latest development of algae-based biochar production technology using thermochemical processes such as pyrolysis, torrefaction and hydrothermal carbonization. This review also aims to provide updated information on the characterization of physical and chemical properties of microalgal biochar to justify and to expand their potential applications. A future recommendation of research work related to algal biochar is also proposed in the review.

2. Algal biomass as the source for producing biofuels and biochar

Fig. 1 shows the schematic view of algal biomass production in renewable energy and carbon sequestration. With the ability in nutrients uptake, algae possess a high growth rate and environmentally tolerant characteristics to rapidly dominate in high nutrients environment. The high nutrient content of algae makes it a suitable feedstock for biochar production for the potential use in soil amendment and implement for long-term carbon sequestration. Algal biochar derived from the remediation of wastewater could provide a notable benefit in the future by utilizing biomass for carbon negative energy generation and application to the environment (Bird et al., 2011). However, the high nutrient content of algal biomass makes it a disadvantage in pyrolysis product distribution where more bio-oil product can be obtained. One way to solve this problem is to extract the lipids from algae for biooil production, while the residues are further used for biochar production to the context of biorefinery (Wang et al., 2013). Algae have been known as one of the promising sustainable energy feedstocks for the future without the dependence on fossil fuels and their growth can efficiently reduce emissions of greenhouse gases. Microalgae are popular choice for biofuel production since it is easy to cultivate them in a large amount under various environments (Vassilev and Vassileva, 2016). All types of biofuels (i.e., solid, liquid and gas biofuels) can be generated from microalgae using several conversion methods such as direct combustion, chemical conversion, biochemical conversion and thermochemical conversion. In addition to the success of algal technology in fuel production, other value-added co-products such as biochar can be produced simultaneously from algal feedstock for a biorefinery concept (Foley et al., 2011; Rashid et al., 2013).

Biochar is gaining more attention on its long term advantage in carbon sequestration and application in agriculture for soil amendment (Ennis et al., 2012). Biochar technology involved the CO$_2$ uptake through photosynthesis. The captured carbon undergoes conversion processes such as pyrolysis to produce biochar with characteristic of long-term carbon storage through soil amendment (Sohi et al., 2009). Biochar production differs from other biomass energy production systems as this technology is carbon-negative. The International Biochar Initiative (2008) estimated that biochar production has the potential of mitigation of climate change by providing 3.67 Gt CO$_2$ per year using only biomass wastes. Biochar is potential to sequester up to 12% of greenhouse gases from anthropogenic sources in ecologically and economically sustainable systems (Ennis et al., 2012). Implementation of biochar’s ability in mitigation of climate change at global scale is recognized (Molina et al., 2009).

As a strategy to store captured carbon for a long time on impact to greenhouse gas accumulation, biomass is converted into biochar that has more than 90% carbon (Heilmann et al., 2010). Biochar derived from microalgae is nutrient-rich (especially nitrogen-rich) so is well-suited to serve as a fertilizer in agriculture soil (Torri et al., 2011). With all the advantages of algal biochar, converting algal biomass into biochar can be economically feasible for algal production enterprise (Bryant et al., 2012). However, to date there is still very limited literature regarding algal biochar and its utilization. This may markedly hinder the future development and application of algae-based biochar (Shukla et al., 2017), suggesting the need for a comprehensive literature review in this promising area.

3. Algal biochar production

Algal biomass is converted into biochar mainly through thermochemical conversions, such as pyrolysis, hydrothermal carbonization and torrefaction. The conventional way of synthesizing biochar is through slow pyrolysis which gives a high char yield. Hydrothermal carbonization produced a final carbonaceous material, which is also denoted as hydrochar. Torrefaction is a pre-treatment method that has been studied extensively to upgrade biomass into carbon-rich solid fuel such as biochar (Chen et al., 2015d; Kumar et al., 2017). Details of biochar synthesis methods are described as follows.

3.1. Conventional and microwave-assisted pyrolysis

Pyrolysis is one of the most promising technologies for converting biomass into valuable biofuels as well as biochars. There are several types of pyrolysis based on their operating conditions such as the conventional slow pyrolysis, fast pyrolysis and also the latest developed microwave-assisted pyrolysis. Each type of pyrolysis produces different composition of solid, liquid and gaseous products according to their operating parameters, such as temperature, heating rate and residence time. Slow pyrolysis gives the highest yield of biochar while fast pyrolysis gives the highest yield of bio-oil with biochar as by-product (Roy and Dias, 2017).

3.1.1. Conventional pyrolysis

Pyrolysis is the heating of biomass with the absence of oxygen or air
at a given rate typically at a temperature range of around 300–700 °C (Chen et al., 2015c). The products obtained from pyrolysis are determined by several factors, in particular the temperature and heating rate (Basu, 2010). Biochar yield increases with a decrease in pyrolysis temperature, an increase in the residence time, and a preferable low heating rate. In addition, feedstock properties, such as moisture content and particle size, also significantly affect the yield of biochar produced via pyrolysis (Tripathi et al., 2016). Slow pyrolysis, the conventional process in charcoal production, could yield the maximum amount of biochar from biomass compared to other processes, such as fast pyrolysis and gasification (Chaiwong et al., 2012; Mohan et al., 2014). Up to 50% of the carbon from biomass may be stored in the stable biochar through pyrolysis (Bird et al., 2011). Biomass undergoes slow pyrolysis process with a vapour residence time from several minutes to hours for char production (Du, 2013). Vapours are restrained and reacted with solid phase extensively for more char yield at the end of the process (Mohan et al., 2014). Slow pyrolysis, in general, carried out at low heating rates of 0.1–1 K/s with a residence time of around 450–550 s. Pre-pyrolysis happens at the beginning, followed by solid decomposition corresponding to the high rate pyrolysis process to form pyrolysis products. Decomposition of the char finally occurs at a very low rate and carbon-rich biochar is formed (Suganya et al., 2016). Most of the traditional slow pyrolysis used fixed bed reactors where heating is provided by heated surface but there are studies that looked into alternative heating methods such as microwave heating (Du, 2013; Wan et al., 2009).

3.1.2. Microwave-assisted pyrolysis

Microwave-assisted pyrolysis is one of the most efficient thermochemical processes in the production of biochar, bio-oil and syngas and it has been successfully applied to plant residues such as wood and sewage sludge (Lei et al., 2011). Some of the advantages of microwave pyrolysis are high products yield, reduction of harmful chemical in bio-oil, energy and cost-saving. Microwave technology uses electromagnetic waves to cause oscillation of material molecules and to produce heat. The technical advantages of microwave-assisted pyrolysis over conventional pyrolysis are (1) uniform microwave heating that is applicable on larger biomass particles, (2) production of higher heating value syngas that can be used for in-situ electricity for microwave generation, (3) cleaner products due to no agitation and fluidization in the process, and (4) microwave heating is a mature technology with scale-up feasibility (Du, 2013). There are some differences between conventional slow pyrolysis and microwave-assisted pyrolysis in the formation of biochar product. Conventional pyrolysis used typical heating process, while microwave pyrolysis required some pre-treatment and catalysts prior to heating. Moreover, in conventional pyrolysis, the pyrolysis gas is the by-product, while bio-oil, hot water and non-condensable gases can be obtained after condensation of microwave pyrolysis. There are numerous studies on the pyrolysis of lignocellulosic biomass but reports on the production of algal biochar via microwave heating are limited (Wan et al., 2009). Biochar that undergoes further chemical or thermal processing after production can be transformed into activated carbon (Spokas et al., 2011). However, previous study mentioned that the decrease of functional groups in biochar due to the release of volatiles during pyrolysis would result in a challenge when using it as an adsorbent (Wang et al., 2015). Microwave-assisted pyrolysis can be used in future scale-up production from algal products into biochar for applications such as soil fertilizer due to its economic production process. Previous reports on the algal biochar production via the pyrolysis process are summarized in Table 1.

3.2. Torrefaction

Torrefaction is a thermochemical conversion process which is performed under atmospheric pressure at the temperature between 200 and 300 °C under an inert condition in the absence of oxygen (Chen et al., 2014a; Chen et al., 2015a). The process partly decomposes biomass and produces a solid product (called torrefied biomass or char) with high carbon content. A general sketch of torrefaction process in algal biochar production is shown in Fig. 2. Torrefaction is used for biofuel production from microalgae and its prime purpose is to produce biochar (Bach et al., 2017b). Torrefaction is an emerging thermal bio mass pre-treatment process able to remove volatiles through different decomposition reactions to reduce major limitations of biomass, upgrade biomass quality and alter the combustion behaviour (Nhuchhen et al., 2014). By altering the combustion behavior, fuel flexibility is enhanced by making a wide range of fuels efficiently applicable in a co-firing power plant. Torrefaction of microalgal biomass grown by using flue gas from the thermal power plant can be made suitable for co-firing in a pulverized coal power (Wu et al., 2012). The thermal pre-treatment of torrefaction can be divided into dry and wet torrefaction, which is also known as hydrothermal torrefaction or hydrothermal carbonization (Chen et al., 2015d; Yan et al., 2009). Hydrothermal carbonization is to be discussed in Section 3.3. Comparison of the characteristics of dry and wet torrefaction is shown in Table 2. The major advantage of wet torrefaction over dry torrefaction is its ability to produce energy-
dense product within a short residence time due to high heat transfer rate in the aqueous media (Coronella et al., 2012; Hoekman et al., 2013). In wet torrefaction, microalgae are treated under hot compressed water, producing a solid product that has high caloric value, better hydrophobicity, and lower ash content (Bach et al., 2017b). Torrefaction could produce biochar with high caloric value or higher heating value so it can be used as an alternative feedstock for clean energy production other than fossil fuel. The hydrophobicity of biochar originating from the surface functional groups and the lower ash content are important properties, determining its effectiveness in applying as an adsorbent for pollutants uptake from soil and water. Bach et al. (2017a) showed that, after wet torrefaction, at least 61.5% of energy in the microalgal biomass is retained. The caloric value intensified up to 21% and there is a decrease in the ash content of the microalgae.

<table>
<thead>
<tr>
<th>Types of process</th>
<th>Biomass feedstock</th>
<th>Temperature (°C)</th>
<th>Biochar production</th>
<th>References</th>
</tr>
</thead>
</table>
| Slow pyrolysis   | Chlorella-based algal residue | 300-700 | • 56.3% at 300 °C  
• 66.2% at 500 °C  
• 65.0% at 700 °C  
• High concentration of nitrogen and other inorganic elements | Chang et al. (2015) |
| Slow pyrolysis   | Brown Laminaria japonica macroalgae | 200-800 | • 78.34% at 200 °C  
• 63.64% at 400 °C  
• 37.96% at 600 °C  
• 27.05% at 800 °C | Jung et al. (2016) |
| Fixed-bed pyrolysis | Chlorella vulgaris | 300-900 | • 19.3–43.46% of biochar yield on different temperatures | Yuan et al. (2015) |
| Fixed-bed pyrolysis | Chlamydomonas reinhardtii | 350 | • Nitrogen-rich biochar  
• Largest fraction in term of mass, 44 ± 1% w/w mass yield of biochar | Torri et al. (2011) |
| Fixed-bed pyrolysis | Scenedesmus dimorphus | 300-600 | • Surface area of biochar increased from 1.72 to 123 m²/g when temperature increased from 300-500 °C, reduced to 89 m²/g at 600 °C  
• The recalcitrance of biochar increased from 0.62 to 0.76 with increasing temperature | Bordoloi et al. (2016) |
| Fixed-bed pyrolysis | Seaweed | 250-600 | • Biochar energy yield of 61.50% at 600 °C to 93.95% at 250 °C  
• 44 wt% yield at 400 °C  
• 40 wt% yield at 500 °C  
• 39 wt% yield at 600 °C | Tag et al. (2016) |
| Fixed-bed pyrolysis | Green macroalgae Cladophora glomerata | 400-600 | • 29–36% of biochar yield  
• Production of biochar with lower heating value due to higher ash content of 41–52% | Norouzi et al. (2016) |
| Fluidized-bed fast pyrolysis | Defatted Chlorella vulgaris | 500 | • 31% of biochar yield  
• Energy recovery of algal biomass in bio-oil and biochar is 94%  
• High inorganic biochar content | Wang et al. (2013) |
| Fluidized-bed pyrolysis | Laminaria digitata, Fucus serratus and mix macroalgae species from Black sea | 500 | • 29–36% of biochar yield  
• Production of biochar with lower heating value due to higher ash content of 41–52% | Yanik et al. (2013) |
| Stepwise and non-stepwise pyrolysis | Wastewater treatment high rate algal pond (WWT HRAP) biomass | 300-500 | • High amount of biochar with more than 50 wt% of the initial biomass was produced under both heating regimes  
• 54.8% of biochar yield | Mehrabadi et al. (2016) |
| Microwave pyrolysis | Macroalgae | 240-400 | • 54.8% of biochar yield | Shuttleworth et al. (2012) |

Table 1
The pyrolysis processes used for algal biochar production.

Table 2
Comparison of the characteristics of dry and wet torrefaction (Yan et al., 2009).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Torrefaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
</tr>
<tr>
<td>Temperature</td>
<td>200–300 °C</td>
</tr>
<tr>
<td>Media</td>
<td>Inert nitrogen gas</td>
</tr>
<tr>
<td>Pressure</td>
<td>Atmospheric pressure</td>
</tr>
<tr>
<td>Residence time</td>
<td>80 min</td>
</tr>
<tr>
<td>Cooling process</td>
<td>Flowing nitrogen; indirect water cooling</td>
</tr>
</tbody>
</table>
| Additional processes | – Filtration and evaporation | |}

Fig. 2. General torrefaction process for algal biochar production.
Torrefaction is usually carried out at a low temperature and short residence time under low heating rate to give a higher yield of solid product (Deng et al., 2009; Nhuchhen et al., 2014). Wu et al. (2012) reported that the solid yield decreased when the torrefaction temperature is increased. The effect of residence time on the mass yield of torrefied biomass at 300 °C shows the mass yield decreased with an increase in the residence time. The study concluded that temperature influenced the mass yield more than residence time. Chen et al. (2014b) shows the isothermal and non-isothermal torrefaction characteristics and kinetics of a macroalga *Scolopodium obliquum* CNW-N. Macroalgae are classified based on the torrefaction temperature, light, mild and severe torrefaction from the maximum decomposition rate and weight loss. Non-isothermal torrefaction required intense pre-treatment than the isothermal torrefaction. Pre-treatment severity is intensified by the increasing of heating rate in non-isothermal torrefaction. Uemura et al. (2015) reported the yields of solid, liquid and gas for a series of torrefaction temperature on a macroalga *Laminaria japonica*. The solid yield decreased when the torrefaction temperature was increased. The decrease in solid yield may be attributed to the decomposition of two major components, alginate and mannotel in *L. japonica*. However, both the liquid and gas yields increased when the temperature was increased in conjunction with a decrease of solid yield with torrefaction temperature. (Bach et al., 2017a) mentioned that the solid yield decreased with an increase in temperature and residence time. The solid yield decreased from 61.68% to 52.58% when the temperature was increased from 160 °C to 180 °C. The solid yield decreased from 62.92% to 51.84% when the residence time increased from 5 min to 30 min. Chen et al. (2016) showed that the solid yield of 51.3–93.9% in the torrefied macroalgae residue at the temperature ranged from 200 to 300 °C with a residence time of 15–60 min. Previous study also shows the solid yield of 50.8–95.7% in macroalgae *Chlamydomonas* sp. JSC4 residue after torrefaction at temperature 200–300 °C for 15–60 min. It is recommended that torrefaction of macroalgae residue should be carried out at an optimum temperature of 250 °C or below for less weight loss and higher energy densification (Chen, 2015). The impact of torrefaction upon biomass properties has been extensively investigated in the last decade. However, there is limited literature on the study of algal biochar from torrefaction process. As torrified algal biomass is a high quality and environmental friendly solid product that may offer considerable opportunities for worldwide greenhouse gas mitigation, future research on this area is suggested.

### 3.3. Hydrothermal carbonization

Hydrothermal carbonization (HTC) is a new thermochemical technique that has gained more attention in the recent years due to its environmental friendly and cost effectiveness (Erlach et al., 2012; Xiao et al., 2012). HTC is a distinctive process that involves the conversion of carbohydrate components of biomass into carbon-rich solids in water where biochar is produced at lower temperatures (180–260 °C) and elevated water or steam pressures (Libra et al., 2011; Titirici et al., 2012). The process takes place in water under a self-generated pressures being less than 10 bar with water as solvent (Titirici et al., 2012). This process can be suitable for concentrating carbon of wet biomass where no drying is required prior to pyrolysis, making it a potential alternative for treatment of some waste streams (Brownsort, 2009). Char produced from hydrothermal carbonization is called hydrochar (Libra et al., 2011). HTC produce a higher product in a shorter period of time and requires lower energy expense than conventional carbonization process (Tekin et al., 2014). The advantages of the HTC process include (1) required only low carbonization temperature, (2) can be synthesized in the aqueous phase, (3) inexpensive process, (4) renewable materials can be used as sources such as biomass and for the use of value-added chemicals, such as nanoparticles in the structure (Kubo, 2013). Char product obtained from HTC has the following properties: uniform spherical particles; controlled porosity; functional surfaces (e.g., —OH, —C=O, —COOH); easily controlled surface chemistry and electronic properties (Titirici et al., 2012).

In a hydrothermal process, biomass can be converted into valuable products such as biochar, bio-oil and gaseous products by manipulating process variables such as temperature, time of reaction, feedstock, the presence of catalysts and pressure (Tekin et al., 2014). Temperature is the most influential variable in the HTC process followed by residence time and the types of feedstock (Nizamuddin et al., 2017). Lower temperature tends to give a higher yield of solid product compared to higher temperatures by affecting its physical and chemical characteristics. At a higher temperature, the carbon content is higher whereas the hydrogen and oxygen contents are lower. This results in a formation of biochar with greater higher heating value (HHV). Char produced from HTC of macroalgae has a unique composition and with bituminous coal quality (Heilmann et al., 2010). Process conditions were under a lower temperature of 200 °C with 0.5 h of reaction time for effective carbonization and production of algal char. The brief reaction time in the batch process suggested the development of a continuous process for HTC processing of algae. There are no specific catalytic agents that significantly enhanced the carbonization process and/or increase the yield of biochar. The most conceivable alternative pathway proposed in the study was carbonization via a dehydration route. Previous literature of algal hydrochar production in HTC is shown in Table 3. As there is very limited literature on algal char production from the HTC process, it would be an interesting topic for future studies. HTC process offers the advantages of lowering the production cost and shortening the time needed for the production of biochar. This can be achieved by utilizing algal biomass residue and converting it into more valuable biofuels and other products. HTC represents a feasible alternative way to convert wet biomass into biochar by omitting the drying process.

### Table 3

| Algal hydrochar production using hydrothermal carbonization (HTC). |
|-----------------|-----------------|-----------------|-----------------|
| **Biomass feedstock** | **Temperature (°C)** | **Reaction time** | **Solid mass yield (%)** | **References** |
| **Microalgae** | | | | |
| *Dunaliella salina* | 190–210 | 30–120 min | 25.3–45.7 | Heilmann et al. (2010) |
| *Arthrobotrys platensis* | 190–210 | 2–4 h | 21.6–36.7 | Yao et al. (2016) |
| *Nannochloropsis* sp. | 180–220 | 15–30 min | 30–47 | Lu et al. (2014) |
| *Nannochloropsis* oculata | 180–215 | 15–45 min | 41–51 | Levine et al. (2013) |
| Whole *Spirulina* | 175–215 | 30 min | 23.3–49.3 | Broch et al. (2014) |
| Lipid extracted *Spirulina* | 175 | 30 min | 44.6 | Broch et al. (2014) |
| **Macroalgae** | | | | |
| *Sargassum horneri* | 180–210 | 2–16 h | 32.7–52.3 | Xu et al. (2013) |
| *Laminaria digitata* | 200–250 | 1 h | 18.4–21.8 | Smith and Ross (2016) |
| *Laminaria hyperborea* | 200–250 | 1 h | 23.6–39.0 | Smith and Ross (2016) |
| *Aralia esculenta* | 200–250 | 1 h | 23.7–30.0 | Smith and Ross (2016) |
4. Algal biochar characterization

Characterization of the physical and chemical properties of algal biochar is of great importance in determining their potential applications. The physical and chemical properties of biochar produced from both microalgae and macroalgae are discussed as follows.

4.1. Physical properties of algal biochar

4.1.1. Biochar yield

Previous studies have demonstrated that algal samples could yield relatively high amounts of biochar per unit biomass. However, comparative analysis of biochar derived from microalgae and macroalgae in terms of their yields under similar experimental conditions is still lacking. As shown in Table 4, the yield of biochar derived from micro- and macroalgae (on a dry weight basis) ranged from 20.0 to 63.0% and 21.4–23.0 MJ/kg, respectively. There are attempts to investigate the factors which affect the yield of algal biochar. Ronsse et al. (2013), for instance, reported that the yield of algal biochar is lower than that of lignocellulosic biochars, which has been reported to exceed 30–40% (Boakye et al., 2016). In general, the HHV of algal biochars is lower than that of lignocellulosic biochars. The HHV of algal biochars is lower than that of lignocellulosic biochars (which has been reported to exceed 28.0–33.5 MJ/kg) and macroalgae (5.2–61.8 MJ/kg) have comparable HHV. In general, the HHV of algal biochars is lower than that of lignocellulosic biochars (which has been reported to exceed 30–40 MJ/kg) and macroalgae (5.2–61.8 MJ/kg) have comparable HHV.

4.1.2. Higher heating value

The higher heating value (HHV) is the amount of heat released when the sample (fuel) is combusted and the products have returned to a temperature of 25 °C. It is typically measured using a bomb calorimeter in the laboratory. As shown in Table 4, biochars derived from microalgae (7.6–23.0 MJ/kg) and macroalgae (5.2–21.2 MJ/kg) have comparable HHV. In general, the HHV of algal biochars is lower than that of lignocellulosic biochars (which has been reported to exceed 30 MJ/kg), is likely attributed to a lower carbon content but higher ash content in algal biomass.

4.1.3. Surface properties

The physical properties of biochars, such as their surface area, porosity, and pore volume, are routinely analyzed. The Brunauer-Emmett-Teller (BET) surface area of biochar can be estimated using a surface area analyzer while a scanning electron microscope (SEM) can be used to profile the surface topography and particle structure. The surface area of algal biochar is generally low but some studies reported that an increase in the pyrolysis temperature could result in a higher surface area. For example, at 350 °C, the BET surface area of K. sp. was 13.9 m²/g, and at 500 °C, the BET surface area of the same sample was 23.0 m²/g. The higher heating value (HHV) is the amount of heat released when the sample (fuel) is combusted and the products have returned to a temperature of 25 °C. It is typically measured using a bomb calorimeter in the laboratory. As shown in Table 4, biochars derived from microalgae (7.6–23.0 MJ/kg) and macroalgae (5.2–21.2 MJ/kg) have comparable HHV. In general, the HHV of algal biochars is lower than that of lignocellulosic biochars (which has been reported to exceed 30 MJ/kg), is likely attributed to a lower carbon content but higher ash content in algal biomass.
the resulting biochar. Wang et al. (2013) reported that the surface area of biochar derived from C. vulgaris (2.4 m$^2$/g) was deemed to be low relative to biochar obtained from lignocellulosic biomass. Working with biochar derived from macroalgae, Roberts et al. (2015b) reported that biochar produced from the macroalgae Eucheuma sp. has a significantly higher surface area (30.03–34.82 m$^2$/g) than those of other species which ranged from 1.29 to 8.87 m$^2$/g.

Findings thus far have indicated that biochar derived from algal samples has distinct structure and characteristics when compared with the biomass before subjected to pyrolysis. For instance, Wang et al. (2013) observed that the particles of biochar derived from a green microalga, Chlorella vulgaris, are compact and irregular, and these are different from the structure of the feedstock before pyrolysis. Similar results were also reported for the biochar derived from Chlamydomonas reinhardtii (Torril et al. 2011). These observations are in contrast with biochars from lignocellulosic biomass, which normally retain their feedstock’s structure. Table 4 summarizes the physical properties of biochars derived from several microalgae and macroalgae species.

4.2. Chemical properties of algal biochar

4.2.1. Proximate and ultimate analysis

In proximate analysis, the moisture, volatile matter, ash, and fixed carbon content of the samples are measured. Ultimate analysis (also termed as elemental analysis), on the other hand, includes the determination of carbon, hydrogen, nitrogen, sulphur, and oxygen within the samples. As shown in Table 5, algal biochars are typically low in C but high in N and minerals (ash) contents. The low C content, in comparison to those derived from lignocellulosic biomass, is the characteristic of biochars produced from micro- and macroalgae.

4.2.2. Inorganic elemental analysis

Inorganic mineral content of algal biochar is typically determined using the inductively coupled plasma atomic emission spectrometry (ICP-AES). Previous work has provided insights into the abundance of various inorganic elements in algal biochar and enables comparison with biochar derived from other feedstock. For example, Wang et al. (2013) reported that biochar derived from C. vulgaris contained higher concentrations of various trace elements, including P, K, Mg and Ca, compared to biochar from lignocellulosic biomass. In a separate study, biochars produced from both red and brown seaweeds have high concentrations of N (0.3–2.8%), P (0.5–6.6 g/kg), and K (5.1–119 g/kg) (Roberts et al., 2015b). Results from both studies, when taken together, seem to suggest that algal biochar has good prospects as fertilizers in view of their mineral contents.

4.2.3. pH

As shown in Table 5, all algal biochar was found to be alkaline. The pH of biochar derived from macroalgae ranges from 7.6 to 13.7, whereas little information is available regarding those derived from microalgae. The pH of biochar is found to be affected by the pyrolysis temperature and the algal samples. According to the study by Ronssse et al. (2013), the pH of biochar is correlated to the presence of oxygen functionalities in the biochar. Tag et al. (2016) noted that the pH of algal biochar (8.7–13.7) increased with an increase in the pyrolysis temperature (250–600 °C). A plausible explanation is the increase in the relative ash content in the biochar caused a rise in the pH of the biochar especially under severe pyrolysis conditions (Ronssse et al., 2013)

4.2.4. Cation exchange capacity

The cation exchange capacity (CEC) of biochar is a measure of the ability of biochar to adsorb cation nutrients. In other words, a biochar with high CEC exerts beneficial effect by preventing nutrient leaching in the soil. Roberts et al. (2015b) showed that seaweed biochar samples have negligible or no exchangeable Al, but have high levels of the remaining exchangeable cations such as Ca, K, Mg and Na. In another study by Tag et al. (2016), algal biochar produced at different pyrolysis temperature was found to have higher CEC (25.6–52.6 cmol/kg) than that produced from vine pruning (32.2–61.0 cmol/kg) and orange pomace (25.6–52.6 cmol/kg) under similar experimental conditions. As CEC correlated with the ash content, it was suggested that the alkali and earth alkali metals in biomass promoted the formation of O-containing surface functional groups in the resulting biochar (Cely et al., 2015).

4.2.5. Functional groups

Fourier transform infrared spectroscopy (FTIR) spectral analysis is used to identify the various functional groups in algal biochar. This technique can be used to compare the chemical profiles of biochar produced under different conditions, as well as between the raw biomass and the resulting biochar. The latter is exemplified by the work of Biswas et al. (2017) whereby FT-IR spectra demonstrated that, following hydrothermal liquefaction, the macromolecular crystal structure of the algae was disrupted and products (biochar and bio-oil) were formed. Table 5 summarizes the chemical properties of biochar derived from some microalgae and macroalgae species.

4.3. Factors affecting the properties of algal biochar

In general, the method and temperature of pyrolysis are two important factors that determine the physical and chemical properties of biochar (Jindo et al., 2014; Mukome et al., 2013). The operating conditions such as heating rate, reaction vessel, chemical activation, residence time, and highest treatment temperature (HTT) also influence the properties of biochar produced. The HTT is regarded to have the greatest effect on the physical properties of biochar produced (Mukome et al., 2013). In a recent study, Palanisamy et al. (2017) reported that biochar of C. vulgaris prepared at higher temperatures (450–600 °C) contained a higher proportion of organic matter (C, H and N) than those produced at lower temperatures.

In addition, the type of feedstock used may affect the chemical composition of the resulting biochar, such as the ash content, pH, H/C ratio, surface area, as well as cation and anion exchange capacities (Sun et al., 2014; Tag et al., 2016). These factors are of great importance when comes to the applications of biochar, particularly in the agriculture sector. In a comparative analysis in the properties of biochar produced by algae, grass, manure, wood, pomace, and nutshell, it was found that feedstock is a better predictor of variation in the ash content and C/N ratio of biochar than pyrolysis temperature (Mukome et al., 2013). However, when one feedstock is being considered, pyrolysis temperature is the best predictor for the surface area.

In terms of biochar production from algal species, the proportion and composition of nutrients of algal-derived biochar is likely influenced by a number of abiotic and biotic factors like species, habitat (e.g. fresh, brackish or saline environment), and other factors. It is evidenced by the findings of a number of researchers. Dealing with seaweed biochars, Roberts et al. (2015b) found that biochars produced from red and brown seaweeds have different elemental composition with biochars from red seaweeds have higher concentrations of S and K and lower concentrations of C and H than biochars produced from the brown seaweeds. There are also variations in most physicochemical characteristics of the biochar between species collected from different locations especially the cation exchange capacity of the biochars. For instance, the exchangeable K in Undaria sp. (13–420 cmol/kg) and Kappaphycus sp. (26–210 cmol/kg) differed by an order of magnitude depending on the location. Bird et al. (2012) also noted a difference in the yield and ash content of the Chadophora vagabunda with their earlier work (Bird et al., 2011). These may be attributed to moving to pilot scale production with commercial pyrolysis equipment rather than controlled laboratory production, purity of the materials collected in the field, and lesser control over pyrolysis conditions.
### 4.4. Comparison of algal biochar with biochars derived from different feedstocks

It is generally accepted that the first critical step in determining the utility and applications of algal biochar is the quantification of the properties of algal biochar and a comparison with biochar produced from other commonly used terrestrial biomass feedstocks (Bird et al., 2011). Studies thus far have pointed to the fact that biochars produced from algal samples are fundamentally different from those produced from lignocellulosic feedstock (Bird et al., 2012; Maddi et al., 2011). In general, biochars produced from various algal species tend to have low carbon content, surface area and cation exchange capacity but high in pH, nitrogen, and extractable inorganic nutrients including P, K, Ca and Mg. In contrast, lignocellulosic materials-derived biochars tend to have higher carbon contents and cation exchange capacities with pH values usually lower than 7, and significantly lower ash and available nutrient contents (Jindo et al., 2014).

The difference in the chemical profiles between algal and other lignocellulosic biochar gives important implications in their applications. The algal biochar is likely to provide significant direct nutrient benefits to soils and crop productivity, and are likely to be particularly useful for application on acidic soils. However, they are volumetrically less able to provide the carbon sequestration benefits that can be provided with the high-carbon-content lignocellulosic biochars. Therefore, Roberts et al. (2015b) proposed that a blending of seaweed and lignocellulosic biochars could provide a soil ameliorant that combines a high fixed C content with a mineral-rich substrate to enhance crop productivity.

### 5. Future challenges and opportunities

Algal biochar could influence the global carbon sequestration on mitigation of climate change from the production of energy to the applications in environmental management. In particular, the use of algal biochar as biosorbents in wastewater treatment should be studied further. Nevertheless, it is important to take note of some of the challenges...
that may lie ahead, such as cost effectiveness of the process and the fact that wastewater contains various impurities that may interfere with the process. In addition, production of algal biochar via the existing methods could be further enhanced with microwave-assisted technology, whereas the additional energy consumption associated with the microwave-assisted process should be well considered and minimized. Microwave-assisted technology in the production of algal biochar is indeed a promising approach that deserves more attention in the future. Furthermore, optimization of algal biochar productivity can also be achieved by employing a continuous process.

In terms of the algal biomass to be used for biochar production, microalgae seem to be a more promising feedstock when compared to macroalgae, in view of their advantages over the latter, such as their rapid growth and the ease of cultivation and harvesting. Macroalgae, on the other hand, require a larger area for cultivation and generally require a longer period of cultivation time. The quality and quantity of macroalgal biochar are also greatly dependent on varieties of abiotic and biotic factors. Moreover, microalgae are deemed to have higher potential in biochar production due to their high nutrient contents which are suitable for the use in agriculture. The recycling of microalgal residue after biofuel production for a biofinery concept is also feasible. Taken together, future research on different aspects pertaining to microalgal biochar, such as production methods and newer applications, is highly recommended in view of the scarcity of information on these aspects.

6. Conclusions

Algal biomass as a third generation feedstock can be utilized in biochar production in the context of biofinery. Pyrolysis, torrefaction or hydrothermal carbonization are suitable processes to produce algal biochar of different composition and properties for varying further applications. Microwave-assisted technology could be an interesting approach in enhancing the current biochar production technologies. Characterization of algal biochar is important for the understanding of their chemical and physical properties, which are useful for determining their potential applications (such as fertilizer for agricultural purpose or adsorbent for water treatment). Development of algal biochar technologies is expected to contribute to a more sustainable environment in the future.

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References


