



Co-pyrolysis of lignocellulosic and macroalgae biomasses for the production of biochar – A review

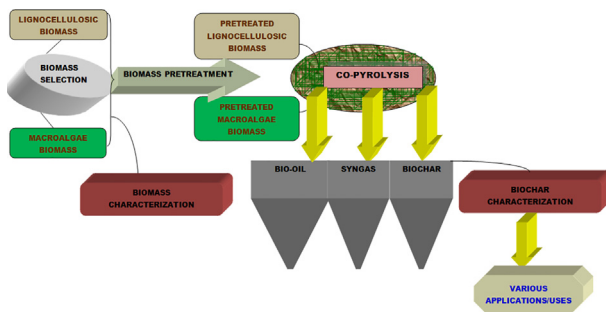
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GRAPHICAL ABSTRACT



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ABSTRACT

Biochar properties are significantly influenced and controlled by biomass feedstock type and pyrolysis operating conditions, and the development of multiple biochar properties for various applications has necessitated the need for blending different feedstocks together. Co-pyrolysis as a potential technology has been proposed to improve the overall performance of biomass pyrolysis and has proved effective in improving biochar properties. Consequently, the combination of lignocellulosic and macroalgae biomasses has been targeted for biochar production and improvement of biochar properties through co-pyrolysis. This paper therefore presents a critical review of biochar production from co-pyrolysis of lignocellulosic and macroalgae biomass (CLMB). It discusses the biomass feedstock selection, characterization, pre-processing and suitability for thermal processing; and analyzes biochar production, characterization and reactor technologies for CLMB. Furthermore, the potential and economic viability of biochar production system from CLMB are highlighted; and finally, the current state and future directions of biochar production from CLMB are extensively discussed.

1. Introduction

Rapid growth in population and industrialization has led to a progressive rise in energy demand, and energy sources development has not been able to meet up with the increasing energy consumption. Over-reliance on fossil fuels, increase in prices, reduced availability,

stringent governmental regulations on exhaust emissions and the quest for a cleaner environment have birthed the adoption of alternative energy sources (Ajav et al., 1999). Conventional energy sources such as coal, oil and natural gas have been the major supply of world energy. However, with the looming predicted future depletion of these conventional energy sources, the use of alternative energy sources has

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become crucial for the sustainability and development of the world's economy, and for the sustainability of the environment in terms of stable energy.

The quest for alternative energy sources has led to the utilization of biomass for energy production. Biomass, an alternative energy source supplies 14% of the world annual energy consumption and is the fourth largest energy system after the conventional energy sources (Xu et al., 2019a). Current research interests on the reduction of green house gases (GHGs) emission through carbon sequestration and the improvement of food production through biochar application in the soil, concomitantly, have furthermore stemmed worldwide interest in the utilization of biomass for sustainable energy production and eco-friendly environment (Kambo and Dutta, 2015).

Biomass can be utilized for energy production via several conversion methods which can be biological (anaerobic digestion and fermentation) or thermochemical (direct combustion, gasification, pyrolysis, liquefaction). However, thermochemical biomass conversion are generally preferred to biological conversion, because of the advantages of short reaction times and high conversion efficiency (Liu et al., 2013). Amongst the various thermochemical methods, pyrolysis has been particularly identified as a viable method which produces energy with high fuel-to-feed ratios (Demirbaş, 2002). Biomass pyrolysis produces a combination of pyrolytic oil (bio-oil), synthesis gas with differing energy values (syngas), and solid product referred to as biochar, with all of these products having promising economic benefits.

Biochar is a carbon-rich solid which is obtained via the reductive thermal processing and/or pyrolysis of biomass feedstocks from various sources (Ahmad et al., 2014). It is a porous carbonaceous solid substance which possesses great aromatization and anti-decomposition characteristics (Wang et al., 2017a); and has energy content which is dependent on the carbon residue in the char (Callegari and Capodaglio, 2018). It is basically produced by slow pyrolysis, characterized by lower temperature, lower heating rate and longer residence time.

Conventional pyrolysis is a relatively simple way for biochar production; however, a single biomass feedstock approach is not promising for the development of multiple properties of biochar used in various applications (Table 1). This has led to the development of co-pyrolysis technology which entails the thermal degradation of a mixture of two or more biomass feedstocks through the generation of synergistic effects between them, achieved through radical interactions during the reaction. Generally, biochar properties such as mineral content, organic carbon, pore structural and surface functional group characteristics are

significantly influenced and controlled by the biomass feedstock type and pyrolysis operating conditions (Dhyani and Bhaskar, 2018; Jafri et al., 2018). Different biomass feedstocks are characterized by different chemical and physical properties; and these varied properties can change the reactivity and thermal characteristics of the samples and products formed, while the generation of synergistic interaction during co-pyrolysis could then result in improved pyrolysis products. Co-pyrolysis as a potential technology has been proposed to improve the overall performance of biomass pyrolysis by adding other biomass feedstocks, and this technology has been shown to effectively improve the properties of biochar (Kambo and Dutta, 2015). In addition, co-pyrolysis technique is mostly employed as an efficient upgrading method for bio-oil production, with biochar as a value-added by-product (Uzoejinwa et al., 2018).

Biochars are obtained from biomasses, which are the principal raw material source, and can either be lignocellulosic or non-lignocellulosic biomasses. Plant and animal bioresources such as agro-industrial residues, forest-industrial residues, energy crops, and municipal solid waste constitute lignocellulosic biomasses. Plant biomass accounts for half of the overall lignocellulosic biomass, and the annual output of terrestrial plants globally is about $1.7\text{--}2.0 \times 10^{11}$ tons (Li et al., 2019); therefore, it has been the most utilized biomass source. Sewage sludge, manure, and algae constitute the non-lignocellulosic biomass. Of recent, the use of aquatic biomass (microalgae and macroalgae) is gradually gaining widespread interest universally, especially in regions with sizeable water bodies. They are regarded as promising feedstock for bioenergy production because of their high energy density, fast growth rate, high photosynthetic capability, CO₂ sequestration rate, high oil content, strong adaptability, high potential in greenhouse gas emissions reduction and lack of competition with lands for food (Xu et al., 2019b; Yuan et al., 2019). However, the use of macroalgae has been more favoured because of the huge cost of harvesting microalgae, due to its small biomass concentration and minute cell size (Hu et al., 2013). Considering these, the combination of lignocellulosic and macroalgae biomasses has been targeted for biochar production and improvement of biochar properties through co-pyrolysis.

There have been several reports on biochar production from the pyrolysis of different biomasses such as bioenergy crops (Brewer et al., 2009), forest residues (McKendry, 2002), aquatic biomass (Ahmed et al., 2019), animal waste (Cao and Harris, 2010), agricultural waste (Colantoni et al., 2016), and sewage sludge (Agrafioti et al., 2013), but only few reports have focused on biochar production from co-pyrolysis

Table 1
Various biochar applications and utilizations.

Application	Purpose
Agriculture	Carbon fertilizer, compost, substitute for peat in potting soil, plant protection, compensatory fertilizer for trace elements. Silage agent, feed additive/supplement, litter additive, slurry treatment, manure composting, water treatment in fish farming. Modifier for several soil properties such as bulk density, water holding capacity, pH, soil aggregation, nutrient availability, and organic carbon availability, improvement of soil fertility, soil moisture retention. Soil additive for soil remediation, soil substrates, treating pond and lake water.
Waste water treatment	Active carbon filter, pre-rinsing additive, soil substrate for organic plant beds and composting toilets. Bio-adsorbent in water treatment to remediate organic/inorganic contaminants due to its abundance of organic functional groups and inorganic minerals. Bio-adsorbent for effective removal of heavy metals, organic chemicals, and microbial contaminants from the aqueous system.
Drinking water treatment	Micro-filters and macro-filters
Building industry	Insulation, air decontamination, decontamination of earth foundations, humidity regulation, protection against electromagnetic radiation ("electromog")
Electrochemical energy storage	Semiconductors, supercapacitor, battery, electrode material or template.
Biogas production	Biomass additive, biogas slurry treatment
Power generation	Pellets, lignite substitute, fuel for power and heat generation
Medicine	Detoxification, carrier for active pharmaceutical ingredients
Industrial materials	Carbon fibres, catalysts and plastics
Metallurgy	Metal reduction
Exhaust filters	Emissions control and room air filters
Cosmetics	Soaps, skin-cream and therapeutic bath additives
Paints and colouring	Food colourants, industrial paints

Adapted from Schmidt and Wilson (2012) with modifications.

of biomasses (Huang et al., 2017; Zhu et al., 2019). Furthermore, while the co-pyrolysis of lignocellulosic biomass with feedstocks like synthetic polymers/plastics (Navarro et al., 2018), tyres (Shah et al., 2019), coal (Wu et al., 2019), sewage and sludge (Wang et al., 2019b) have been extensively utilized, only few works have focused on biochar production from the co-pyrolysis of lignocellulosic and macroalgae biomass (Wang et al., 2018c; Xu et al., 2019b). In addition, several techniques of biochar production processes have been extensively reviewed such as torrefaction, pyrolysis, gasification, microwave heating and hydrothermal processing (Tripathi et al., 2016; Zhang et al., 2019); and while there have been reviews on biochar production from the individual pyrolysis of lignocellulosic biomass (Chemerys and Baltrėnaitė, 2018; Rangabhashiyam and Balasubramanian, 2019) and macroalgae biomass (Yu et al., 2017), there is no review on the biochar obtained from the co-pyrolysis of lignocellulosic and macroalgae biomass (CLMB), which has caught the attention of these authors. Hence, this paper presents a comprehensive and critical review of biochar production from CLMB. It discusses the biomass feedstock selection, characterization, pre-processing and suitability for thermal processing; and analyzes biochar production, characterization and reactor technologies for CLMB. Furthermore, the potential and economic viability of biochar production system from CLMB are highlighted; and finally, the current state and future directions of biochar production from CLMB are extensively discussed.

2. Biomass feedstock selection

Amongst the most important criteria for sustainable biomass feedstock selection for biochar production are abundance of feedstock, ready availability and low cost (Jang and Kan, 2019). The choices of lignocellulosic and macroalgae biomasses have been established in Section 1; therefore, this review focuses on the potential of lignocellulosic and macroalgae biomasses as co-feedstocks in co-pyrolysis for biochar production.

2.1. Biomass feedstock characterization

The distinct chemical and physical properties of biomass feedstocks for biochar production are vital during thermal conversion processes; therefore, biomass feedstock characterization is very important before the co-pyrolysis process. The characterization entails proximate and ultimate analyses measurement. The proximate analysis involves the determination of the compound contained in the sample which include percentage moisture content, ash content, fixed carbon and volatiles, while the ultimate analysis involves the determination of the elements contained in the sample which include percentage of carbon, hydrogen, oxygen, nitrogen, sulphur and their associated ratios (H/C, O/C). Depending upon the species, biomass type, growing conditions, and geographical location, some other elements might be present in the biomass such as potassium, magnesium and chlorine (Tripathi et al., 2016). The hydrogen to carbon effective ratio (H/C_{eff}) is the most important factor which limits biomass conversion to high grade fuels or chemicals (Rezaei et al., 2014). Also, high oxygen content in biomass reduces the number of C–H bonds, heating value, energy density and thermal stability (Bach and Skreiberg, 2016; Dai et al., 2019). Table 2 shows the proximate and ultimate analyses of selected lignocellulosic and macroalgae biomasses. Comparatively, it was observed that in most cases, lignocellulosic biomasses have higher carbon, hydrogen, and oxygen values; and lower nitrogen and sulphur values than the macroalgae biomasses. Also, the higher heating value (HHV) of the lignocellulosic biomasses is comparatively observed to be significantly higher than that of the macroalgae biomasses. This is due to the presence of higher ash content in the macroalgae biomass (Ross et al., 2008). The amount of carbon and hydrogen directly influence HHV, while nitrogen and oxygen contents have an inverse relationship with HHV. Besides the biomass specie type, seasonal variation could

significantly affect the various chemical compositions (Ross et al., 2008).

In addition to the aforementioned proximate and ultimate analyses components, the main components of macroalgae biomass are proteins, carbohydrates and lipids, while the main components of lignocellulosic biomass are lignin, cellulose and hemicellulose (Wang et al., 2018b). The synergistic interaction of these components influence the characteristics of co-pyrolysis products produced. Wang et al. (2018a) established that product distributions were similar between different biomass feedstocks, but varied significantly during co-pyrolysis. According to Xu et al. (2019b), as the organic matter of the biomass composition converts into gas volatiles, the elements on the surface of biochar change during the release of the gas volatiles. In addition, since pyrolysis of biomass feedstocks usually occurs in the pores of the biomass particles, the synergistic reaction causes significant changes in the structures of the pores in the biochar particles. These changes in pore structure consequently affect the progress of the reaction. The diverse thermal degradation behaviour is caused by the variations found in the structure and chemical property of the feedstocks that are associated with their specific components. For lignocellulosic biomass, hemicellulose degradation mainly occurs at 220–315 °C, while the degradation of cellulose occurs at 315 to 400 °C. Because of the complex structure of lignin, it has a slow pyrolysis rate and a wide pyrolysis temperature range between 160 and 900 °C (Yang et al., 2007). For macroalgae biomass, dehydration stage occurs within the temperature range between ambient and 200 °C, followed by devolatilization stage within the temperature range of 200–600 °C, and the decomposition of carbonaceous solid residues which proceeds after 500 °C, but becomes intense beyond 600 °C (Hu et al., 2013; Uzojinwa et al., 2018). The normal pyrolysis of macroalgae biomass is exothermic (Li et al., 2012), while the cellulose pyrolysis of lignocellulosic biomass is endothermic, and hemicellulose and lignin pyrolysis are exothermic (Collard and Blin, 2014). For their interaction, many researchers have observed synergistic effects during co-pyrolysis process (Uzojinwa et al., 2019; Wang et al., 2015), and according to Onay and Kockar (2003), the blending feedstock types influence the synergistic effects significantly. Even though many macroscopic kinetic models with comprehensive mechanism schemes have been developed, such as distributed activation energy model (DAEM), isoconversional method, detailed lumped kinetic model, kinetic Monte Carlo model (Wang et al., 2017b; White et al., 2011), the detailed mechanism of this synergistic effects is still unclear as contended by some authors; and is under critical investigation due to the complicated interactions between different feedstocks and the varying operating conditions (Abnisa and Daud, 2014; Wang et al., 2018a).

2.2. Biomass feedstock pre-processing and suitability for thermal processing

Biochar production is dependent on several key factors, amongst which is the pre-treatment of biomass feedstock, such as the extent of processing parameters (principally the reaction temperature and reaction time), pre-processing and post-processing requirements like drying, cooling, sizing, shaping, and condensation amongst others (Mosier et al., 2005). The technologies for biomass pretreatment prior to pyrolysis can be categorized as physical (grinding/milling, densification, extrusion), chemical (acid, alkali and ionic liquid pretreatments, hydrothermal pretreatment, steam explosion, ammonia fiber expansion), thermal (drying, torrefaction, steam explosion/liquid hot water pretreatment and ultrasound/microwave irradiation) and biological (fungal, microbial consortium and enzymatic pretreatments). A combination of two or more of these pretreatment methods can also be employed. These biomass pretreatment technologies have been extensively reviewed (Dhyani and Bhaskar, 2018; Kan et al., 2016; Wang et al., 2017b).

A basic knowledge of the different pretreatment methods facilitates matching the best pretreatment method/combination for a specific

Table 2
Compositional characteristics and ultimate analysis of selected lignocellulosic and macroalgae biomasses.

	MS (%)	AC (%)	VM (%)	FC (%)	C (%)	H (%)	O (%)	N (%)	S (%)	HHV (MJ/kg)	Refs.
Lignocellulosic Biomass											
Almond shell	8.70	2.30	79.70	4.90	54.70	7.50	37.40	0.30	0.30	20.20	Caballero et al. (1997)
Barley straw	2.69	4.38	75.64	17.28	44.83	6.25	42.43	0.93	1.18	17.95	Aqsha et al. (2017)
Banana waste	7.80	11.4	78.20	15.6	43.50	6.20	42.30	0.86	0.95	17.10	Sellin et al. (2016)
Corn stover	7.69	3.85	82.44	6.02	44.92	5.77	41.00	0.98	0.21	16.82	Cong et al. (2018)
Flax straw	4.75	1.12	74.80	19.32	46.76	6.34	43.53	1.11	1.14	18.62	Aqsha et al. (2017)
Rapeseed cake	1.50	4.90	75.50	18.10	55.00	7.80	31.10	4.70	1.40	25.40	Smets et al. (2011)
Rice husk	10.60	11.41	61.99	16.00	40.20	4.68	31.77	1.20	0.14	15.38	Yuan et al. (2019)
Sugarcane bagasse	5.40	3.10	80.20	11.30	44.86	5.87	48.97	0.24	0.06	18.00	Varma and Mondal (2017)
Walnut shell	5.43	5.00	74.00	15.57	45.32	5.54	46.17	1.12	1.81	16.68	Yildiz and Ceylan (2018)
Wheat straw	9.10	5.10	3.70	3.70	44.87	5.74	43.69	0.36	0.24	17.66	Lazdovica et al. (2017)
Macroalgae Biomass											
<i>Chorda filum</i>	13.1	9.90	52.2	24.90	39.14	4.69	37.23	1.42	1.62	15.55	Ross et al. (2008)
<i>Enteromorpha clathrata</i>	6.80	28.56	53.95	10.69	29.42	3.96	21.76	7.05	2.45	12.10	Yuan et al. (2019)
<i>Fucus serratus</i>	11.4	18.60	45.50	24.20	33.50	4.78	34.44	2.39	1.31	16.66	Ross et al. (2008)
<i>Fucus vesiculosus</i>	12.3	11.80	51.40	23.80	32.88	4.77	35.63	2.53	2.44	15.00	Ross et al. (2008)
<i>Laminaria digitata</i>	13.7	10.00	53.40	25.30	31.59	4.85	34.16	0.90	2.44	17.60	Ross et al. (2008)
<i>Laminaria japonica</i>	7.65	28.28	53.10	10.97	30.60	4.89	62.44	1.51	0.56	6.41	Bae et al. (2011)
<i>Macrocystis pyrifera</i>	8.00	18.50	42.40	33.40	27.30	4.08	34.80	2.03	1.89	16.00	Ross et al. (2008)
<i>Porphyra tenera</i>	6.41	10.44	69.66	13.49	40.60	4.65	47.40	6.13	1.26	12.29	Bae et al. (2011)
<i>Sargassum natans</i>	10.46	29.09	48.85	11.60	25.90	5.57	24.18	3.58	1.22	8.68	Wang et al. (2013)
<i>Undaria pinnatifida</i>	9.50	25.84	53.62	11.04	34.01	4.99	56.95	3.34	0.71	7.68	Bae et al. (2011)

MS– Moisture, AC– Ash content, VM– Volatile matter, FC– Fixed carbon, HHV– Higher heating value.

biomass feedstock. While several pretreatment methods have been studied, many more are still being developed. However, the evaluation and comparison of pretreatment technologies are difficult because they involve upstream and downstream processing cost, capital investment, chemical recycling and waste treatment systems (Isahak et al., 2012). The effectiveness of any biomass feedstock pretreatment process, as an integrated part of an industrial system or biorefinery, requires sound economic analysis to establish the best method suitable for a particular biomass feedstock for an industrial process, with certain considerations such as co-location with existing plants where inexpensive power, steam or default treatment is available (Czajczyńska et al., 2017). In addition, biomass availability and characteristics, capital, and low negative environmental impacts can be considered in the selection of the best pretreatment method.

For high quality biomass, torrefaction is a viable option that is being employed. Torrefaction has been used as pretreatment methods for both lignocellulosic and macroalgae biomasses and significant influence on yield and quality of pyrolysis biochar was obtained (Uemura et al., 2015; Zhang et al., 2016). Dai et al. (2019) reported that structural modification of lignocellulosic biomass by torrefaction pretreatment is favourable for co-pyrolysis process; while Zhu et al. (2019) demonstrated that torrefaction pre-treatment combined with co-pyrolysis is effective to upgrade biochar. In both the torrefaction and co-pyrolysis stages, positive synergistic effects on the yield of torrefied feedstocks and biochar were observed. Torrefaction is performed within a temperature range of 200–300 °C at atmospheric pressure, under an inert atmosphere without oxygen (Chen et al., 2015). It is a thermal pretreatment process of biomass feedstock aimed at reducing moisture content and superfluous volatiles through several decomposition reactions. It helps to eliminate the limitations of biomass, upgrade the quality and alter the combustion characteristics (Nhuchhen et al., 2014). In this process, biomass is partly decomposed to produce torrefied char containing high carbon content (Yu et al., 2017). The thermal treatment destructs the fibrous structure and tenacity of biomass feedstock and also increases the calorific value (Isahak et al., 2012). In addition, after torrefaction pretreatment, the biomass has more hydrophobic characteristics which make the storage of the torrefied biomass more attractive. During torrefaction process, the biomass partly devolatilizes, which leads to a decrease in mass. However, the initial energy content of the torrefied biomass is generally preserved

in the solid product, making the energy density of the biomass to be higher than the original biomass (Isahak et al., 2012).

There are different approaches for biochar production based on the feedstock characteristics (wet or dry) and the expected properties for varied utilizations. Biomass feedstock with moisture content > 30% or < 30% during harvest, are referred to as wet or dry respectively (Kambo and Dutta, 2015). While the high moisture content inherent in wet biomass can be reduced by drying methods, this generates additional cost as the drying techniques are energy intensive, thereby decreasing the economic feasibility of the system (Mani et al., 2006). In addition, high water content in biomass reduces the heating value and the efficiency of the conversion process, while it equally increases the storage and transportation costs, and corrosion due to water condensation in flue gas. Biomasses that are hygroscopic in nature absorb moisture during storage which increases the risks of biological degradation. Biomass with low bulk and energy density also increases the storage and transportation costs and requires high feeding capacity (Bach and Skreiberg, 2016; Dai et al., 2019). The particle size is also very important as high energy utilization for pyrolysis is required for wet biomass feedstocks with large particle sizes. Part of the carbon contained in the biomass feedstock is burnt for the required energy supply which consequently leads to low feedstock conversion to biochar and other pyrolysis products (Kwapinski et al., 2010). High moisture level biomass increases grinding energy, whereas, low moisture level promotes easy and efficient grinding of the dried samples, after which the sample is screened to a desired particle size. Biomass is a poor heat conductor leading to a problematic heat transfer process. The feedstock's particle size curtails the inherent heat transfer problems which consequently determines the pyrolysis product yields (Akhtar and Amin, 2012). Smaller size particles lead to faster and uniform heating during pyrolysis because they mitigate against internal heat transfer limitations (El Hanandeh, 2013; Sharma et al., 2015). The moisture content and particle size also determine the type of pyrolysis process to be employed. Slow pyrolysis is suited to particle size range of 5–50 mm, while intermediate pyrolysis can process a wide range of biomasses with bigger particle size up to pellets and chips, and biomasses with moisture content up to 40%. Biomasses with low moisture content (< 10 wt%), and finely ground to a particle size range of < 1 mm are favourable for fast pyrolysis, while particle size of < 0.2 mm is suited to flash pyrolysis (Chang et al., 2016; Pandey et al., 2015). When the

Table 3
Summary of studies on co-pyrolysis of lignocellulosic biomass and macroalgae biomass.

Biomass feedstocks	Reactor type	Process conditions	Biochar yield (%)	Major findings	References
<i>Enteromorpha clathrata</i> and rice husk	Fixed bed reactor	Temperature: 550 °C N ₂ gas flow rate: 200 ml.min ⁻¹	41.82	The biochar yield remained unchanged, but the H/C ratio and the calorific value in solid chars decreased. Results demonstrated that fast co-pyrolysis had a small influence on biochar yield. Experimental value of biochar yield was almost the same with theoretical value.	Hu et al. (2018)
<i>Enteromorpha clathrata</i> volatiles (EN) and rice husk biochar (HU)	Sectional tubular pyrolysis furnace	Temperatures: 250, 400 and 550 °C N ₂ gas flow rate: 50 ml.min ⁻¹ Residence time: 45 min	*68	At 250 °C, EN + bio-coke was slightly higher than that of EN, while the yield of EN + bio-coke was lower than that of EN at 400 °C Compared with separate pyrolysis, the interaction resulted in a decrease in the yield of EN + bio-coke at medium temperature and an increase in the bio-coke yield at low and high temperatures. HU volatiles promoted decarboxylation process of EN + bio-coke at medium temperature, but it was inhibited at high temperature due to adsorption effect of EN bio-coke. The interaction reaction at 550 °C resulted in an increase in the number of pores of the EN + bio-coke, while also allowing the micropores to expand and merge with the adjacent pores forming mesopores. The changes in specific surface area of the pyrolyzed bio-coke indicated the significant effect of HU volatiles on EN bio-coke microstructure. Owing to the free radicals in HU volatile, polycondensation and aromatization reactions were enhanced in EN bio-coke resulting in aromatic compounds with higher cyclization of nitrogenous compounds. The yield of the HU + biochar was higher than that of HU biochar at all tested temperatures. Increment in yield of biochar at 400 °C is stronger than others. Compared with the individual pyrolysis, the yield of HU biochar increased at all studied temperatures. EN volatiles accelerated the carbonation and deepen the aromatic degree of HU biochar at high temperatures.	(Wang et al. (2018b))
<i>Enteromorpha clathrata</i> volatiles (EN) and rice husk biochar (HU)	Sectional tubular pyrolysis reactor	Temperatures: 250, 400 and 550 °C N ₂ gas flow rate: 50 ml.min ⁻¹ Residence time: 45 min	*30–57	The yield of the HU + biochar was higher than that of HU biochar at all tested temperatures. Increment in yield of biochar at 400 °C is stronger than others. Compared with the individual pyrolysis, the yield of HU biochar increased at all studied temperatures. EN volatiles accelerated the carbonation and deepen the aromatic degree of HU biochar at high temperatures.	Wang et al. (2018c)
<i>Enteromorpha clathrata</i> (EN) and rice husk (HU)	Fixed bed reactor	Temperature: 550 °C N ₂ gas flow rate: 200 ml.min ⁻¹ Catalysts: ZSM-5 and MCM-41	38.10–43.25	The experimental yield of biochar was consistent with the theoretical yield. Biochar yield of the co-pyrolysis of EN and HU was higher than that of the individual pyrolysis of HU, but lower than that of the individual pyrolysis of EN. The combination of ZSM-5 and MCM-41 catalysts promoted the formation of biochar. The effect of MCM-41 on the yields of the pyrolysis products was weaker than those of ZSM-5. Compared with the individual pyrolysis of EN, the co-pyrolysis of EN and HU significantly improved the pore structural characteristics. Co-pyrolysis of EN and HU contributed to the mass and heat transfer and the chemical reactions of the char/coke. The release of nitrogenous substances was inhibited by the addition of the HU at the low temperature range (< 190 °C). The addition of the HU promoted the pyrolysis of the aliphatic C–O functional groups at the middle temperature range and the cleavage of ether bonds of some water-soluble polysaccharides at 320–550 °C, generating the aromatic compounds. Significant synergistic effects exist between the EN and HU and the actual pore structure parameters of the char/coke are higher than the theoretical values, indicating that more volatiles are released during the co-pyrolysis which promotes the process.	Wang et al. (2019a)
<i>Enteromorpha clathrata</i> (EN) and rice husk (HU)	Fixed bed reactor	Temperatures: 190, 320 and 550 °C N ₂ gas flow rate: 200 ml.min ⁻¹	–	The combination of ZSM-5 and MCM-41 catalysts promoted the formation of biochar. The effect of MCM-41 on the yields of the pyrolysis products was weaker than those of ZSM-5. Compared with the individual pyrolysis of EN, the co-pyrolysis of EN and HU significantly improved the pore structural characteristics. Co-pyrolysis of EN and HU contributed to the mass and heat transfer and the chemical reactions of the char/coke. The release of nitrogenous substances was inhibited by the addition of the HU at the low temperature range (< 190 °C). The addition of the HU promoted the pyrolysis of the aliphatic C–O functional groups at the middle temperature range and the cleavage of ether bonds of some water-soluble polysaccharides at 320–550 °C, generating the aromatic compounds. Significant synergistic effects exist between the EN and HU and the actual pore structure parameters of the char/coke are higher than the theoretical values, indicating that more volatiles are released during the co-pyrolysis which promotes the process.	Xu et al. (2019b)

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Table 3 (continued)

Biomass feedstocks	Reactor type	Process conditions	Biochar yield (%)	Major findings	References
<i>Enteromorpha prolifera</i> (EP) and sugarcane bagasse (SA)	Fixed bed reactor	Temperature: 550 °C Heating rate: 20 °C/min	*31–35	Changes in the experimental and theoretical value yields of biochars are not so significant. The co-pyrolysis biochars had higher calorific values compared to that obtained through pyrolysis of EP alone. The HHV of char obtained from co-pyrolysis is higher than the pyrolysis of EP alone. The HHVs of the char from the co-pyrolysis of the blends increased. The yield of biochar decreased with the increasing HU mass percentage in the feedstock mixture, but increased with the increasing mass percentage of EP in the feedstock mixture. The maximum biochar yield was obtained when the feedstock blend contains almost EP. Higher pyrolysis temperatures led to lower char yields, while extremely low heating rates led to higher yields of biochar. Biochar yield of SA + CE was higher than biochar yield of EN + CE. The lowest biochar yield was recorded for CE. Co-pyrolysis of polysaccharides with cellulose promoted biochar production over the theoretical values. Biochar yield of normal co-pyrolysis was higher than catalytic pyrolysis. A synergy in biochar yield was observed for ESBC, whereas SK10BC experienced no improvements in biochar yield when compared to that of KBC and SMSBC. KBC showed least biochar yield due to high potassium amount. Total carbon was highest for SMSBC, followed by ESBC, SK10BC and KBC in that order. SK10BC and ESBC exhibited higher oxygen contents in comparison to SMSBC. Nitrogen contents did not vary much across all the biochars. Fixed carbon content was higher in ESBC than SK10BC with KBC showing the least value. Ash content was highest for KBC and was observed to increase in SK10BC and ESBC when compared to SMSBC although differences were not drastic. KBC had the highest BET surface area, followed by ESBC, SMSBC and SK10BC. Average pore diameter remained in the mesoporous range for SK10BC and ESBC, just like in the case of SMSBC, although KBC was microporous.	Hua and Li (2016)
<i>Enteromorpha prolifera</i> (EP) and rice husk (HU)	Fixed bed reactor	Temperatures: 400–600 °C Heating rate: 5–25 (°C/min) N ₂ gas flow rate: 100 ml.min ⁻¹	21.5–28.8		Uzojinwa et al. (2019)
<i>Enteromorpha clathrata</i> polysaccharides (ENP), <i>Sargassum fusiforme</i> polysaccharides (SAP) and cellulose (CE).	Fixed bed reactor	Temperature: 550 °C N ₂ gas flow rate: 0.2 L.min ⁻¹ Catalyst: ZSM-5	*28–30		Cao et al. (2018)
<i>Saccharina japonica</i> and spent mushroom substrate	Fixed-bed reactor	Temperature: 500 °C N ₂ gas flow rate: 200 ml.min ⁻¹ Residence time: 60 min	*27–32		Sewu et al. (2017)

*Approximated values obtained from figures. KBC, SMSBC, SK10BC and ESBC representing *Saccharina japonica*, spent mushroom substrate, co-pyrolysed *Saccharina japonica* and spent mushroom substrate and *Saccharina japonica*-extract treated spent mushroom substrate biochars respectively.

Table 4
Comparison of the effect of processing conditions on biochar yield and ultimate analysis during co-pyrolysis of macroalgae and lignocellulosic biomasses.

	Yield (%)	C (%)	H (%)	N (%)	S (%)	O (%)	H/C Ratio	HHV (MJ/kg)	Reference
EN + HU	41.82	34.66	1.25	1.68	–	–	0.43	–	Hu et al. (2018)
EN	46.76	22.86	1.17	2.14	–	–	0.61	–	
HU	34.39	47.23	1.14	0.58	–	–	0.30	–	
EN volatile + HU biochar at 250 °C	*57	49.20	4.05	0.71	–	–	0.08	–	Wang et al. (2018c)
HU at 250 °C	*55	50.08	3.89	0.64	–	–	0.08	–	
EN volatile + HU biochar at 400 °C	*38	50.48	2.64	0.68	–	–	0.05	–	
HU at 400 °C	*37	49.83	2.62	0.61	–	–	0.05	–	
EN volatile + HU biochar at 550 °C	*30	50.4	1.79	0.59	–	–	0.04	–	
HU at 550 °C	*28	50.22	1.86	0.58	–	–	0.04	–	
EN at 250 °C	*67	*33	*3	*4	–	–	–	–	Wang et al. (2018b)
EN volatile + HU biochar at 250 °C	*65	*34	*3	*4	–	–	–	–	
EN at 400 °C	*49	*27	*2	*3	–	–	–	–	
EN volatile + HU biochar at 400 °C	*52	*28	*2	*3	–	–	–	–	
EN at 550 °C	*43	*25	*1	*2	–	–	–	–	
EN volatile + HU biochar at 550 °C	*42	*26	*1	*2	–	–	–	–	
BA	26.27	–	–	–	–	–	–	21.27	Hua and Li, (2016)
EP 30%	*31	–	–	–	–	–	–	22.43	
EP 40%	*32	–	–	–	–	–	–	19.47	
EP 50%	*33	–	–	–	–	–	–	17.57	
EP 60%	*34	–	–	–	–	–	–	16.81	
EP 70%	*35	–	–	–	–	–	–	15.51	
EP	44.44	–	–	–	–	–	–	12.74	
EN Non-catalyst	46.76	–	–	–	–	–	–	–	Wang et al. (2019a)
EN ZSM-5	44.90	–	–	–	–	–	–	–	
EN MCM-41	48.54	–	–	–	–	–	–	–	
HU Non-catalyst	34.39	–	–	–	–	–	–	–	
HU ZSM-5	34.40	–	–	–	–	–	–	–	
HU MCM-41	35.29	–	–	–	–	–	–	–	
EN:HU 1:1 Non-catalyst	40.58	–	–	–	–	–	–	–	
EN:HU 1:1 ZSM-5	38.10	–	–	–	–	–	–	–	
EN:HU 1:1 MCM-41	42.38	–	–	–	–	–	–	–	
EN:HU 1:1 ZCM-5: MCM-41 1:1	43.25	–	–	–	–	–	–	–	
#HU:EN 0:100	39.40	52.72	4.93	5.20	–	37.15	1.12	31.60	Uzoejinwa et al. (2019)
#HU:EN 25:75	44.50	50.07	5.97	4.87	–	39.09	1.43	30.98	
#HU:EN 50:50	46.50	48.06	6.59	2.51	–	42.84	1.65	29.83	
#HU:EN 75:25	47.70	46.43	6.90	1.92	–	44.75	1.78	28.68	
#HU:EN 100:0	47.00	45.93	6.98	1.10	–	45.99	1.82	26.88	
EN	*41	–	–	–	–	–	–	–	Cao et al. (2018)
EN (Catalytic)	*38	–	–	–	–	–	–	–	
SA	*43	–	–	–	–	–	–	–	
SA (Catalytic)	*37	–	–	–	–	–	–	–	
CE	*8	–	–	–	–	–	–	–	
CE (Catalytic)	*7	–	–	–	–	–	–	–	
EN + CE	*28	–	–	–	–	–	–	–	
EN + CE (Catalytic)	*27	–	–	–	–	–	–	–	
SA + CE	*30	–	–	–	–	–	–	–	
SA + CE (Catalytic)	*28	–	–	–	–	–	–	–	
EN + HU at 250 °C	*67	–	–	–	–	–	–	–	
EN at 250 °C	*65	–	–	–	–	–	–	–	Wang et al. (2018b)
EN + HU at 400 °C	*49	–	–	–	–	–	–	–	
EN at 400 °C	*52	–	–	–	–	–	–	–	
EN + HU at 550 °C	*43	–	–	–	–	–	–	–	
EN at 550 °C	*42	–	–	–	–	–	–	–	
KBC	*27	29.93	0.11	1.90	–	8.71	–	–	Sewu et al. (2017)
SMSBC	*28	69.79	0.49	3.24	–	1.38	–	–	
SK10BC	*28	65.38	0.52	4.49	–	1.23	–	–	
ESBC	*32	69.39	< 0.01	4.93	–	1.59	–	–	

*Approximately obtained from Figures.

All values to 2 decimal places.

#(Performed at heating rate of 20 °C/min and a temperature of 500 °C).

moisture content is air-dried, it can be reduced to acceptable levels for thermal processing.

3. Biochar production from CLMB

The mechanisms and kinetics of pyrolysis are practically close to that of co-pyrolysis process, apart from the synergistic reaction mechanisms based on the nature, compositions, interactions and blending ratio of the feedstocks' constituents. Therefore, co-pyrolysis, like pyrolysis, can broadly be classified as slow or fast depending on the

operating conditions. Slow co-pyrolysis produces biochar, generally at a lower temperature, heating rate and longer residence time, while fast co-pyrolysis produces bio-oil, predominantly at a higher temperature, heating rate and shorter residence time. This makes temperature and heating rate particularly important for biochar production, with the former supplying the heat requirement for biomass bond fragmentation. It was observed from Tables 3 and 4 that higher temperatures produced lower yields of biochar (Uzoejinwa et al., 2019; Wang et al., 2018b; Wang et al., 2018c). This was due to the pyrolysis primary reactions and the acceleration of the secondary decomposition of char to

gaseous products generation (Aysu and Sanna, 2015). At high temperatures, the produced biochar during the pyrolysis reaction goes through secondary reactions. These secondary reactions favour the production of syngas and bio-oil at the expense of biochar. Consequently, low temperature is necessary for higher biochar yield. At high temperature, the temperature applied to the biomass feedstock can exceed the bond cessation energy, consequently releasing the volatiles components of the biomass which come out in liquid and gaseous forms (Akhtar and Amin, 2012). In a similar vein, it was observed that increase in the heating rate led to low biochar production (Uzoejinwa et al., 2019). This was attributed to the rapid high molecular volatiles removal at higher heating rates. At lower heating rates, there is no thermal cracking of biomass, and there is less tendency for secondary pyrolysis reactions, which leads to high production of biochar. High heating rate aids biomass fragmentation which favours the production of gaseous and liquid yields (Tripathi et al., 2016).

Feedstock compositions of the lignocellulosic and macroalgae biomasses, their blending ratio and extent of contact are crucial in establishing the synergistic effect in the co-pyrolysis process. These compositions (aforementioned in Section 2.1) determine the characteristics of pyrolysis products produced. The feedstock blending ratio is salient in co-pyrolysis, in distinction to normal pyrolysis, as it has been reported to significantly influence the solid, liquid and gas distribution (Aboyade et al., 2013). From Table 3, it was observed that increase in the amount of macroalgae in the feedstock favours biochar production. Comparatively, biochar yield of the individual pyrolysis of macroalgae > co-pyrolysis of macroalgae and lignocellulosic biomass > pyrolysis of lignocellulosic biomass (Hu et al., 2018; Hua and Li, 2016; Uzoejinwa et al., 2019). This, as observed by many researchers, was due to the ash content inherent in macroalgae (Hua and Li, 2016; Uzoejinwa et al., 2019; Wang et al., 2019a). The higher biochar yield from macroalgae in comparison to lignocellulosic biomass has been attributed to the alkali content in the ash which acts as catalysts for char formation (Xu et al., 2015).

The higher heating value (HHV), also known as the gross calorific value of the co-pyrolysis process is dependent on the biomass co-feedstocks. In Table 3, Hua and Li (2016) observed that the higher the percentage of sugarcane bagasse in the co-pyrolysis with *Enteromorpha prolifera*, the higher the HHV of biochar produced. However, Uzoejinwa et al. (2019) observed that as the percentage of rice husk increased in the co-pyrolysis with *Enteromorpha prolifera*, the HHV of the biochar produced decreased. The pyrolysis of *Enteromorpha prolifera* alone produced the highest biochar HHV. Even though the results from the two studies appear contrasting, the mutual understanding was the amount of ash contained in the biomass feedstock. In comparison, rice husk has notably higher amount of ash than sugarcane bagasse. Hua and Li (2016) obtained ash content of 5.45 (wt%) on dry basis for sugarcane bagasse, while Uzoejinwa et al. (2019) obtained ash content of 11.41 (wt%) on dry basis for rice husk. While the presence of high amounts of ash in biomass could favour biochar formation, it leads to reduction in HHV. Maddi et al. (2011) in their study, observed that the HHV of biochar obtained from lignocellulosic biomasses are mostly higher than the ones obtained from macroalgae biomass, except rice husk. This was because the ash contents of the macroalgae biomasses considered in their study were higher than the other lignocellulosic biomasses, except rice husk. Ash contents of 4.3, 1.5, 19.7, 25.7 and 13.3 (wt%) on dry basis were obtained for corncob, woodchips, rice husk, *Lyngbya* sp. and *Cladophora* sp. respectively. The high ash content in rice husk has been attributed to the presence of silica (Zaid and Taiwo, 2008). From the foregoing, the ash content significantly influences the biochar HHV. This was consistent with the report of Yu et al. (2017) which observed that the HHV of algal biochars is comparatively lower than lignocellulosic biochars (which has been reported to exceed 30 MJ/kg). This was attributed to lower carbon content and higher ash content in algal biomass. High biochar HHV values show the potential of the biochar to be utilized as a biofuel.

The degree of the contact between the co-feedstocks is very essential to obtaining positive synergistic effects, and this is vastly controlled by the pyrolysis reactor type. While the fluidized bed reactor has been employed mostly for fast pyrolysis due to its relative ease of scalability and simple operation in comparison with other reactor types (Abnisa and Daud, 2014), most studies on co-pyrolysis were performed using a fixed-bed reactor (Cao et al., 2018; Hua and Li, 2016; Sewu et al., 2017). Onay and Kockar (2003) reported that the extent of contact between the biomass feedstock is very essential to achieve the synergistic effect and is more likely to occur when pyrolysis is carried out in a fixed-bed reactor as compared to a fluidized-bed reactor. The fixed-bed reactor is discussed comprehensively in Section 5.

The presence of catalyst is used to alter product distribution during pyrolysis process. Sometimes, the biomass feedstock constituents like ash can act as catalyst for biochar production also. However, the presence of metals in the ash of raw biomass feedstock partially eliminates the formation of char (Tripathi et al., 2016). Various catalysts have been studied to increase the product yield ranging from solid acid catalysts, solid base catalysts, ionic catalysts, HZSM-5 catalyst and aluminum silicate catalysts. Acid catalysts have been found to increase the biochar yield; and among the acid catalysts, ZSM-5 zeolite is the most frequently studied catalyst and considered the most efficient, due to its unique three-dimensional microporous structure and relatively strong Brønsted acidity (Jae et al., 2011). Recently, the utilization of a metal (mono-metallic) or two metals (bi-metallic) has been introduced to further improve the catalytic activities and catalysts stability (Ren et al., 2018).

The influence of catalysts on biochar production during CLMB showed that while some catalysts increased biochar production at the cost of the other two phases, some decreased biochar production, thereby enhancing the other two phases. Wang et al. (2019a) observed that in the catalytic co-pyrolysis process, MCM-41 significantly improved biochar yield, while the effect of ZSM-5 on biochar yield was weaker comparatively. Cao et al. (2018) reported that biochar yields of all observed treatments decreased in the presence of ZSM-5. This might be due to the insolubility of ZSM-5 in water, which makes it difficult while spreading uniformly. While the use of ZSM-5 catalyst is very common in pyrolysis and co-pyrolysis studies, there have been conflicting results in the studies. While some studies have reported increased biochar yield with the use of ZSM-5 catalyst (Smets et al., 2013; Stefanidis et al., 2011), other studies revealed that ZSM-5 led to reduction in biochar yield (Wang et al., 2006; Zhang et al., 2009). In finding a common ground, Tripathi et al. (2016) submitted that biomass feedstocks have varied chemical compositions as well as ash and water contents, which makes it extremely difficult to generalize the catalytic effect on the product yield. This is because catalysts function differently for each biomass. Considering this submission, studying the catalytic effect on biochar production from co-pyrolysis of two or more biomass feedstocks can be very complex. A very important point worthy of consideration also is the mode of catalyst application in pyrolysis which can be *in-situ* or *ex-situ* mode. In the former, catalyst is mixed with feedstocks and placed in the pyrolysis reactor, whereas, in the latter, catalyst is situated in a different reactor, positioned downstream of pyrolysis reactor (Muneer et al., 2019). For *in-situ* mode, since the catalysts are thoroughly mixed with the feedstocks, they interfere with the pyrolysis and cracking processes of the biomass feedstock at an earlier stage. This could increase the decomposition of larger pyrolysis fragments and decrease the secondary char formation. For the *ex-situ* mode however, since the catalyst is separate from the feedstocks, the char formed in the pyrolysis process can be simply separated and collected as a potential valuable solid product (Luo and Resende, 2016).

4. Biochar characterization

Biochar characterization is classified as physical or chemical. Physical characterization includes determination of moisture content,

ash content, bulk density, particle size distribution, pore volume, SEM/TEM and X-ray absorption near-edge structure; while chemical characterization includes determination of elemental analysis, pH measurement, gas chromatography, FTIR/FTIS, X-ray photoelectron spectroscopy (XPS), BET, CEC analysis C-NMR, Boehm titration and zeta potential of biochar colloids (Nartey and Zhao, 2014). The purpose of elemental analysis is for the determination of the degree of aromaticity, polarity and maturation (Lehmann et al., 2006). The elemental analysis components for biochar characterization are the same as for feedstock characterization; however, there is significant difference in their values. Feedstock blending (Hu et al., 2018; Sewu et al., 2017), temperature (Wang et al., 2018b), and percentage feedstock in co-pyrolysis (Hua and Li, 2016) have been established to have significant effects on the characterization of biochar obtained from CLMB (Table 4). The SEM and pore structure analyses are used in the morphological changes detection on the solid residue when bio-macromolecules are transformed into small molecules and several pores, which are formed and distributed on the biochar surface (Chen et al., 2008); while BET is used in the determination of the surface area, pore structures, average pore diameter, pore volume, and average pores of biochar produced (Ghani et al., 2013). XPS is a sensitive quantitative spectroscopic technique utilized in material surface chemistry to show the surface compositions and binding interactions in it (Zhang and Cresswell, 2016), while FTIR/FTIS determines the various changes that occur in biochar preparations and the variations in the chemical functional groups existing in the original biochar due to dehydration, pyrolysis, graphene nucleation, and carbonization (Lee et al., 2010; Nartey and Zhao, 2014).

Hu et al. (2018) reported a significant change in the FTIR analysis of biochar from the co-pyrolysis of *Enteromorpha clathrata* and rice husk and discovered that there was no C–H bond from the rupture of C–H bond in hydroxyl group. No signals of aromatic ring frame vibration and C–H bending vibration were detected, which implied that there was no aromatization in the produced biochar. During the co-pyrolysis of *Enteromorpha clathrata* volatiles and rice husk biochar, Wang et al. (2018c) established that the interactive effect caused polycondensation reaction which led to the formation of aromatic compounds. Furthermore, *Enteromorpha clathrata* volatiles accelerated the fragmentation of some glycosidic bonds and pyranose rings in rice husk residual cellulose and hemicellulose, thereby strengthening the formation of aromatic compounds. The XPS spectra revealed significant removal of oxygen functional groups in the rice husk biochar by the free radicals of *Enteromorpha clathrata* volatiles. Wang et al. (2018c) in the same study, determined the morphological characteristics and fractal dimensions of the biochar produced and observed an insignificant changes in the surface morphology of the residue at 550 °C as the fractal dimension was almost the same. Nonetheless, during co-pyrolysis, a decrease in the specific surface area was observed. A closure of some micropores (< 2 nm) and mesopores (2–50 nm) was observed for the biochar produced at 550 °C, caused by organic compounds deposition after interaction with *Enteromorpha clathrata* volatiles. Xu et al. (2019b) used XPS to analyze the surface functional groups of the biochar obtained from the co-pyrolysis of *Enteromorpha clathrata* and rice husk. Analyses of the carbon-containing, oxygenated and nitrogen-containing functional groups were carried out. For the carbon-containing functional group, four major types of carbon were identified viz. C–C–C–H, C–O, C–O and COO– (in ascending order of bond energy); while for the oxygenated functional group, four peaks were identified viz. –OH, C–O, C–O–C and COO– (in ascending order of bond energy); and for the nitrogen-containing functional group, three main peaks were observed namely pyridine nitrogen, protein nitrogen and ammonium salt nitrogen (in ascending order of bond energy), with protein nitrogen being the dominant because *Enteromorpha clathrata* cells consists of numerous proteins. Rice husk addition prevented nitrogenous substances release at low temperatures (< 190 °C), and favours the pyrolysis of the aliphatic C–O functional groups at medium temperature range. Also, aromatic compounds were generated by the cleavage of

ether bonds of some water-soluble polysaccharides at 320–550 °C. In the same study, the SEM analysis revealed that as the temperature increased, the pores on the biochar surface appeared to collapse and melt. Mesopores and macropores were found on the pore structure of the biochar surface at the end of the reaction, caused by the further polycondensation of the C–H and C–O bonds in the biochar. In another study by Wang et al. (2019a) on the co-pyrolysis of *Enteromorpha clathrata* and rice husk, the XPS analysis of the carbon-containing and nitrogen-containing functional groups showed that the carbon spectrum of biochar comprises of four peaks which are aliphatic carbon C–C/C=C/C–H groups, C–O/C–O–C groups in alcohol, ether groups, C=O groups in carbonyl groups and COO– groups in carboxyl and/or ester groups (in ascending order of bond energy). For the nitrogen-containing functional group, three main peaks were discovered namely pyridine nitrogen, protein nitrogen and ammonium salt nitrogen (in ascending order of bond energy). Hua and Li (2016) studied the functional characteristics of biochar and observed that the stretching vibration absorption peaks of C–H disappeared during the co-pyrolysis of sugarcane bagasse with *Enteromorpha prolifera* at feedstock ratio of 50/50. Decomposition of aliphatic hydrocarbon occurred due to the C–H bonds of alkyls which causes the rise of some hydrocarbon gases, such as methane and ethane. There was increase in the infrared absorbance of C–O and the stretching vibration absorption peaks of C–H aromatic, which was attributed to aromatic hydrocarbons formation at feedstock ratio of 50/50.

These aforementioned studies showed the morphological and surface compositional changes in the biochar produced from CLMB which are important in the various utilizations of the biochar in different applications.

5. Biochar reactor technologies for CLMB

The choice of a particular pyrolysis reactor technology over other reactors is basically dependent on the intended final products (biochar, bio-oil or syngas). Many reactors are available for co-pyrolysis which include fixed bed, fluidized bed, circulating fluidized bed, rotating cone, ablative pyrolysis, entrained flow, auger, pyros and plasma pyrolysis reactors, amongst others. An overview of the various reactor types used in pyrolysis process has been presented in other studies (Czajczyńska et al., 2017; Dhyani and Bhaskar, 2018; Isahak et al., 2012). Each of the reactors has their various advantages and disadvantages in operation and scaling. For the CLMB, the fixed bed pyrolysis reactor was the most utilized (Table 3).

The fixed bed pyrolysis reactor system basically consists of a fixed bed reactor, a liquid condenser, liquid collectors and a biomass source heater. The fixed bed reactor is maintained at the desired temperature, depending on the type of pyrolysis (slow, intermediate, fast or flash) and at an apparent vapour residence time. Heat is supplied to the reactor through the pre-heater in order to maintain the desired temperature in the reactor. Nitrogen gas is the most commonly used carrier gas throughout the system to create an inert atmosphere inside the reactor (Table 3). This is due to its easy availability, cost-effectiveness and inert behaviour. Nitrogen is utilized as a purging agent for the vapour generated during co-pyrolysis to prevent the vapour from taking part in the secondary reactions which significantly affect the composition and nature of the co-pyrolysis products. A nitrogen gas pressure regulator is used to control and regulate the gas pressure from the cylinder. The outlet gauge is set at atmospheric pressure, while a nitrogen gas flow-meter with a variable control valve is used to control and measure the gas flow rate. Different nitrogen gas flow rates have been used ranging mostly from 50 to 200 ml/min during the pyrolysis operation (Table 3). Water cooled condenser is used for the rapid cooling of condensable pyrolysis vapour in the reactor to be condensed into liquid product. Liquid collectors are positioned in the system for additional condensation of the vapour (in order to be ice-cooled), while the non-condensable gases are flared into the atmosphere. Fig. 1 shows a

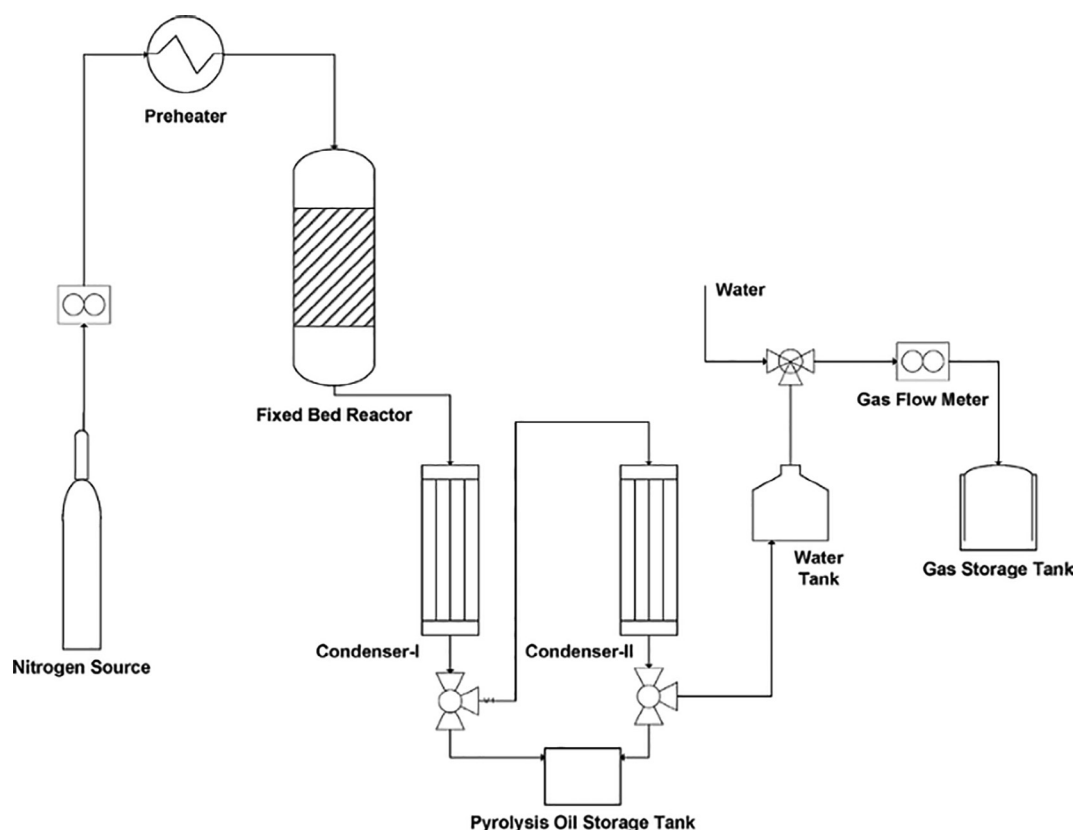


Fig. 1. Schematic of a typical fixed bed reactor. Source: (Kanaujia et al., 2016).

schematic of a typical fixed bed reactor.

New findings have suggested auger reactors to be a more versatile and attractive option for the co-pyrolysis of several biomass feedstocks; and this is being utilized presently in pyrolysis studies (Lazdovica et al., 2017; Martínez et al., 2014). Auger/screw reactors can easily vary and control feedstocks rate and have the capability to produce liquid, gaseous and solid products at slow, intermediate and fast conditions, which is not achievable using any other technology (Campuzano et al., 2019). They are characterized by simple construction and operation, little or no carrier gas, low energy consumption and easier control of the residence time of biomass in the heated zone through the adjustment of the speed of rotation of the screw or the flight-pitch (Brassard et al., 2017). Fig. 2 shows a schematic of a semi-continuous pilot screw reactor.

A search of literature revealed that the auger reactor has not been utilized for co-pyrolysis studies at present. However, with the various advantages of the reactor, it is expected to gain considerable attention sooner, as research on co-pyrolysis continues.

6. Potential and economic viability of biochar production system from CLMB

Co-pyrolysis process offers simplicity in design and operation which makes the technology so important in the biomass energy industry development. However, before this method can be fully integrated, the economic feasibility needs to be considered and this can be achieved by evaluating the net present value. The economic assessment of biochar production from lignocellulosic biomass using pyrolysis method has been reported (Giwa et al., 2019; Ji et al., 2018). However, since co-pyrolysis process is a relatively new technology, to the best of the authors' knowledge, there is no report on the economic feasibility of biochar production from the process; more so, from the CLMB, especially on a large industrial scale. The economic feasibility of co-

pyrolysis is very similar to that of pyrolysis, with the basic difference being the combination of feedstocks involved in co-pyrolysis. This has significant effects on the energy value generated in the process, production and collection costs of the feedstock, transportation cost for both the feedstock and the biochar product, capital cost of feedstock processing, total operating costs for feedstock processing, and the biochar value. For CLMB, the extra costs of drying and handling macroalgae is taken into consideration as it substantially increases the costs.

The economic feasibility of biochar production is a bit complex, as it is influenced by several factors which include valuable energy product yield, cost of biochar application, important GHG offsets obtained via offsetting fossil fuels, emissions reduction from agricultural input utilization and sequestering carbon, and cost of remaining value added chemicals (Roberts et al., 2009). The economic costs and benefits components are the feedstock production and collection, feedstock hauling, feedstock storage and pre-processing, feedstock processing, co-pyrolysis operation, energy sales, and biochar hauling and application. The costs of biomass feedstock production and collection also include costs of assembly, harvesting, collection and compaction (Caputo et al., 2005).

The operating cost of pyrolysis plant includes biomass preparation cost (reception, drying, comminution, storage and feeding), cost of pyrolysis process (slow or fast) to produce bio-oil, biochar and syngas, and cost of electricity generation. The production economy analyses take into consideration the total investment cost, total revenue, total fixed cost, total variable cost, total cost, break-even-point, net present value, benefit/cost ratio, payback period, internal rate of return, and return on investment (Harsono et al., 2013).

The net profit (NP) of the biochar production system is obtained using the method described by Roberts et al. (2009):

$$NP = BC + E - F - T - O - C - A$$

BC is the biochar value, E is the energy value generated in the process, F is the production and collection costs of the feedstock, T is

utilization of the biochar from the co-pyrolysis process has often been overlooked and ignored in the published literatures. However, understanding how biochar properties are related to precursor material and heat-treatment parameters is essential to the development of biochar for specific application in different fields. Initially, biochar utilization was focussed on the soil amendment characteristics because of the potential of biochar for carbon sequestration and soil quality improvement. However, extensive investigations of the biochar properties (physical, chemical and biological) as well as the production technologies, have shifted the attention from just soil improvement alone to several industrial applications, notably in the areas of health, science and engineering (Chemerys and Baltrėnaitė, 2018). Biochars show wide changes in physical and chemical properties which significantly influence their various utilizations (Gul et al., 2015). Feedstock type and the conversion technique influence the biochar characteristics (concentrations of elemental constituents, pH, porosity, density amongst others), and significantly determine the suitability of the biochar for different utilizations (Daful and Chandraratne, 2018). They consist of different surface functional groups which are influenced by thermal modifications of the parent organic materials (Ahmad et al., 2014). Temperature, pressure, duration and biomass feedstock physical characteristics are critical variables for consideration in biochar commercial production; most especially temperature, as it influences the density and nature of functional groups of the resulting biochar (Uchimiya et al., 2012). These parameters control the biochar quality variability, vis-à-vis, biochar utilization, so they should be effectively studied, understood and controlled during the production process.

Biomass feedstock pretreatment, prior to pyrolysis is fast attracting considerable interest as it improves the quality through the removal or modification of the undesired functional groups and structures of the biomass, which in turn advances the biomass conversion process and optimizes pyrolysis product formation (Wang et al., 2017b). Torrefaction gives high quality biochar production and provides huge benefits in logistics, handling and storage, as well as opening up a wide range of potential uses. Torrefaction of biomass can also enhance the fuel properties of biochar for combustion, pyrolysis, liquefaction, and gasification (Ong et al., 2019). Thus, the development of a tandem torrefaction-pyrolysis technology is highly recommended; which requires an understanding of the integration of torrefaction and advanced co-pyrolysis techniques. Diverse effect mechanism of torrefaction on co-pyrolysis should be explored after thorough knowledge of torrefaction chemistry, including interactions between all biomass components (cellulose, lignin, hemicellulose, carbohydrates, protein, lipids) and self-catalysis of light organic acids. Thereafter, an efficient integration system which considers the structural variations in biomass feedstock and the biomass pre-treatment properties, amongst other important factors should be developed.

Biomass feedstock storage is an important requirement that should be appraised, which hitherto has been ignored by many researchers. Equally, the short-term storage of intermediate products like biochar should be explored, while the properties of the biochar components over time should be properly monitored.

Finally, the economic analysis of biochar production from the CLMB needs to be fully explored. This should be compared with the economics of the pyrolysis of individual biomasses (that is, lignocellulosic and macroalgae biomasses). A comprehensive sensitivity analysis should be performed to determine how variations in different parameters of the biochar production will influence the investment in terms of overall profit and/or loss. This is important to determine the economic vulnerability of the biochar production against potential fluctuations during the lifetime of the investment. Possible variations might be in terms of the feedstocks production, collection, transportation and storage costs, co-pyrolysis (slow or fast) type, bio-oil yield, syngas yield, pyrolysis plant construction cost, design parameters, capital costs, change in fuel prices, electricity price, GHG price, yield implications of biochar application, biochar sales price amongst others. The sensitivity

analysis is imperative in making critical decisions on investments, most especially with a rise in raw material prices, increase fuel prices and decrease sales prices of biochar products (Harsono et al., 2013). This is important in making informed and appropriate decisions about the investment in terms of the uncertainties, pros and cons with the limitations and scope of the project.

8. Conclusions

Biochar production is attracting keen interest because of its promising potentials in energy and environmental aspects. Merging lignocellulosic and macroalgae biomass feedstocks can be successfully employed for biochar production in the energy biorefinery. Biomass feedstock pretreatment is important to improve the biomass quality vis-à-vis the biochar produced. Biochar characterization provides adequate knowledge of the physical and chemical properties, hence, the potential utilizations in the various applications. Exploring more lignocellulosic and macroalgae biomass types is encouraged, and a comprehensive sensitivity analysis to determine the economic vulnerability of the biochar production against potential fluctuations during the lifetime of the investment is recommended.

9. Declaration of competing interests

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

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References

- Abnisa, F., Daud, W.M.A.W., 2014. A review on co-pyrolysis of biomass: an optional technique to obtain a high-grade pyrolysis oil. *Energy Convers. Manage.* 87, 71–85.
- Aboyade, A.O., Carrier, M., Meyer, E.L., Knoetze, H., Görgens, J.F., 2013. Slow and pressurized co-pyrolysis of coal and agricultural residues. *Energy Convers. Manage.* 65, 198–207.
- Agrafioti, E., Bouras, G., Kalderis, D., Diamadopoulos, E., 2013. Biochar production by sewage sludge pyrolysis. *J. Anal. Appl. Pyrol.* 101, 72–78.
- Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. *Chemosphere* 99, 19–33.
- Ahmed, M., Okoye, P., Hummadi, E., Hameed, B., 2019. High-performance porous biochar from the pyrolysis of natural and renewable seaweed (*Gelidium acerosa*) and its application for the adsorption of methylene blue. *Bioresour. Technol.* 278, 159–164.
- Ajav, E., Singh, B., Bhattacharya, T., 1999. Experimental study of some performance parameters of a constant speed stationary diesel engine using ethanol–diesel blends as fuel. *Biomass Bioenergy* 17 (4), 357–365.
- Akhtar, J., Amin, N.S., 2012. A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. *Renew. Sustain. Energy Rev.* 16 (7), 5101–5109.
- Aqsha, A., Tijani, M.M., Moghtaderi, B., Mahinpey, N., 2017. Catalytic pyrolysis of straw biomasses (wheat, flax, oat and barley) and the comparison of their product yields. *J. Anal. Appl. Pyrol.* 125, 201–208.
- Aysu, T., Sanna, A., 2015. Nannochloropsis algae pyrolysis with ceria-based catalysts for production of high-quality bio-oils. *Bioresour. Technol.* 194, 108–116.
- Bach, Q.-V., Skreiberg, Ø., 2016. Upgrading biomass fuels via wet torrefaction: a review and comparison with dry torrefaction. *Renew. Sustain. Energy Rev.* 54, 665–677.
- Bae, Y.J., Ryu, C., Jeon, J.-K., Park, J., Suh, D.J., Suh, Y.-W., Chang, D., Park, Y.-K., 2011. The characteristics of bio-oil produced from the pyrolysis of three marine macroalgae. *Bioresour. Technol.* 102 (3), 3512–3520.
- Brassard, P., Godbout, S., Raghavan, V., 2017. Pyrolysis in auger reactors for biochar and bio-oil production: a review. *Biosyst. Eng.* 161, 80–92.
- Brewer, C.E., Schmidt-Rohr, K., Satrio, J.A., Brown, R.C., 2009. Characterization of biochar from fast pyrolysis and gasification systems. *Environ. Prog. Sustain. Energy* 28 (3), 386–396.
- Caballero, J., Conesa, J., Font, R., Marcilla, A., 1997. Pyrolysis kinetics of almond shells and olive stones considering their organic fractions. *J. Anal. Appl. Pyrol.* 42 (2),

- 159–175.
- Callegari, A., Capodaglio, A., 2018. Properties and beneficial uses of (bio) chars, with special attention to products from sewage sludge pyrolysis. *Resources* 7 (1), 20.
- Campuzano, F., Brown, R.C., Martínez, J.D., 2019. Auger reactors for pyrolysis of biomass and wastes. *Renew. Sustain. Energy Rev.* 102, 372–409.
- Cao, B., Xia, Z., Wang, S., Abomohra, A.E.-F., Cai, N., Hu, Y., Yuan, C., Qian, L., Liu, L., Liu, X., 2018. A study on catalytic co-pyrolysis of cellulose with seaweeds polysaccharides over ZSM-5: towards high-quality biofuel production. *J. Anal. Appl. Pyrol.* 134, 526–535.
- Cao, X., Harris, W., 2010. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresour. Technol.* 101 (14), 5222–5228.
- Caputo, A.C., Palumbo, M., Pelagagge, P.M., Scacchia, F., 2005. Economics of biomass energy utilization in combustion and gasification plants: effects of logistic variables. *Biomass Bioenergy* 28 (1), 35–51.
- Chang, G., Huang, Y., Xie, J., Yang, H., Liu, H., Yin, X., Wu, C., 2016. The lignin pyrolysis composition and pyrolysis products of palm kernel shell, wheat straw, and pine sawdust. *Energy Convers. Manage.* 124, 587–597.
- Chemerys, V., Baltrėnaitė, E., 2018. A review of lignocellulosic biochar modification towards enhanced biochar selectivity and adsorption capacity of potentially toxic elements. *Ukrainian J. Ecol.* 8 (1), 21–32.
- Chen, H., Luo, Z., Yang, H., Ju, F., Zhang, S., 2008. Pressurized pyrolysis and gasification of Chinese typical coal samples. *Energy Fuels* 22 (2), 1136–1141.
- Chen, W.-H., Huang, M.-Y., Chang, J.-S., Chen, C.-Y., 2015. Torrefaction operation and optimization of microalga residue for energy densification and utilization. *Appl. Energy* 154, 622–630.
- Colantoni, A., Evcic, N., Lord, R., Retschitzegger, S., Proto, A., Gallucci, F., Monarca, D., 2016. Characterization of biochars produced from pyrolysis of pelletized agricultural residues. *Renew. Sustain. Energy Rev.* 64, 187–194.
- Collard, F.-X., Blin, J., 2014. A review on pyrolysis of biomass constituents: mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. *Renew. Sustain. Energy Rev.* 38, 594–608.
- Cong, H., Mašek, O.E., Zhao, L., Yao, Z., Meng, H., Hu, E., Ma, T., 2018. Slow pyrolysis performance and energy balance of corn stover in continuous pyrolysis-based poly-generation systems. *Energy Fuels* 32 (3), 3743–3750.
- Converti, A., Casazza, A.A., Ortiz, E.Y., Perego, P., Del Borghi, M., 2009. Effect of temperature and nitrogen concentration on the growth and lipid content of *Nannochloropsis oculata* and *Chlorella vulgaris* for biodiesel production. *Chem. Eng. Process. Process Intensif.* 48 (6), 1146–1151.
- Czajczyńska, D., Anguilano, L., Ghazal, H., Krzyżyńska, R., Reynolds, A., Spencer, N., Jouhara, H., 2017. Potential of pyrolysis processes in the waste management sector. *Therm. Sci. Eng. Prog.* 3, 171–197.
- Daful, A.G., Chandraratne, M.R., 2018. Biochar production from biomass waste-derived material. In: Reference Module in Materials Science and Materials Engineering. Elsevier Inc. (S&T Books and Cell Press), United Kingdom, pp. 11249–11258.
- Dai, L., Wang, Y., Liu, Y., Ruan, R., He, C., Yu, Z., Jiang, L., Zeng, Z., Tian, X., 2019. Integrated process of lignocellulosic biomass torrefaction and pyrolysis for upgrading bio-oil production: a state-of-the-art review. *Renew. Sustain. Energy Rev.* 107, 20–36.
- Demirbaş, A., 2002. Analysis of liquid products from biomass via flash pyrolysis. *Energy Sources* 24 (4), 337–345.
- Dhyani, V., Bhaskar, T., 2018. A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renewable Energy* 129, 695–716.
- El Hanandeh, A., 2013. Carbon abatement via treating the solid waste from the Australian olive industry in mobile pyrolysis units: LCA with uncertainty analysis. *Waste Manage. Res.* 31 (4), 341–352.
- Ferreira, S.D., Altafini, C.R., Perondi, D., Godinho, M., 2015. Pyrolysis of Medium Density Fiberboard (MDF) wastes in a screw reactor. *Energy Convers. Manage.* 92, 223–233.
- Ghani, W.A.W.A.K., Mohd, A., da Silva, G., Bachmann, R.T., Taufiq-Yap, Y.H., Rashid, U., Alaa, H., 2013. Biochar production from waste rubber-wood-sawdust and its potential use in C sequestration: chemical and physical characterization. *Ind. Crops Prod.* 44, 18–24.
- Giwa, A., Yusuf, A., Ajumobi, O., Dzdizienyo, P., 2019. Pyrolysis of date palm waste to biochar using concentrated solar thermal energy: economic and sustainability implications. *Waste Manage.* 93, 14–22.
- Goyal, H., Seal, D., Saxena, R., 2008. Bio-fuels from thermochemical conversion of renewable resources: a review. *Renew. Sustain. Energy Rev.* 12 (2), 504–517.
- Guedes, R.E., Luna, A.S., Torres, A.R., 2018. Operating parameters for bio-oil production in biomass pyrolysis: a review. *J. Anal. Appl. Pyrol.* 129, 134–149.
- Gul, S., Whalen, J.K., Thomas, B.W., Sachdeva, V., Deng, H., 2015. Physico-chemical properties and microbial responses in biochar-amended soils: mechanisms and future directions. *Agric. Ecosyst. Environ.* 206, 46–59.
- Harsono, S.S., Grundman, P., Lau, L.H., Hansen, A., Salleh, M.A.M., Meyer-Aurich, A., Idris, A., Ghazi, T.I.M., 2013. Energy balances, greenhouse gas emissions and economics of biochar production from palm oil empty fruit bunches. *Resour. Conserv. Recycl.* 77, 108–115.
- Hu, Y., Wang, S., Li, J., Wang, Q., He, Z., Feng, Y., Abomohra, A.E.-F., Afonaa-Mensah, S., Hui, C., 2018. Co-pyrolysis and co-hydrothermal liquefaction of seaweeds and rice husk: comparative study towards enhanced biofuel production. *J. Anal. Appl. Pyrol.* 129, 162–170.
- Hu, Z., Zheng, Y., Yan, F., Xiao, B., Liu, S., 2013. Bio-oil production through pyrolysis of blue-green algae blooms (BGAB): product distribution and bio-oil characterization. *Energy* 52, 119–125.
- Hua, M.-Y., Li, B.-X., 2016. Co-pyrolysis characteristics of the sugarcane bagasse and *Enteromorpha prolifera*. *Energy Convers. Manage.* 120, 238–246.
- Huang, H.J., Yang, T., Lai, F.Y., Wu, G.Q., 2017. Co-pyrolysis of sewage sludge and sawdust/rice straw for the production of biochar. *J. Anal. Appl. Pyrol.* 125, 61–68.
- Isahak, W.N.R.W., Hisham, M.W., Yarmo, M.A., Hin, T.Y., 2012. A review on bio-oil production from biomass by using pyrolysis method. *Renew. Sustain. Energy Rev.* 16 (8), 5910–5923.
- Jae, J., Tompsett, G.A., Foster, A.J., Hammond, K.D., Auerbach, S.M., Lobo, R.F., Huber, G.W., 2011. Investigation into the shape selectivity of zeolite catalysts for biomass conversion. *J. Catal.* 279 (2), 257–268.
- Jafri, N., Wong, W., Doshi, V., Yoon, L., Cheah, K.H., 2018. A review on production and characterization of biochars for application in direct carbon fuel cells. *Process Saf. Environ. Prot.* 118, 152–166.
- Jang, H.M., Kan, E., 2019. A novel hay-derived biochar for removal of tetracyclines in water. *Bioresour. Technol.* 274, 162–172.
- Ji, C., Cheng, K., Nayak, D., Pan, G., 2018. Environmental and economic assessment of crop residue competitive utilization for biochar, briquette fuel and combined heat and power generation. *J. Cleaner Prod.* 192, 916–923.
- Jung, K.A., Lim, S.-R., Kim, Y., Park, J.M., 2013. Potentials of macroalgae as feedstocks for biorefinery. *Bioresour. Technol.* 135, 182–190.
- Kambo, H.S., Dutta, A., 2015. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renew. Sustain. Energy Rev.* 45, 359–378.
- Kan, T., Strezov, V., Evans, T.J., 2016. Lignocellulosic biomass pyrolysis: a review of product properties and effects of pyrolysis parameters. *Renew. Sustain. Energy Rev.* 57, 1126–1140.
- Kanaujia, P.K., Naik, D.V., Tripathi, D., Singh, R., Poddar, M.K., Konathala, L.S.K., Sharma, Y.K., 2016. Pyrolysis of *Jatropha Curcas* seed cake followed by optimization of liquid-liquid extraction procedure for the obtained bio-oil. *J. Anal. Appl. Pyrol.* 118, 202–224.
- Kwapinski, W., Byrne, C.M., Kryachko, E., Wolfram, P., Adley, C., Leahy, J.J., Novotny, E.H., Hayes, M.H., 2010. Biochar from biomass and waste. *Waste Biomass Valoriz.* 1 (2), 177–189.
- Lazdovica, K., Kampars, V., Liepina, L., Vilka, M., 2017. Comparative study on thermal pyrolysis of buckwheat and wheat straws by using TGA-FTIR and Py-GC/MS methods. *J. Anal. Appl. Pyrol.* 124, 1–15.
- Lee, J.W., Kidder, M., Evans, B.R., Paik, S., Buchanan Iii, A., Garten, C.T., Brown, R.C., 2010. Characterization of biochars produced from cornstovers for soil amendment. *Environ. Sci. Technol.* 44 (20), 7970–7974.
- Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems—a review. *Mitig. Adapt. Strat. Glob. Change* 11 (2), 403–427.
- Li, D., Chen, L., Chen, S., Zhang, X., Chen, F., Ye, N., 2012. Comparative evaluation of the pyrolytic and kinetic characteristics of a macroalga (*Sargassum thunbergii*) and a freshwater plant (*Potamogeton crispus*). *Fuel* 96, 185–191.
- Li, X., Xu, R., Yang, J., Nie, S., Liu, D., Liu, Y., Si, C., 2019. Production of 5-hydroxymethylfurfural and levulinic acid from lignocellulosic biomass and catalytic up-gradation. *Ind. Crops Prod.* 130, 184–197.
- Liu, Z., Quek, A., Hoekman, S.K., Balasubramanian, R., 2013. Production of solid biochar fuel from waste biomass by hydrothermal carbonization. *Fuel* 103, 943–949.
- Luo, G., Resende, F.L., 2016. In-situ and ex-situ upgrading of pyrolysis vapors from beetle-killed trees. *Fuel* 166, 367–375.
- Maddi, B., Viamajala, S., Varanasi, S., 2011. Comparative study of pyrolysis of algal biomass from natural lake blooms with lignocellulosic biomass. *Bioresour. Technol.* 102 (23), 11018–11026.
- Mani, S., Sokhansanj, S., Bi, X., Turhollow, A., 2006. Economics of producing fuel pellets from biomass. *Appl. Eng. Agric.* 22 (3), 421–426.
- Martínez, J.D., Veses, A., Mastral, A.M., Murillo, R., Navarro, M.V., Puy, N., Artigues, A., Bartroli, J., García, T., 2014. Co-pyrolysis of biomass with waste tyres: upgrading of liquid bio-fuel. *Fuel Process. Technol.* 119, 263–271.
- McKendry, P., 2002. Energy production from biomass (part 1): overview of biomass. *Bioresour. Technol.* 83 (1), 37–46.
- Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y., Holtzapple, M., Ladisch, M., 2005. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour. Technol.* 96 (6), 673–686.
- Muneer, B., Zeeshan, M., Qaisar, S., Razaq, M., Iftikhar, H., 2019. Influence of in-situ and ex-situ HZSM-5 catalyst on co-pyrolysis of corn stalk and polystyrene with a focus on liquid yield and quality. *J. Cleaner Prod.* 237, 117762.
- Nartey, O.D., Zhao, B., 2014. Biochar preparation, characterization, and adsorptive capacity and its effect on bioavailability of contaminants: an overview. *Adv. Mater. Sci. Eng.* 2014.
- Navarro, M.V., López, J.M., Veses, A., Callén, M., García, T., 2018. Kinetic study for the co-pyrolysis of lignocellulosic biomass and plastics using the distributed activation energy model. *Energy* 165, 731–742.
- Nhuchhen, D.R., Basu, P., Acharya, B., 2014. A comprehensive review on biomass torrefaction. *Int. J. Renew. Energy Biofuels* 2014, 1–56.
- Onay, O., Kocak, O.M., 2003. Slow, fast and flash pyrolysis of rapeseed. *Renew. Energy* 28 (15), 2417–2433.
- Ong, H.C., Chen, W.-H., Farooq, A., Gan, Y.Y., Lee, K.T., Ashokkumar, V., 2019. Catalytic thermochemical conversion of biomass for biofuel production: a comprehensive review. *Renew. Sustain. Energy Rev.* 113, 109266.
- Pandey, A., Bhaskar, T., Stöcker, M., Sukumaran, R., 2015. Advances in thermochemical conversion of biomass—Introduction. In: *Recent Advances in Thermochemical Conversion of Biomass*, first ed. Elsevier, pp. 504.
- Rangabhashyam, S., Balasubramanian, P., 2019. The potential of lignocellulosic biomass precursors for biochar production: performance, mechanism and wastewater application-A review. *Ind. Crops Prod.* 128, 405–423.
- Ren, X.-Y., Cao, J.-P., Zhao, X.-Y., Yang, Z., Liu, T.-L., Fan, X., Zhao, Y.-P., Wei, X.-Y., 2018. Catalytic upgrading of pyrolysis vapors from lignite over mono/bimetal-loaded mesoporous HZSM-5. *Fuel* 218, 33–40.
- Rezaei, P.S., Shafaghath, H., Daud, W.M.A.W., 2014. Production of green aromatics and olefins by catalytic cracking of oxygenate compounds derived from biomass

- pyrolysis: a review. *Appl. Catal. A* 469, 490–511.
- Roberts, K.G., Gloy, B.A., Joseph, S., Scott, N.R., Lehmann, J., 2009. Life cycle assessment of biochar systems: estimating the energetic, economic, and climate change potential. *Environ. Sci. Technol.* 44 (2), 827–833.
- Ross, A., Jones, J., Kubacki, M., Bridgeman, T., 2008. Classification of macroalgae as fuel and its thermochemical behaviour. *Bioresour. Technol.* 99 (14), 6494–6504.
- Sellin, N., Krohl, D.R., Marangoni, C., Souza, O., 2016. Oxidative fast pyrolysis of banana leaves in fluidized bed reactor. *Renewable Energy* 96, 56–64.
- Sewu, D.D., Boakye, P., Jung, H., Woo, S.H., 2017. Synergistic dye adsorption by biochar from co-pyrolysis of spent mushroom substrate and *Saccharina japonica*. *Bioresour. Technol.* 244, 1142–1149.
- Schmidt, H.-P., Wilson, K., 2012. 55 uses of biochar. *Ithaca J.* 1, 286–289.
- Shah, S.A.Y., Zeeshan, M., Farooq, M.Z., Ahmed, N., Iqbal, N., 2019. Co-pyrolysis of cotton stalk and waste tire with a focus on liquid yield quantity and quality. *Renew. Energy* 130, 238–244.
- Sharma, A., Wang, S., Pareek, V., Yang, H., Zhang, D., 2015. Multi-fluid reactive modeling of fluidized bed pyrolysis process. *Chem. Eng. Sci.* 123, 311–321.
- Smets, K., Adriaensens, P., Reggers, G., Schreurs, S., Carleer, R., Yperman, J., 2011. Flash pyrolysis of rapeseed cake: influence of temperature on the yield and the characteristics of the pyrolysis liquid. *J. Anal. Appl. Pyrol.* 90 (2), 118–125.
- Smets, K., Roukaerts, A., Czech, J., Reggers, G., Schreurs, S., Carleer, R., Yperman, J., 2013. Slow catalytic pyrolysis of rapeseed cake: product yield and characterization of the pyrolysis liquid. *Biomass Bioenergy* 57, 180–190.
- Stefanidis, S., Kalogiannis, K., Iliopoulou, E., Lappas, A., Pilavachi, P., 2011. In-situ upgrading of biomass pyrolysis vapors: catalyst screening on a fixed bed reactor. *Bioresour. Technol.* 102 (17), 8261–8267.
- Tripathi, M., Sahu, J.N., Ganesan, P., 2016. Effect of process parameters on production of biochar from biomass waste through pyrolysis: a review. *Renew. Sustain. Energy Rev.* 55, 467–481.
- Uchimiya, M., Bannon, D.I., Wartelle, L.H., 2012. Retention of heavy metals by carboxyl functional groups of biochars in small arms range soil. *J. Agric. Food. Chem.* 60 (7), 1798–1809.
- Uemura, Y., Matsumoto, R., Saadon, S., Matsumura, Y., 2015. A study on torrefaction of *Laminaria japonica*. *Fuel Process. Technol.* 138, 133–138.
- Uzoejinwa, B.B., He, X., Wang, S., Abomohra, A.E.-F., Hu, Y., He, Z., Wang, Q., 2019. Co-pyrolysis of macroalgae and lignocellulosic biomass. *J. Therm. Anal. Calorim.* 136 (5), 2001–2016.
- Uzoejinwa, B.B., He, X., Wang, S., Abomohra, A.E.-F., Hu, Y., Wang, Q., 2018. Co-pyrolysis of biomass and waste plastics as a thermochemical conversion technology for high-grade biofuel production: recent progress and future directions elsewhere worldwide. *Energy Convers. Manage.* 163, 468–492.
- Varma, A.K., Mondal, P., 2017. Pyrolysis of sugarcane bagasse in semi batch reactor: effects of process parameters on product yields and characterization of products. *Ind. Crops Prod.* 95, 704–717.
- Wang, B., Gao, B., Fang, J., 2017a. Recent advances in engineered biochar productions and applications. *Crit. Rev. Environ. Sci. Technol.* 47 (22), 2158–2207.
- Wang, J., Zhang, M., Chen, M., Min, F., Zhang, S., Ren, Z., Yan, Y., 2006. Catalytic effects of six inorganic compounds on pyrolysis of three kinds of biomass. *Thermochim. Acta* 444 (1), 110–114.
- Wang, L., Chai, M., Liu, R., Cai, J., 2018a. Synergetic effects during co-pyrolysis of biomass and waste tire: a study on product distribution and reaction kinetics. *Bioresour. Technol.* 268, 363–370.
- Wang, S., Cao, B., Feng, Y., Sun, C., Wang, Q., Abomohra, A.E.-F., Afonaa-Mensah, S., He, Z., Zhang, B., Qian, L., 2019a. Co-pyrolysis and catalytic co-pyrolysis of *Enteromorpha clathrata* and rice husk. *J. Therm. Anal. Calorim.* 135 (4), 2613–2623.
- Wang, S., Dai, G., Yang, H., Luo, Z., 2017b. Lignocellulosic biomass pyrolysis mechanism: a state-of-the-art review. *Prog. Energy Combust. Sci.* 62, 33–86.
- Wang, S., Jiang, D., Cao, B., Hu, Y., Yuan, C., Wang, Q., He, Z., Hui, C.-W., Abomohra, A.E.-F., Liu, X., 2018b. Study on the interaction effect of seaweed bio-coke and rice husk volatiles during co-pyrolysis. *J. Anal. Appl. Pyrol.* 132, 111–122.
- Wang, S., Jiang, D., Cao, B., Qian, L., Hu, Y., Liu, L., Yuan, C., Abomohra, A.E.-F., He, Z., Wang, Q., 2018c. Bio-char and bio-oil characteristics produced from the interaction of *Enteromorpha clathrata* volatiles and rice husk bio-char during co-pyrolysis in a sectional pyrolysis furnace: a complementary study. *J. Anal. Appl. Pyrol.* 135, 219–230.
- Wang, S., Wang, Q., Hu, Y., Xu, S., He, Z., Ji, H., 2015. Study on the synergistic co-pyrolysis behaviors of mixed rice husk and two types of seaweed by a combined TG-FTIR technique. *J. Anal. Appl. Pyrol.* 114, 109–118.
- Wang, S., Wang, Q., Jiang, X., Han, X., Ji, H., 2013. Compositional analysis of bio-oil derived from pyrolysis of seaweed. *Energy Convers. Manage.* 68, 273–280.
- Wang, Z., Xie, L., Liu, K., Wang, J., Zhu, H., Song, Q., Shu, X., 2019b. Co-pyrolysis of sewage sludge and cotton stalks. *Waste Manage.* 89, 430–438.
- White, J.E., Catallo, W.J., Legendre, B.L., 2011. Biomass pyrolysis kinetics: a comparative critical review with relevant agricultural residue case studies. *J. Anal. Appl. Pyrol.* 91 (1), 1–33.
- Wu, Z., Li, Y., Xu, D., Meng, H., 2019. Co-pyrolysis of lignocellulosic biomass with low-quality coal: optimal design and synergistic effect from gaseous products distribution. *Fuel* 236, 43–54.
- Xu, S., Hu, Y., Wang, S., He, Z., Qian, L., Feng, Y., Sun, C., Liu, X., Wang, Q., Hui, C., 2019a. Investigation on the co-pyrolysis mechanism of seaweed and rice husk with multi-method comprehensive study. *Renew. Energy* 132, 266–277.
- Xu, S., Uzoejinwa, B.B., Wang, S., Hu, Y., Qian, L., Liu, L., Li, B., He, Z., Wang, Q., Abomohra, A.E.-F., 2019b. Study on co-pyrolysis synergistic mechanism of seaweed and rice husk by investigation of the characteristics of char/coke. *Renew. Energy* 132, 527–542.
- Xu, Y.-P., Duan, P.-G., Wang, F., 2015. Hydrothermal processing of macroalgae for producing crude bio-oil. *Fuel Process. Technol.* 130, 268–274.
- Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C., 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 86 (12–13), 1781–1788.
- Yildiz, Z., Ceylan, S., 2018. Pyrolysis of walnut shell biomass in fluidized bed reactor: determination of optimum conditions for bio-char production. *Environ. Res. Technol.* 1 (4), 47–51.
- Yu, K.L., Lau, B.F., Show, P.L., Ong, H.C., Ling, T.C., Chen, W.-H., Ng, E.P., Chang, J.-S., 2017. Recent developments on algal biochar production and characterization. *Bioresour. Technol.* 246, 2–11.
- Yuan, C., Wang, S., Cao, B., Hu, Y., Abomohra, A.E.-F., Wang, Q., Qian, L., Liu, L., Liu, X., He, Z., 2019. Optimization of hydrothermal co-liquefaction of seaweeds with lignocellulosic biomass: merging 2nd and 3rd generation feedstocks for enhanced bio-oil production. *Energy* 173, 413–422.
- Zaid, A.A., Taiwo, G., 2008. Comparative utilization of biodegraded ricehusk. *J. Fish. Aquat. Sci.* 3 (5), 312–319.
- Zhang, H., Xiao, R., Huang, H., Xiao, G., 2009. Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor. *Bioresour. Technol.* 100 (3), 1428–1434.
- Zhang, S., Hu, B., Zhang, L., Xiong, Y., 2016. Effects of torrefaction on yield and quality of pyrolysis char and its application on preparation of activated carbon. *J. Anal. Appl. Pyrol.* 119, 217–223.
- Zhang, X., Cresswell, M., 2016. Chapter 3—materials characterization of inorganic controlled release. *Inorg. Controlled Release Technol.* 57–91.
- Zhang, Z., Zhu, Z., Shen, B., Liu, L., 2019. Insights into biochar and hydrochar production and applications: a review. *Energy*.
- Zhu, X., Luo, Z., Diao, R., Zhu, X., 2019. Combining torrefaction pretreatment and co-pyrolysis to upgrade biochar derived from bio-oil distillation residue and walnut shell. *Energy Convers. Manage.* 199, 111970.