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Chapter

A Mini Review of Biochar Synthesis, Characterization, and Related Standardization and Legislation

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Abstract

The abundance of biomass in Malaysia creates an avenue for growth of bio-economic sector through the research and development (R&D) activities on the biochar production. Biochar that is described as a carbonaceous material derived from the thermochemical process at temperature of usually lower than 700°C is promising due to its applicability in wider range of applications, such as in soil amendment (fertilizer) and as a low-cost adsorbent for the pollution remediation, apart from minimizing the solid waste disposal problems. Therefore, this chapter discusses the current trends on various production techniques of biochar from both the lignocellulosic (plantation based waste materials) and non-lignocellulosic sources, as well as the physiochemical characteristics of the resulting biochar. In addition, overview of the biochar industry in Malaysia is presented in this chapter. Lastly, recap of standardization and legislation particularly related to the biochar utilization as a soil amendment agent is included to grasp readers' attention prior to the large scale applications.

Keywords: biochar, biomass, environmental standardization and legislation, pyrolysis, soil amendment, waste management

1. Introduction

Biochar, which is a subset of carbon-rich and black powder, is generally defined as a porous solid that is produced from biomass via pyrolysis process and in the absence of oxygen (O_2) [1]. Nevertheless, based on literatures, there are various definitions of the biochar [2–4]; accordingly, Sohi et al. [5] reported that the term of biochar remains ill-defined. Thus, the International Biochar Initiative (IBI) standardized the biochar "as a solid material obtained from the thermochemical conversion of biomass in O_2 -limited environments." While the production route of biochar and charcoal is similar where both materials are derived from the carbonaceous feedstock through the pyrolysis process [6], but the distinct features that can distinguish these two materials lies in their starting material and end application. Biochar that contains high porosity, high nutrient content, and waterstorage-capability is applied for soil amelioration or an adsorbent, whereas charcoal that is usually derived from the petroleum-based feedstock is used for heat generation (energy/fuel) purposes [3, 7]. In a nutshell, Mesa et al. [2] reported that the term biochar is not applicable for the charred materials used as a solid fuel, and to exclude the black carbon produced from non-renewable resources such as coal and petroleum. Besides, Abdelhafez et al. [8] reported that biochar contains lower ash compounds as compared to charcoal, due to an incomplete carbonization process. Further, due to wider application of biochar in both agronomic sector as well as in environmental management, Verheijen et al. [9] reported that the global market of biochar is rapidly growing, with the global market price is estimated around \$80–13,480/oven dried metric ton (ODMT). In addition, Hersh et al. [10] reported that the global biochar market is projected to increase up to \$3.14 billion by 2025, and expand at an average rate of 13.1% annually [11]. Due to the growing interest of the biochar production and application, number of scientific publications related to the biochar is gradually increasing (as presented in Figure 1), where most of these publications (since 2016) are from Republic of China, USA, Australia, South Korea, and India. Herein, this chapter aims to highlight the recent advancement of the biochar production from various processing techniques, as well as an overview on the biochar standardization (quality standard) and legislation, particularly for its application as soil amendment agent.

So far, research work on the biochar-related field in Malaysia is extensive in local universities and research institutes, where Universiti Putra Malaysia (UPM) is the leading organization in the biochar research. Being a pioneer in biochar research, UPM researchers in collaboration with Nasmech Technology has successfully built the first large scale biochar production plant within the region (as shown in **Figure 2**) in January 2010 [12, 13], where the carbonator is capable to accommodate up to 20 tons of different types of waste materials daily for the biochar production. Hypothetically, opportunities of biochar industry in Malaysia can be attributed to lower labor cost, low or no cost incurred of biomass, large agricultural industry, as well as fast-growing biomass. In fact, Ozturk et al. [14] reported that Malaysia produces about 168 million tons of biomass annually. Nevertheless, Kong et al. [15]

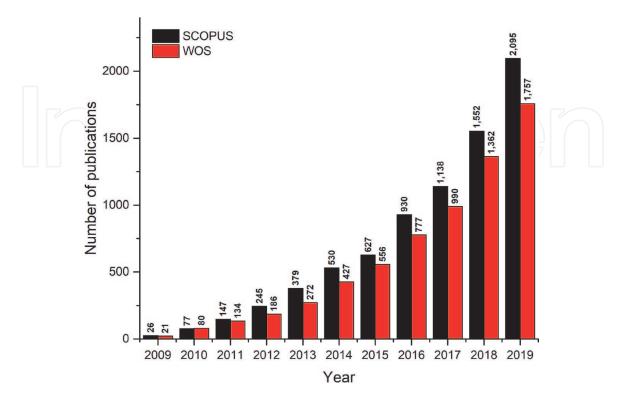


Figure 1. Number of biochar-related publications from 2009 to 2019 from Web of Science (WOS) and SCOPUS database.



Figure 2. Biochar plant in Dengkil, Selangor, Malaysia [18].

reported that the main challenge in biochar production in Malaysia is due to the physiochemical nature of biomass (particularly oil palm biomass) itself; where wet biomass will result in transportation problems from the source to production sites, thus need an additional drying process apart from normal pre-treatments such as chopping, shredding, and grinding stages. Consequently, this will increase both production cost and equipment's capital investment. Besides, difficulty in gaining a long-term contract basis between the biomass suppliers, producers, investors, and potential end users, is one of the major barriers in the biochar production in Malaysia [15, 16]. Due to these problems and the lack of key players along the value chain, biochar's production is rather costly, accordingly, Tang et al. [17] reported that commercialization of biochar in Malaysia is relatively new and still at an early stage. Based on literatures, biochar providers in Malaysia include the following: Global Green Synergy Sdn. Bhd., Pakar Go Green Sdn. Bhd., Usaha Strategik Sdn. Bhd., and CH Biotech Sdn. Bhd. In addition, realizing the prominence of the biochar industry toward the socio-environmental economy, Biochar Association Malaysia (BMA) has been established in 2014 with the missions are to promote the biochar production and application in both agricultural and industrial sector, to stimulate publics' awareness on the role of biochar as a carbon sequester, and as a platform for idea and information exchange in promoting the biochar industry in Malaysia. In addition, to further promote the advancement of biochar industry in Malaysia, key players including researchers, authorities, and business analysts should work closely together.

2. Production of biochar

Biochar can be produced from various types of biomass which include the lignocellulosic (i.e., bioenergy crop, agricultural waste, forestry residues) and non-lignocellulosic groups (i.e., manure, sewage sludge, microalgae) [19, 20]. To date, agricultural waste is the primary feedstock used for the biochar production, as confirmed in **Table 1**. Regardless of the different types of feedstock, the biochar's

Biomass	Process conditions		Fir	Findings	
	Temp (°C)	time (min)	Yield (%)	Capacity	-
Heavy metals remova	ıl (i.e., cadmium,	copper, lead, zii	nc, etc.)		
Cocoa pod	500	120	n/a	69.9 mg/g	[24]
EFB	615	128	25.49	15.18 mg/g	[25]
EFB	300	180	n/a	85 mg/g	[26]
Sludge	n/a	60	n/a	19 mg/g	[27]
Sludge	400	90	64.2	48.8 mg/g	[28]
Color/dyes removal (i.e., methylene b	lue, malachite gr	een)		
Cassava stem	500	120	11.94	40.5 mg/g	[29]
Coconut frond	800	240	n/a	126.58 mg/g	[30]
Palm shell	700 W	25	33	48 mg/g	[31]
Seaweed	800	90	n/a	512.67 mg/g	[32]
Sugarcane bagasse	600	120	n/a	99.47%	[33]
Phenolic compounds	removal				
EFB	500	80.27	n/a	7.38%	[34]
Gas/vapor adsorption	n (i.e., CO ₂ , merc	ury, sulfur dioxi	de)		
Coconut pith	900	60	27.76	6067.49 µg/g	[35]
Coconut pith	700	60	31.42	10 mmol/g	[36]
Sludge	405	88	54.25	9.75 mg/g	[37]
Wood sawdust	650	60	n/a	18 mg/g	[38]
Soil-based application	n (herbicides/pes	ticides removal,	fertilizer)		
EFB	300	60	n/a	4.497	[39]
Rice husk	300	180	n/a	4.742	[39]
Palm shell	700 W	25	33	450 g	[31]

Table 1.

Summary of recent biochar production in Malaysia from local biomass and the corresponding optimum conditions.

skeleton is primarily comprised of carbon and ash, where the overall compositions and characteristics of each biochar varied, depending on the types of feedstock and the process conditions. Filiberto et al. [20] reported that the significant difference between the nutrient-rich feedstocks such as animal manure and sewage sludge, compared to the lignin-rich biomass feedstock is that the former materials contain considerably high nutrient and mineral compositions (i.e., nitrogen, phosphorus, potassium, etc.). In context of heavy metal removal application, Zhao et al. [21] reported that the sewage sludge biochar that has higher mineral contents (161 g/kg) compared to corn biochar (28.6 g/kg) and poplar wood biochar (19.5 g/kg) contributes to higher heavy metal removals from wastewater (sewage sludge > corn > poplar wood), thus implies the importance of the mineral compositions in heavy metal adsorption process. Likewise, for the soil amendment application (in terms of element supplementation and liming effect), Zhang et al. [22] also agreed that the biochar should contain a sufficient mineral composition. Meanwhile in context of the process technologies, biochar can be produced from four thermochemical routes that include pyrolysis, torrefaction, hydrothermal carbonization, as well as gasification, [23]; which is thoroughly described in the following subsections.

2.1 Pyrolysis

By definition, pyrolysis is the thermal conversion process conducted in absence of O₂; producing biochar, condensable liquid (i.e., bio-oil), and non-condensable gas (i.e., syngas). The yield distribution depends on the type of pyrolysis process—slow, fast, and flash pyrolysis; where it differs in terms of reaction temperature, heating rate, and holding time (as summarized in **Table 2**).

Referring to **Table 2**, the ideal route for the biochar production is through slow pyrolysis, also known as conventional carbonization, as compared to fast or flash pyrolysis that targets bio-oil production. Recently, Yuan et al. [42] confirmed that walnut shell biochar obtained through slow pyrolysis process has greater biochar yield as compared to the fast pyrolysis, irrespective of reaction temperature, thus it confirms the effectiveness of the slow pyrolysis mechanism toward the biochar production. Furthermore, slow pyrolysis for the biochar production is promising due to lower capital investment as compared to fast pyrolysis scheme (\$132 vs. \$200 million) [43]. Basically, Daful et al. [44] reported that biochar from slow pyrolysis route refers to primary and secondary char, where the mechanism of the process is simplified in Eqs. (1)-(3) [45]. The pre-pyrolysis reaction [Eq. (1)] involves the water elimination and evaporation from the biomass structure. During the primary reaction, devolatilization process including the dehydration, decarboxylation, and dehydrogenation occurs. Then upon the completion of primary decomposition, the secondary reaction (at high temperature) that refers to cracking of heavy organic compounds as well as repolymerization ensues, producing a stable and carbondense solid product (i.e., biochar) and non-condensable syngas such as methylene (CH_2) , methane (CH_4) , carbon monoxide (CO), and carbon dioxide (CO_2) [45–48].

 $Biomass \rightarrow water + unreacted residue (Pre-pyrolysis)$ (1)

Unreacted residue \rightarrow (volatiles + gases) + char (Primary reaction) (2)

 $Char \rightarrow (volatiles + gases) + char (Secondary reaction)$ (3)

2.2 Torrefaction

Torrefaction or known as a mild pyrolysis refers to the thermochemical process at temperature of 200–300°C at atmospheric pressure and inert atmosphere, heating rate of \leq 50°C/min, with residence time of 30 min to 2 h [44, 49].

Conditions		Slow pyrolysis	Fast pyrolysis	Flash pyrolysis
Temperature (°C)		300–700	550-1000	800–1100
Heating rate (°C/sec)		0.1–1	10–200	>1000
Vapor residence time (sec)		450–550	0.5–10	< 0.5
Particle size (mm)		5–50	<1	< 0.2
Yield (wt. %)	Biochar	35	20	12
	Bio-oil	30	50	75
	Syngas	35	30	13

Bold value refers to the highest product yield of slow pyrolysis, fast pyrolysis and flash pyrolysis. In summary, for the slow pyrolysis, the bold value is for biochar, while for fast and flash pyrolysis, the bold value is for the bio-oil. In other words, the slow pyrolysis favors the biochar production, and both fast and flash pyrolysis targets the bio-oil.

Table 2.

Process conditions for slow (conventional), fast, and flash pyrolysis and product distribution [40, 41].

Nevertheless, it has been reported that the torrefaction process is not a promising technique for the biochar production, regardless of higher product yield (70–80 wt. %), since the torrefied biomass still contains a significant fraction of volatile components from the raw biomass, and the physiochemical properties are in between raw biomass and biochar [44, 50]. For example, oxygen to carbon (O/C) ratio of the torrefied biomass which is >0.4 contradicts with the European Biochar Certification (EBC) of biochar [44]. Therefore, this torrefaction process is often being applied as a pre-treatment process for moisture removal, biomass densification, and to improve the biomass properties. Besides, while the torrefaction process alone cannot be used for biochar production, combination of torrefaction pretreatment and pyrolysis is feasible for the exceptional biochar production (in terms of yield) in addition to the physiochemical characteristics (i.e., surface area) [51–54].

2.3 Hydrothermal carbonization

Opposite to the slow pyrolysis and torrefaction process that is normally carried out under dry atmosphere, hydrothermal carbonization can also be referred as wet pyrolysis or wet torrefaction; since this process is performed in a biomass-water solution at temperature of 180–250°C at high pressure (subcritical condition) for several hours [50, 55–57]. Similar to pyrolysis, this hydrothermal carbonization produces 50-80 wt. % solid char (termed as hydrochar), bio-oil and water mixture (5–20 wt. %), and synthetic gas that is mainly CO_2 (2–5 wt. %) [58]. The great interest in this hydrothermal technology for the biochar production is that it can avoid the preliminary energy-intensive drying process that is usually required for the conventional pyrolysis, and thus it will minimize the operational costs. Besides, Oktaviananda et al. [59] agreed that such process is convenient for the biomass having >50 wt. % moisture content. On top of that, it has been reported that the energy requirement for hydrothermal carbonization and pyrolysis process for 1 kg of feedstock of 80% moisture content is 2.5 and 3.20 MJ, respectively [60]. Moreover, this hydrothermal technology offers the lowest reaction temperature as compared to other thermochemical conversion techniques. During the process, water (H_2O) acts as a solvent, reactant, catalyst, and as a medium for both mass and energy transfer [61], where it will facilitate the hydrolysis, dehydration, decarboxylation and depolymerization process [62]. Besides, at temperature of 200–280°C, H₂O that possesses similar behavior to mild acid and mild base at the same time results in an acceleration of biomass decomposition [61, 63]. Specifically, Libra et al. [64] reported that during the hydrothermal carbonization, hemicellulose decomposes at temperature of 180–200°C, lignin decomposition takes place at 180–220°C, whereas cellulose decomposition occurs at 220°C. However, most often, the hydrochar cannot be described as biochar since the reaction temperature is too low, low carbon contents, as well as an intolerable O/C and hydrogen to carbon (H/C) ratio [65, 66]. Yet, recent work shows that integration of this hydrothermal carbonization with pyrolysis process positively contributes toward the high-quality biochar production and can stabilizes the heavy metal in solid products [67]. For example, by referring to the experimental findings by Olszewski et al. [68], the preliminary hydrothermal treatment of brewery spent grains (that contains 70–90 wt. % moisture) prior to the pyrolysis process produces biochar with greater product yield and carbon contents as well as reduced ash compositions; where the corresponding value is varied, subjected to the intensity of the hydrothermal carbonization process. Likewise, Garlapalli et al. [69] confirmed that the carbon compositions of biochar from the combined hydrothermal and pyrolysis process (at 260 and 800°C, respectively) increases to 82 wt. % compared to standalone hydrothermal process, where the carbon contents is merely 70 wt. %. Moreover,

such combined processes also show an improvement of the surface area (63.48 m²/g vs. 2.93 m²/g). In overall, the upgrading of hydrochar is crucial since the hydrochar that possesses low surface area (<30 m²/g), low porosity, and presence of noxious chemicals (i.e., furan, furfural, and phenolic compounds) limits its application in soil amelioration [69].

2.4 Gasification

The gasification process takes place at the temperature range of 600-1200°C, heating rate of 50–100°C/min, with vapor residence time of 10–20 s. Unlike the pyrolysis, gasification process is carried out in the presence of O_2 (including O_2 , air, steam, CO_2 , or mixture of the gases) and primarily used for the syngas production (i.e., CO, CO_2 , CH₄, hydrogen [H₂]) instead of the biochar production. Due to this, the biochar yield is minimal (<10 wt. %) [44, 56]. With regards to this limitation, there are limited research works on the feasibility of biochar from the gasification process especially for soil amendment purpose [70]. In addition, Wang and Wang [71] reported that the charred product from the gasification process do not satisfy the biochar's definition; in addition to presence of hazardous polycyclic aromatic hydrocarbons (PAHs) as well as alkaline and alkaline heavy metals within the structure [55, 56].

3. Biochar's characterization, standardization, and legislations

The detailed characterization of biochar prior to any applications is significant in order to determine the relationship between nature and operating conditions with the physiochemical properties of biochar, to evaluate the suitability of biochar in desired target application, and to examine the presence of contaminants and eco-toxicology properties [72]. The overall characterization techniques that have been applied for biochar are summarized in **Table 3**.

Given that the biochar's characteristics is mainly influenced by various parameters such as feedstocks' type, technology (i.e., process type, reactor configuration), and process condition (i.e., temperature, heating rate, residence

Characterization	Detailed analysis			
Physical property	 Surface area, pore volume and size (N₂ gas sorption) Particle size distribution (Laser sizing) Density (Mercury porosity, Pycnometer) 			
Chemical property	 pH (<i>pH meter</i>) Electrical conductivity (<i>Conductivity meter</i>) Cation exchange capacity (<i>Ion chromatography</i>) Biochar compositions (<i>CHNS, EDS, XPS</i>) Metallic/ash contents (<i>XRD, ICP, XRF</i>) Proximate analysis (<i>Muffle furnace, TGA</i>) Surface functionality (<i>FTIR, Raman</i>) Surface acidity/alkalinity (<i>Boehm titration</i>) Surface aromaticity (¹³C NMR, Raman spectroscopy) 			
Surface structure & morphology	 SEM/FESEM TEM Crystallinity (<i>XRD</i>, <i>Raman</i>) 			
Stability behavior	• TGA-DSC			

Table 3.

Summary of biochar's detailed characterization [19, 46, 64, 71–74].

Applications of Biochar for Environmental Safety

Property	IBI-BS	EBC		BQM	
		Basic	Premium	Standard	High gr.
Organic C (wt. %)	≥10	≥50		≥1	0
H:C molar ratio	≤0.7	≤0.7		≤0.7	
O:C molar ratio	_	≤0.4		_	
Moisture	_		≥30	≥20	
Fotal ash (wt. %)	1		/	\checkmark	
Conductivity		1		Optional	
Liming equiv. pH			$\frac{1}{\sqrt{2}}$	$\left - \right\rangle \left(\frac{4}{5} \right)$	
Particle size distr.					
Surface area	v			-	
		0	ptional	Optional	
Water holding capacity	Ontional	0	-	<i>√</i>	
Volatile matter (%) Germination test	Optional Pass/fail				
	Pass/Tall	0	ptional		-
Macro-nutrients (wt. %)					
Total N		v			
Total P, K, Mg, Ca	Optional		\checkmark	✓ (Total	Р&К)
Organic pollutants (mg/kg)	6.000				
PAH (US EPA 16)	6–300	<12	<4	<20	<20
B(a) P toxic equi.	≤3	—	—	—	—
РСВ	0.2–0.5	<0.2		< 0.5	
PCDDs/Fs	<17	<20		<20	
Heavy metals (mg/kg)—maxi	mum limit				
Arsenic	12–100		_	100	10
Cadmium	1.4–39	1.5	1	39	3
Chromium	64–1200	90	80	100	15
Cobalt	40–150	_		_	
Copper	63–1500	100	100	1500	40
Lead	70–500	150	120	500	60
Mercury	1–17	1	1	17	1
Manganese	_	_	_	n/a	3500
Molybdenum	5–20	_	_	75	10
Nickel	47–600	50	30	600	10
Selenium	2–36	_	_	100	5
Zinc	200–7000	400	400	2800	150
Boron	1		_		-
Chlorine	1		_		-
Sodium	1		_		_

Table 4.Summary of biochar certification based on IBI-BS (Ver. 2.0), EBC (Ver. 4.8), and BQM Ver. 1.0.

time, pressure, carrier gas); the corresponding properties of biochar are widely varied. Therefore, the standardization of biochar prior to applications is significant as their performance can be generalized and predicted [64, 75]. To date, the biochar standards have been established by the International Biochar Initiative (IBI-BS), European Biochar Foundation (European Biochar Certificate, EBC); as well as the British Biochar Foundation (Biochar Quality Mandate, BQM) [76–78]. Referring to Verheijen et al. [9], the common objectives of these certifications are to provide the quality and safety indicator for biochar utilization as a soil amendment agent, to promote the biochar's industrial growth and commercialization, as well as for future legislative or regulations. Besides, development of such certifications assists in improving the confidence level of consumers and regulators of the biochar's safe application [79]. Thereby, the parameters and their corresponding threshold values in each biochar certificate are tabulated in **Table 4**.

However, Gelardi et al. [80] reported that variation between these certifications will led to inconsistencies in both scientific and legislative framework, accordingly, there is an urgent need to come out with a unified regulations that can benefit the communication in academics field and in the biochar market. In addition, it should be noted that these certifications are only applicable for the biochar categorization and their suitability as soil amendment agent, and to exclude the hydrochar [65]. Hence, more data and research work toward the hydrochar characterization and appropriate certificates that enable commercial hydrochar utilization is strongly recommended. In addition, since these certifications are only valid for the biochar usage in soil application, it is recommended to produce a detailed assessment and guideline for the biochar utilization in other environmental applications too [74].

4. Conclusions and future outlook

Biomass valorization to biochar materials has gained a significant attention due to its exceptional characteristics—high surface area, high pore volume, long-term stability, and presence of various surface functionalities, as well as wider potential application including energy and biomaterial development, agronomy sector (i.e., soil amelioration, fertilization), and environment pollution control; among others. Given the slow pyrolysis process is the most promising technique for the biochar production, more research studies on the various types of biomass need to be considered as the biochar field is rather a non-exhaustive subject, in addition to the continuous advancement toward cleaner, simpler, and inexpensive biochar production. In addition, a comprehensive analysis on different types of biomass (including agricultural, aquaculture, forestry, human and animal waste, as well as industrial waste) will result in a complete database; mainly focus on the influence of operating parameters toward the process performance, in terms of reaction rate and underlying mechanism, yield, selectivity, biochar's characteristics, as well as energy and mass balance; which are useful for practitioners and future researchers. In addition, from the databases, it is practical for ranking the biomass suitability for the biochar production for specific applications, accordingly facilitates a proper planning on biomass utilization in biochar industry. Besides, the recent work on both the biochar production and utilization is limited to the laboratory scale, thus upscaling the research work to a larger scale is necessary in order to determine the practicality. Finally, techno-economic analysis as well as life cycle assessment of the biochar production through various technologies is recommended. Overall, viability of the biochar industrial sector needs to incorporate the social, technical, economic, and environmental aspects to ensure its sustainability.

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Conflict of interest

The auth	ors declare no	conflict of i	nterest.

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