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Impact of Pyrolysis Temperature and Water Quenching on Hydrophilicity of Biochar derived from Durian Wood Waste

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It becomes critical to have knowledge of the physicochemical properties of hydrophilic biochar. This study was aimed to analyze the water quenching effect on biochar hydrophilicity at various pyrolysis temperatures. The raw material was obtained from durian wood (Durio zibethinus) waste. Biochar was produced by durian wood waste pyrolysis with oxygen absence in temperature pyrolysis of 350 °C, 450 °C, 550 °C for 2 hours. Following the pyrolysis process, hot biochars were guenched with water for 30 minutes. In particular, the hydrophilicity of biochar was measured using contact angle measurement. Furthermore, we analyzed the proximate and elemental composition of biochar, including pH. Morphological features of biochar were examined by SEM and the characterization of the biochar structure was analyzed using FTIR. The results indicated that water quenching of biochar resulted in hydrophilic biochar pyrolyzed starting at 450 °C. The morphology of biochar showed an increase in the number of pore structure and generated highly ordered microporous biochar due to hot quenching. The high pyrolysis temperature increased pH, fixed carbon, C and ash content of biochar, whereas vice versa for the yield, volatile matter, oxygen, hydrogen, O/C and H/C ratios. There was no different organic functional group between water-guenched biochars and fresh biochars. However, they became more aromatic with increasing temperatures. Water-quenched biochar at 550 °C, with contact angle 48.85°, volatile matter 13.93%, fixed carbon 78.07%, total carbon 82.03%, hydrogen 3.11%, oxygen 11.29%, and pH 9.07, was highly recommended to improve acidic soil.

Keywords: pyrolysis temperature, water quenching, hydrophilic biochar, physicochemical analysis, contact angle

INTRODUCTION

Biochar is charcoal form, made from many feedstocks including dairy manure, municipal solid and lignocellulosic biomass (Demirbas, 2004, Demirbas, 2006, Kwapinski et al. 2010, Chowdhury et al. 2016, Li et al. 2016). Several authors proved that the lignocellulosic biochar can increase characteristic of soil, for instance pH, nutrient contents, water storage capacity and microbial diversity (Joseph et al. 2010, Yuan and Xu, 2011, Liu et al. 2012, Abel et al. 2013, Jien and Wang, 2015, de Melo Carvalho et al. 2014, Hardie et al. 2014, Frišták and Soja, 2015, Lehman and Joseph, 2015, Burrell et al. 2016). Lianocellulosic materials. includina woodv biomass (Esmaeelnejad et al. 2017, Rhoades et al. 2017), corn cob (Chen et al. 2015, Shariff et al. 2016), rice husk (Cheng and Wang, 2017), have significantly been used to produce biochar. Materials derived from wood and waste wood contain a high content of lignin and cellulose and low nutrients (Suliman et al. 2016, Domingues et al. 2017). In consequence of variation in lignin content of lignocellulosic materials, the biochars may vary in yield. Pyrolysis of wood-derived biomass has the highest yield of biochar (Kloss et al. 2012, Li et al. 2014, Yargicoglu et al. 2015, Wang et al. 2015, Bandara et al. 2016, Zhao et al. 2017). Having a tropical climate, Indonesia has an abundance of sources of woody biomass (Wulandari et al. 2014, Yuliansyah and Amirta, 2016) and tropical soils (Wulandari et al. 2014). Woody biochar is believed able to increase C storage and improve soil characteristic (Jeffery et al. 2013, Domingues et al. 2017, Chao et al. 2018, Cornelissen et al. 2018, Lin et al. 2018, Pandit et al. 2018). Hence woody biomass has a high prospect to be used as biochar feedstock in Indonesia.

Biochar characterization is the main factor to determine their industrial and environmental application (Zhu et al. 2018). Biochar is being considered for various applications in agriculture as a soil amendment or in ecological remediation (Sizmur et al. 2016, Igalavithana et al. 2016, Muegue et al. 2017). It must be well understanding to have a concept about how to produce high quality of biochar (Sing et al. 2010. Das and Sarmah, 2015) which cause it hydrophilic or hydrophobic due to its utilities. Biomass which is pyrolyzed at low temperatures will become hydrophobic (Novak et al. 2009, Kinney et al. 2012, Das and Sarmah, 2015). Hydrophobic biochar has aliphatic functional groups (Novak et al. 2009) which can remove harmful organic and inorganic materials from the polluted substance (Sarmah et al. 2010). In agricultural application, interactions of biochar/soil are occasionally complicated. One key factor of biochar-soil interactions is the ability of biochar to absorb and resist water. Fresh biochar produced by low pyrolysis tends to be hydrophobic (Basso et al. 2013, Brantley et al. 2015, Blanco-cangui, 2017, Zhu et al. 2018) due to many chemical compounds on biochar surface (Brantley et al. 2015, Zhu et al. 2018). As nutrient exchange site, hydrophobic biochar can improve soil quality.

However, it is not recommended for soil water storage because it is water-repellent (Sun et al. 2011). Previous studies have been notified that produced hydrophobicity of biochar from conventional pyrolysis. Very few studies to date have investigated the pyrolysis condition to the hydrophilicity of biochar (Yi et al. 2015, Bubici et al. 2016, Zornoza et al. 2016). Hydrophilic biochar improves water permeability by giving high soil wettability (Rattanakam et al. 2017) due to its ability to absorb and retain water. Hence the soil's performance can be improved and available during periods of low precipitation and hot or dry soil conditions (Taylor, 2010). Feedstocks and pyrolysis conditions affect the biochar hydrophilicity (Aston et al. 2014). Pyrolysis temperature influences biochar alkalinity (Sun et al. 2018) and its physicochemical properties (Yargicoglu et al. 2015. Khanmohammadi et al. 2015, Jiang et al. 2016, Widowati et al., 2017, Wei et al. 2019). Its alkalizing effect is recommended to increase acidic soil pH and provide a longer-term nature as a stable organic matter (Šimanský and Klimaj, 2017). Méndez et al. (2012) stated that sewage sludge biochar which pyrolyzed above 500 °C would produce high alkalinity. Moreover, structural modification of biochar has appeared when biochar is pyrolyzed until 550 °C (Pituello et al. 2015). Biochar surfaces become hydrophilic when oxidized on contact with air and water (Basso et al. 2013). The principle of water quenching processes is to minimize potential blockages (Brown, 2009). When hot biochar is guenched with water, the biochar dust will be decreased (Major, 2010). In addition, when the water is added to the hot biochar, it evaporates and become active. The hot water vapor is released and reacted with biochar pore condensate to produce cleaned biochar. Therefore the biochar porosity and its inner surface area are increased (Schmidt et al. 2014). Hence water guenching can trigger of biochar to be more efficient and partly activates. It is clear that the post-pyrolysis step can be undertaken that modify the original biochar and affects the subsequent performance in the soil. The modification through water guenching is a part of creating the initial biochar. Therefore the biochar should be tested post-modification.

In this context, we hypothesized that water quenching would provide hydrophilic biochar. However, it can be effected by pyrolysis temperature as well as by feedstock and posttreated modification. In consequence, this study was aimed to analyze the water quenching effect on the biochar hydrophilicity at various pyrolysis temperatures derived from durian wood waste. Physicochemical properties of durian wood waste biochar were examined in this study.

MATERIALS AND METHODS Feedstock Preparation

Durian wood wastes for biochar production were collected from the sawmill industry in South Kalimantan, Indonesia. The wood wastes were air dried for the removal of moisture. For biochar production in agricultural purposes, it is recommended to have a small sized of feedstock to mix well with soil (Page-Dumroese et al. 2017). Hence the dried wood wastes were ground to the smaller size. After that, the wood particles were separated by size using a sieve–only particles which passed an 18-mesh screen and were retained on a 40-mesh screen selected for the sample. The particle size was maintained at about 0.42–1.00 mm.

Characteristic of Durian Wood Waste

The analysis of basic physicochemical properties of durian wood waste was conducted according to the ASTM: fixed carbon (D.3172), volatile matter (D.3175), ash content (D.3174), moisture content (D.3173), total carbon (D.5373), hydrogen (D.4239), oxygen (D.3176). Cellulose and lignin testing were carried out by the Chesson method.

Biochar Production

The 1.5 kg biomass was pyrolyzed using electric reactor (5000 W) by 10 °C/min heating rate with limited oxygen condition. Biomass was pyrolyzed until the temperature of 350 °C. 450 °C. and 550 °C respectively, for two hours. The biochar produced was instantly cooled by guenching from top to bottom with water in the container until the biochar was entirely under water for 30 min. The quenched biochars were then filtered by a strainer and dried in the sun to reduce moisture content before analyzed. The biochar obtained were labeled according to pyrolysis temperature as Water-Quenched Biochar BCW350, BCW450 and BCW550. To compare the results, biochar was also analyzed without water quenching treatment, called Fresh Biochar, and labeled as fresh biochar BCF350, BCF450, BCF550. The raw sample and biochar obtained from different treatment were characterized.

Characterization of Biochar Hydrophilicity of Biochar

The hydrophilicity of biochar was analyzed by contact angle measurement system (Letey et al., 2000), which measure the angle when liquid interface meets a solid surface (Letey et al. 2000, Sakti et al. 2017). Biochar is called hydrophilic when it has contact angle < 90°. Vice versa, biochar become hydrophobic when its contact angle > 90° (Gray et al. 2014). To measure contact angle, biochar was put on the top of glass microscope slides (76.2×25.4×1.2 mm) which platted with double-sided adhesive and held on until 30 s. Biochars that were not firmly bound to the slide were disposed of (Shang et al. 2008, Nowak et al. 2013). The glass microscope slide was dripped by 20 µL of distilled water and put on the apparatus holder which upright position to the camera. The slide surface was captured through the optical lens (Sakti et al. 2017).

Proximate Analysis and pH

Proximate analysis of durian wood waste and biochar included fixed carbon (FC), volatile matter (VM), ash content and moisture content. ASTM method was used as a base to analyze FC (D.3172), VM (D.3175), ash content (D.3174) and moisture content (D.3173). Fixed C is considered as total ash, volatile and moisture content subtracted from 100. The pH of biochar was measured by pH meter in 1:5 biochar: water (Zhao et al. 2017).

Elemental Analysis

An elemental analyzer (LECO CHN 628) was used to determine carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) contents according to ASTM D.5373, while S and Oxygen (O) were analyzed according to ASTM D.4239 and D.3176. Oxygen (O) content was computed by the sum of percentage C, H, N, S, ash, subtracted from 100 percent (D.3176). The ratio of O:C and H:C was also counted.

Surface Properties of Biochar

Fourier Transform Infrared (FT-IR) Spectrophotometer (8400S, Shimadzu, Japan) was utilized to analyze a different kind of functional groups in biochar. The FTIR spectra were collected with a spectrometer using potassium bromide (KBr) pellets and wavenumber between 400–4000 cm⁻¹ (Trakal et al. 2013). The biochar morphology was analyzed by scanning electron microscope (SEM) method (Tescan Vega 3SB) at 1000x magnification in the scales of 50 μ m with an acceleration voltage of 15 kV.

Statistical Analysis

Data were analyzed using ANOVA (analysis of variance) test and reported as an average and standard variation. DMRT (Duncan's Multiple Range Test) was used to compare the significant difference of treatment at 5% level of confidence by SAS 9.1 version.

RESULTS

Water Quenching Effect to Hydrophilicity of Biochar

Quenching took place from the top to the bottom of the hot freshly biochar. Hot biochar which was quenched with water could inhibit its hydrophobicity. Based on CA measurement, water could be able to immediately absorbed by waterquenched biochar (Figure 1). The magnitude of left and right contact angles are asymmetric because of the wide droplet position and surface flatness (Sakti et al. 2017).

To compare the hydrophilicity, the fresh biochar was also tested for CA measurement. Table 1 showed the contact angle measurement for both water-quenched biochar (BCW) and fresh biochar (BCF) with different pyrolysis temperature. All fresh biochars were hydrophobic. Quenching hot biochar with water produced in high temperature caused biochar hydrophilic. Based on the Analysis of Variance (ANOVA) there was a significant difference in contact angle in all treatments (Table 2).

Table 1.	The average surface	contact angle of BCW an	d BCF from different pyrol	ysis temperature

Post-treated Biochar	Temperature (°C)	Contact Angle (°)		
	350	117.77 ± 1.11 d		
BCW	450	81.23 ± 1.10 e		
	550	48.85 ± 0.76 f		
	350	137.90 ± 1.09 a		
BCF	450	124.08 ± 0.79 c		
	550	129.30 ± 0.81 b		

Remarks: water-quenched biochar (BCW); fresh biochar (BCF). Numbers followed by the different letter within each column were significantly different based on DMRT α = 5%

Table 2. Analysis of variance of surface contacts angle of biochars

Source	DF	SS	MS	F Value	Pr > F	R-Square	Coeff Var	Root MSE
Model	5	17712.29	3542.46	3892.53	<.0001	0.9993	0.8955	0.9540
Error	12	10.921	0.910					
Corrected Total	17	17723.21						

Remarks: DF: degree of freedom; SS: sum of squares; MS: mean square



Figure 1. CA measurement (Left: 50.403°, right: 47.780°)

Post-treated biochar played the important role in an attempt to achieve hydrophilic biochar. As shown in Table 1, all BCFs resulted from various pyrolysis temperature were hydrophobic (>90°). Similarly, Smetanová et al., (2012) stated that biochar hydrophobicity resulted from biochar pyrolyzed at low temperature. Hydrophobicity of the fresh biochar was often compared to charcoal, which was composed of residues derived from burning. Pyrolysis temperature of 350 °C and water rinsing for 24 h could decrease biochar coatings due to the releasing of various salt and small molecules from the surface of biochar. Therefore the pore of biochar might open, and the surface roughness could increase (Spokas et al., 2014), which could improve water retention properties.

On the contrary, in this study water-guenched biochar produced at 350 °C was still hydrophobic because of the absence of its polar oxygen-based functional groups. With increasing pyrolysis temperature, water quenching treatment decreased the hydrophobicity of the wood biochar. According to Smetanová et al., (2012), hydrophobic biochar derived from bark and wood was still found at pyrolysis temperature 500-600 °C. The new findings, this study resulted in hydrophilic wood biochar at 450 °C pyrolysis temperature by water quenching treatment. Quenching hot biochar with water was an excellent method because hot steam produced may potentially crack open more pores, rinse residual tars, remove the ash, oxygen and other minor components of the biochar. Hence, water quenching treatment after pyrolysis was able to create pure biochar (activated carbon). The pure biochar surface had a lot of pores for water absorbing and retaining, which was enabled to interact with the air and soil in addition to water. We used FTIR and SEM analyses to investigate the surface functional group of biochar further.

Based on the Analysis of Variance (ANOVA) as shown in Table 2, there was a significant difference in contact angle in all treatments. Table 1 showed post-treated biochar affected the surface contact angle. As increasing pyrolysis temperature, the contact angle of BCW was decreased.

Pyrolysis Temperature Effect to Biochar Characteristics and Surface Properties

Proximate Analysis and pH

As increasing pyrolysis temperature, the biochar moisture and yield were decreased (Table 3). The lowering of biochar yield was consistent with other studies regarding the woody biomasses pyrolysis (Keiluweit et al. 2010, Wang et al. 2013). The organic substance was more decomposed at higher pyrolysis temperature, which could promote the volatile compound releasing. Pyrolysis of biomass caused a mass loss in which the shrinking and diminishing of its volume did not cause many modifications compared to the raw material structure (Kloss et al., 2012). The yield decreasing was usually related to its moisture loss. The level of thermal decomposition was also affected by the moisture content of the feedstock. The higher pyrolysis temperature, the lower moisture content, and yield (Nsamba et al., 2015).

As shown in Table 3, The high pyrolysis temperature could increase biochar ash content. Ash content in fresh biochar was higher than water-quenched because of C, H and O decreasing (Angın and Sevgi, 2014). In contrary, water-quenched biochar had lower ash content than a fresh one because guenching hot biochar with water not only prevented further burning but also kept nutrient as well as removed dust (Sohi et al. 2013). The ash content reflected the noncombustible component and non-volatile matter of the biochar (Angin, 2013). Generally, the high pyrolysis temperature caused the increasing of biochar ash content because there was molecule volatilization enriched by inorganic matters (Kloss et al., 2012). As a consequence of that enrichment of inorganic elements, the pH value of biochars was raised (Novak et al., 2009) as increasing of pyrolysis temperature. Waterquenched biochar produced at 350 °C,450 °C, 550 °C had a pH value of 6.51, 8.07, 9.07, respectively, while the fresh biochar 5.35, 7.23, 8.22, respectively. The water-quenched biochar had higher pH than fresh one due to leaching of ash minerals from the hot biochar. pH value of BCW 550 resulted in this study was higher than durian wood biochar produced by Krishnan et al. (2016) at 600-700 °C (8.37-8.56) and Chowdhury et al., (2016) at 350-550 °C (6.1-6.8). The alkalinity effect of water-quenched biochar could. therefore, be used to neutralize acidic soil, which could potentially substitute the use of lime (Nurhidayati and Mariati, 2014, Hüppi et al., 2015), increase soil characteristic and crop productivity.

The fixed carbon and volatile matter represented the recalcitrant and available carbon fraction (Basso et al., 2013). Recalcitrant carbon indicated that the carbon had been converted to stable benzene rings that could not degrade quickly. As recalcitrant carbon, lignin was the main compound in woody biomass. Generally, the VM content in biochar was decreased as increasing pyrolysis temperature, while the opposite trend was found in FC. The low VM of biochar was likely due to complete decomposition of the predominantly cellulosic feedstock at 550 °C temperature concurrent with a period of devolatilization during pyrolysis (McBeath et al., 2014). As temperatures increased over 500 °C, the biochar would consist mainly of FC due to the hemicellulose and cellulose were mostlv decomposed, while lignin was slowly decomposed (Dufour et al., 2012, Wang and Howard, 2018). The content of VM for the water-quenched biochars and fresh biochars ranged from 13.93% to 33.48% and 20.73% to 38.25%, respectively, while the FC ranged from 57.25% to 78.07% and 52.66% to 68.12%, respectively. These VM and

FC analyses results were similar to that reported for woody biochars with VM 19.42%–32.06% and FC 62.2%–70.8% (Jindo et al. 2014, Domingues et al. 2017), The VM of water-quenched biochar resulted was lower than fresh biochar and higher in FC. It was worth noting that water-quenched biochars derived from woody feedstock had the high FC content and the low inorganic substances as well as volatile matters. Biochar which contained of high FC and low VM might be suitable as organic fertilizer (Garrido et al. 2017).

Samples	Yield (%)	Moisture in air dried (%)	Ash content (%)	Volatile Matter (%)	Fixed C (%)	рН
BCW350	33.09 ± 1.01 b	7.20 ± 0.23 a	2.07 ± 0.38 e	33.48 ± 1.1 b	57.25 ± 0.96 d	6.51 ± 0.47 d
BCW450	27.20 ± 0.84 c	6.47 ± 0.20 b	2.64 ± 0.55 de	23.18 ± 0.99 d	67.71 ± 0.70 b	8.07 ± 0.26 b
BCW550	20.53 ± 1.16 d	4.77 ± 0.30 c	3.23 ± 0.75 cd	13.93± 0.94 f	78.07 ± 1.06 a	9.07 ± 0.17 a
BCF350	46.67 ± 0.75 a	4.96 ± 0.37 c	4.13 ± 0.68 c	38.25 ± 0.86 a	52.66 ± 0.97 e	5.35 ± 0.29 e
BCF450	33.05 ± 1.03 b	3.07 ± 0.16 d	5.47 ± 0.53 b	25.73 ± 0.81 c	65.73 ± 1.03 c	7.23 ± 0.33 c
BCF550	27.16 ± 0.86 c	3.06 ± 0.45 d	9.09 ± 0.77 a	20.73 ± 0.62 e	68.12 ± 1.23 b	8.22 ± 0.24 b
DW	-	9.3 ± 0.55	1.43 ± 0.14	73.00 ± 1.26	16.27 ± 0.36	-

Remarks: water-quenched biochar 350 °C (BCW350); water-quenched biochar 450 °C (BCW450); waterquenched biochar 550 °C (BCW550); fresh biochar 350 °C (BCF350); fresh biochar 450 °C (BCF450); fresh biochar 550 °C (BCF550); durian wood (DW). Numbers followed by the different letter within each column were significantly different based on DMRT α = 5%

Table 4. Elemental components of biochar and durian wood waste								
Samplas	Elemental analysis (%)						Atomic Ratio	
Samples	С	Н	Ν	0	S	O/C	H/C	
BCW350	68.98 e	4.12 ab	0.31 c	24.49 a	0.03 b	0.36	0.06	
BCW450	73.67 d	3.62 bc	0.38 b	19.76 c	0.03 b	0.27	0.05	
BCW550	82.03 a	3.11 cd	0.41 b	11.29 e	0.03 b	0.14	0.04	
BCF350	68.61 e	4.26 a	0.28 c	22.69 b	0.03 b	0.33	0.06	
BCF450	75.26 c	3.81 ab	0.37 b	15.05 d	0.04 b	0.20	0.05	
BCF550	77.48 b	2.74 d	0.50 a	10.13 e	0.06 a	0.13	0.04	
DW	47.42	6.52	0.15	44.43	0.05	0.04	0.14	

Table 4. Elemental components of biochar and durian wood waste

Remarks: water-quenched biochar 350 °C (BCW350); water-quenched biochar 450 °C (BCW450); waterquenched biochar 550 °C (BCW550); fresh biochar 350 °C (BCF350); fresh biochar 450 °C (BCF450); fresh biochar 550 °C (BCF550); durian wood (DW); sulphur (S); oxygen (O); nitrogen (N); hydrogen (H); carbon (C). Numbers followed by the different letter within each column were significantly different based on DMRT $\alpha = 5\%$

Elemental Analysis

Table 4 summarized the elemental analysis of biochars and durian wood. As increasing pyrolysis temperature, C content was raised from 68.98–82.03% for BCW and 68.61–77.48% for BCF. The

highest C content was in BCW550 (82.03%), which the lowest content was observed in BCF350 (68.61%). N content also increased from 350 to 550 °C pyrolysis temperature for both BCW and BCF. These results were in line with previous woody biochar results (Kloss et al. 2012, Crombie et al. 2013, Jindo et al. 2014, Zhao et al. 2017) which implied that high pyrolysis temperature could increase carbonization degree of biochars (Chen et al. 2012). Meanwhile, the low H and O contents in biochars resulted in the progressive reduction of H:C and O:C ratios. The low contents of O and H at high pyrolysis were due to oxygen bond fission, which could release low-molecular compound contained of O and H (Fu et al., 2012, Suliman et al., 2016).

BCW and BCF atomic ratio at various pyrolysis temperature was figured by Van Krevelen plot (Figure 2). As shown in Figure 2, biochar was gradually lost in O/C and H/C at high pyrolysis temperature because of progressive dehydration and decarboxylation reactions. It was such an indication of aromatic compound formation which was appeared in 1600 and 1038 cm⁻¹ (Wu et al., 2012). Furthermore, the decrease of O-containing molecule could produce carbonrich biochar (Fu et al., 2012). Low ratio of O/C was further evidence of successful biomass conversion to biochar which showed the higher aromaticity level and environmentally more stable (Kumar et al., 2013, Melo et al., 2013). So the O:C and H:C ratios were usually counted for determining the level of biochar aromaticity (Wu et al., 2012).

Meanwhile, the relatively high H/C ratio at lower pyrolysis temperatures indicated a partial lignocellulose conversion in decomposition (Brewer et al., 2014). Of the biochars produced, O/C was similar even same with H/C ratio for BCW and BCF at each pyrolysis temperature. All biochars produced from this study complied with the European Biochar Certificate (EBC) Version 4.8, which constrain a maximum O:C ratio of 0.4. The O:C and H:C decreasing at high temperature implied that pyrolysis at 550 °C yielded the highest stability of biochar. Generally, the high carbon content and the low volatile component were the best properties for the use of biochar in agriculture (Ścisłowska et al., 2015). Hence from the view of elemental analyses, BCW550 these was recommended to improve the soil.

Surface Morphology (Scanning Electron Microscopy) Analysis

Morphology of durian wood waste as raw material was shown in Figure 3, while biochar transformation on its surface could be observed by comparing the SEM profile of biochar pyrolyzed at various temperatures (Figure 4). From SEM images, biochars resulted in this study were porous due to the devolatilization process of pyrolysis or derivative from feedstock porous surface (Brewer et al. 2009). The pores had the honeycomb shape characteristic.

As shown in Figure 3, longitudinal fibrous on the woody material surface appeared from the existence of cellulose in sawdust which could be classified as prismatic, fibrous and spherical geometries (Pituello et al., 2015). Likewise, biochar on 350 °C pyrolysis temperature (Figure 4a.d arrow) retained the longitudinal fibrous structures. Biochar produced at 350 °C also exhibited a partially smooth surface which visually had irregular porosity. This phenomenon could be explained that cellulose and hemicellulose decomposition were terminated in the temperature of 400 °C, whereas lignin was gradually decomposed between 200-500 °C (Brebu and Vasile, 2010). When pyrolysis temperature reached 550 °C, the morphology of biochar became more complicated (Figure 4c,f). As a result of thermal decomposition, the pores in the fresh biochar (Figure 4d-f) might be part was blocked by created tarry substances and ash. Post-pyrolysis quenching was a part of a physical treatment potentially cleansed biochar from surface dust.

During pyrolysis, the more volatile matter was released from the biomass, and it resulted in vesicles (Rajapaksha et al., 2014). Hot quenching could cause biochar cracking which generated vesicles on its surface. Therefore the surface properties of woody biochar were highly porous and generated well-ordered macroporous woody biochar (Figure 4c). It seemed the possibility of fragmentation because several cracks of the volatile fractions passed through the particle. Gasior (2017) stated that biochar with a large number of pores was excellent water absorbing and retaining material; therefore, it might be used for insulating material and adjusting moisture.

Fourier-Transform Infrared and Functional Groups Analyses

Figure 5 showed the feedstock, BCW and BCF spectra pyrolyzed at various temperatures, while Table 5 listed the functional groups and peak description of biochars.



Ratio of O/C Figure 2. Van Krevelen plot of BCW and BCF at different pyrolysis temperature



Figure 3. SEM images of durian wood at 1000x magnification



Figure 4. Biochar profile: [a] BCW 350; [b] BCW450; [c] BCW550; [d] BCF 350; [e] BCF450; [f] BCF550 (Magnification 1000x, 15.0 kV)



Wavenumber (cm⁻¹) Figure 5. FTIR of DW, BCW and BCF at various temperature: water-quenched biochar 350 °C (BCW350); water-quenched biochar 450 °C (BCW450); water-quenched biochar 550 °C (BCW550); fresh biochar 350 °C (BCF350); fresh biochar 450 °C (BCF450); fresh biochar 550 °C (BCF550); durian wood (DW)

Type of	Wavenumber (cm ⁻¹)							Functional
Vibrations	DW	BCW350	BCW450	BCW550	BCF350	BCF450	BCF550	Group
O-H stretch, H-bonded	3167.66	-		-	-	-	-	Alcohol, phenol
C-H stretch	2901.50	-	-	-	-	-	-	Alkanes
C=O stretch	1736.58 1661.36	1694.15	1705.72	1699.93	1699.93	1690.29	1703.79	Ketone/carbo- xylic acid
C=C stretch	1603.50 1508.99	1601.57 1512.85	1595.78	1568.78	1601.57 1514.78	1595.78	1566.85	Aromatic
-CH ₃ bend	1456.92	1427.99	1426.05	1412.56	1460.78	1427.99	-	Alkane
C-O stretch	1373.99 1329.63 1250.55 1115.54 1049.97	1366.27 1316.12 1264.05 1213.90 1119.40	1264.05	1264.05	1262.12 1210.05 1113.61	1265.98	1258.26	Ether, esher, carboxylic acid, alcohol
C-H bend	901.46	862.88 783.81	878.31 826.24 760.66	878.31 822.38 754.88	857.10, 706.66	870.60 816.52	876.38 824.31 756.81	Aromatic

Table 5. Functional groups and Peaks of DW, BCW and BCF

Remarks: water-quenched biochar 350 °C (BCW350); water-quenched biochar 450 °C (BCW450); waterquenched biochar 550 °C (BCW550); fresh biochar 350 °C (BCF350); fresh biochar 450 °C (BCF450); fresh biochar 550 °C (BCF550); durian wood (DW)

As seen in Table 5, generally there was no different phenomenon encountered between BCW and BCF. In all pyrolysis temperatures, there was the similarity of functional groups between BCW and BCF (Figure 5, Table 5). The feedstock showed strong peaks at 3167.66 cm⁻¹, commonly found in phenolics (O-H stretch) lignin (Poletto and Zattera, 2013), 2901.50 cm-1 indicative of conjugated C-H stretch (alkanes), while the other peaks showed the presence of cluster C=C, C=O, aliphatic and aromatic C-H, C-O. Similar findings with Kumar et al. (2018), spectral analysis at 1661.36 cm⁻¹ and 1736.58 cm⁻¹ was assigned to the non-conjugated carbonyl group in hemicellulose, where the band at 1508.99 cm⁻¹ and 1603.50 cm⁻¹ was derived from an aromatic compound of lignin. During pyrolysis, spectra analysis showed the loss process in O-H stretching and C-H aliphatic (Jindo et al., 2014) due to the further reaction of dehydration, which a large amount of water was released simultaneously (Chen et al., 2012). Meanwhile, oxygen and hydrogen were released as volatile matter; thus the aliphatic and oxygen functional group intensities were decreased (Yin et al., 2018). Hence groups of C aliphatic decreased but C aromatic increased at high temperature (Lee et al., 2010). The biochar spectra at 1119.40-1366.27 and 1601.57-1705.72 cm⁻¹ could be attributed to aromatic carbonyl (C-O) and carboxyl groups (C=O), which meant that there was still retained oxygen-containing organic groups in biochar produced. Furthermore, the increasing of C-H bend in aromatic indicated that the biochar was more aromatic at higher pyrolysis temperature. This study was in line with Ahmad et al., (2012), Keiluweit et al., (2012), Budai et al., (2014), Devi and Saroha (2015), Zielinska and Oleszczuk (2016), Banik et al., (2018), Weidemann et al., (2018), Wei et al., (2019) and Yin et al., (2018).

CONCLUSION

Quenching of hot biochar with water resulted in hydrophilic biochar pyrolyzed starting at 450 °C. As increasing pyrolysis temperature, water auenchina treatment decreased the hydrophobicity of the durian wood biochar. Hot quenching yielded cracked biochar on its surface; therefore the surface properties of woody biochar was highly porous and generated well-ordered macroporous as increasing temperature. This study showed that higher pyrolysis increased ash content, total carbon, fixed carbon, and pH, but decreased yield, moisture, volatile matter, hydrogen, and oxygen content. There was no different organic functional group encountered between water-guenched biochar and fresh biochar. Biochars became more aromatic with increasing temperatures which characterized by the increase in the aromatic C-H bend. The waterquenched biochar had a higher pH than the fresh one. Water-guenched biochar at 550 °C, with contact angle 48.85°, volatile matter 13.93%, fixed carbon 78.07%, total carbon 82.03%, hydrogen 3.11%, oxygen 11.29%, and pH 9.07, was recommended to improve the quality of acidic soil. The study represented that the temperature of pyrolysis and water quenching of biochar postpyrolysis created a possibility to yield hydrophilic biochar

CONFLICT OF INTEREST

The authors declared that the present study was performed in the absence of any conflict of interest.

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AUTHOR CONTRIBUTIONS

ES designed and performed the experiment and also wrote the manuscript. Dr. DM and Dr. CP designed the experiment and analyzed the data. Prof. SP supervised the experiments and reviewed the manuscript. Prof. S designed the experiment and reviewed the manuscript. All authors read and approved the final version.

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