Effects of Pyrolysis Temperature and Residence Time on Rice Straw-derived Biochar for Soil Application

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Authors' contributions

This works carried out in collaboration among all authors. Author SS planned the research, conducted the experiment, data analyses, data interpretation and wrote the first draft of the manuscript. Author MRI allocated the research fund, reviewed and revised the manuscript. Author TRP contributed on the statistical analyses, native English speaker, proofread manuscript. Author HMS provided laboratory facilities. Author RI Contributed on the soil and biochar data interpretation, reviewed and revised the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Aims: A study was conducted to assess the rice straw-derived (Rsd) biochar in relation to temperature and residence time.

Study Design: Rsd biochar was pyrolyzed at different temperatures (300ºC, 400ºC, 500ºC and 600ºC) in a combination of different residence times (45 min, 60 min and 120 min) namely 300-45, 300-60, 300-120, 400-45, 400-60, 400-120, 500-45, 500-60, 500-120, 600-45, 600-60, and 600-120, respectively.

Place and Duration of Study: The study was conducted in the laboratory of Institute of Tropical Agriculture and Food Security, Universiti Putra Malaysia, Malaysia, between July to September 2014.

Methodology: A suite of analytical procedures was performed to evaluate the Rsd biochar characteristics.

Results: The results showed that the biochar yield decreased when the pyrolysis temperature increased. The physicochemical and structural characteristics of the biochar were significantly influenced by pyrolysis temperature. Scanning Electron Microscope (SEM) images indicate significant macro-porosity (size between 1-10 μm) and were clearly visible across the surface of 300ºC (60 min) compared to other temperature values and residence times. Increase in temperature gave rise to a nodule-like visible indicator of silicate presence on the surface. Macro-porosity presence in biochar is an indicator that it can adsorb and retain water and nutrient for plant-root hair uptake. Meanwhile, Brunauer-Emmett-Teller (BET)-N_2 surface area ranged from 2.36-6.26 $m^2\ g^{-1}$, for 300 to 500ºC, respectively. Surface area controls materials' ability to adsorb chemical compounds, as larger surface area means more porous structures within biochar. H/C and O/C ratio decreased as the temperature increased, indicating condensed carbon in biochar. The pH increased with the increment of pyrolysis temperature.

Conclusion: Rsd biochar at 300-60 and 400-60 showed good potential characteristic with macro-porosity and surface area increases, and should thus be suitable as a soil amendment for agricultural activity.

1. INTRODUCTION

Rice (*Oryza sativa* L.) is the most important food crop globally, inclusive of Malaysia. As of the year 2016, Malaysia produces about 2.74 million tons $year^{-1}$ of rice grains [1] with cultivation area of 699,800 ha [1] paddy fields. The paddy is normally harvested and sold to Beras Nasional (BERNAS), the governing body to purchase and distribute the national paddy for the local market consumption. After the paddy harvest, about 1.3 million tons of rice straw is left at the paddy field, and this becomes a by-product. According to MOA [2], this by-product has a potential to be utilized as a soil amendment for further paddy cultivation cycle; internationally recognized as rice straw-derived biochar. However, the common practice is the direct burning of rice straw. Direct burning of rice straw in paddy fields is a common practice among local farmers to dispose of this organic waste. Although this practice helps the improvement of soil fertility and reduce pest infestation in the subsequent rice farming cycle to some extents, it has been noted by Tipayarom and Oanh [3] and Zhang et al. [4] to emit carbon dioxide (CO_2) to the atmosphere.

Carbon dioxide emission from agricultural activities have been estimated to be about 5.1–6.1 Pg CO_2-equivalents $year^{-1}$, that contributes to 10–12% of the total global anthropogenic emissions [5] of Green House Gaseous (GHGs). Globally, the increment of CO_2 in the atmosphere is well recorded to affect farming activities in terms of yield and quality [5,6]. As such, farming practices that are able to reduce/minimize the CO_2 release can support sustainable rice farming.

The net GHGs emission (CO_2-equivalent) from farming activities can be reduced by enhancing soil organic carbon (SOC) storage as stated by Mosier et al. [7] and further supported by Smith et al. [5]. A key point in supporting sustainable agriculture is to make full use of crop residue such as rice straw from rice fields as a soil amendment.

Biochar is defined as charcoal materials produced by incomplete combustion of biomass

which is often produced under a low-temperature pyrolysis and/or under oxygen-limited condition [8–10]. In recent years, biochar has been attracting a widespread attention due to its multi-potential such as; i) carbon sequester [11,12], ii) soil amendment to improve soil fertility [10,13] and thus crop yield [14] and also as, iii) an agent which can mitigate greenhouse gas emission [14–16].

In agriculture, rice straw could be used as a source of materials to produce biochar, due to high availability in paddy farming system as a by-product. Rice straw-derived (Rsd) biochar appears to be a promising technique to address the problem of reductions in soil nutrients and C storage, plus mitigate GHGs emissions. In Peninsular Malaysia granary area, it has been estimated about 1.3 million tons of rice straw is generated after paddy harvest, thus have the potential to be utilized as Rsd biochar.

It has been reported that biochar is highly resistant to microbial decomposition, thus very durable in natural environments and agro-ecosystems [17]. However, biochar often varies in characteristics based on their production process of pyrolysis (i.e. temperature and residence time), therefore may exhibit different chemical and physical properties [18].

Based on a study by Wu et al. [19], the increment in pyrolysis temperature, shows increment in the degree of aromaticity, noted with a decrease in both Hydrogen/Carbon (H/C) and Oxygen/Carbon (O/C) ratios, to less than 0.5. The lower ratio value indicates condensed carbon formed in biochar through pyrolysis process. The condensation of carbon improves the stability of biochar [19].

However, the information on chemical and physical properties of Rsd biochar in relation to pyrolysis temperature and residence time is still lacking, which is the major constraint for utilization of Rsd biochar in Malaysia. The objective of this study was to determine and characterize Rsd biochar produced under different pyrolysis temperatures and residence times. It is, therefore, essential to determine and characterize Rsd biochar prior to large-scale application to agricultural fields.

2. MATERIALS AND METHOD

2.1 Rice Straw Preparation

Rice straw sample was collected from a paddy field in Kelantan, Malaysia. The sample was first air-dried for 24 hours, then oven-dried at 60ºC for 24 hours [19].

2.2 Pyrolysis of Rice Straw

For the pyrolysis process, the rice straw was ground to pass through Endecott® 2 mm brass sieve and then placed in a custom-made lab-scale tubular furnace. The set-up as follows: a corundum tube (70 mm in diameter; 508 mm in length), and LED control panel with N_2 purge (400 cm^3 min^{-1} flow rate) to ensure an oxygen-free atmosphere. In this study, two factors were focused. Factor 1: pyrolysis temperatures (300, 400, 500, and 600ºC); Factor 2: residence times (45, 60 and 120 min). The treatments are named 300-45, 300-60, 300-120, 400-45, 400-60, 400-120, 500-45, 500-60, 500-120, 600-45, 600-60, and 600-120, respectively. Two replicates have been pyrolyzed for all treatments. The heating rate was at 6ºC min^{-1}. The yield of Rsd biochar was determined.

2.3 Laboratory Analyses of Rice Straw

The pH_{H2O} of Rsd biochar was measured at 1:20 (w/v) ratio after 1h [20]. Carbon (C), hydrogen (H), and nitrogen (N) content were determined with a CHN Elemental Analyzer (NA-1500, Carlo-Erba, USA). Oxygen (O) content was estimated by difference, assuming biochar to be composed of C, H, N, and O only [19]. Ash contents determined by combusting the biochar at 700°C for 12h in open crucibles [21]. Extractable cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and cation exchange capacity (CEC) were measured with 1 M NH_4OAc (pH 7) method [22]. Available phosphorus (P_{avail}) was extracted by the Bray no. 2 method for soil (pH > 7.5) and determined by the molybdenum blue method [23]. Surface area of Rsd biochar was determined by the BET (Brunauer–Emmett–Teller) nitrogen method. Image analyses conducted with Scanning Electron Microscope (SEM) (TM-1000, Hitachi, Japan). Fourier Transform Infrared (FTIR) spectra (range: 4,000 to 650 cm^{-1}) of the rice straw and biochar samples were recorded with Spectrum 100 (Perkin Elmer, USA) equipped with a ZnSe flat crystal using the attenuated total reflectance (ATR) technique.

2.4 Statistical Analyses

Difference between the Rsd biochar treatments was analyzed by analysis of variance (ANOVA) in SAS Version 9.4 (SAS Institute, Inc.; Cary, NC, USA). The Tukey test for comparison of

means was used when the F-test was significant at $P < .05$.

3. RESULTS AND DISCUSSION

3.1 Characterization and Yield of Rsd Biochar

Initial chemical composition prior to pyrolysis, shows that the rice straw contained total value of C = 413.4 g kg^{-1}, N = 13.8 g kg^{-1}, P = 0.01 g kg^{-1}, K = 0.2 g kg^{-1}, Ca = 0.03 g kg^{-1}, Mg = 0.02 g kg^{-1}, Na = 0.01 g kg^{-1}, and H = 61.4 g kg^{-1}.

The yield of Rsd biochar decreased with increment in pyrolysis temperature (Table 1), from 48% in 300-45 to 31% in 600-120). However, there was no significant effect on residence time. The yield decrease of biochar with increase in pyrolysis temperatures is in accordance with Peng et al. [24]. The H/C and O/C ratios progressively decreased due to the increase in condensed carbon. These ratios indicate the aromaticity of the biochar and are an indication of its susceptibility to mineralization. As the H/C and O/C decrease with rising temperature, biochar mineralization resistance increases [19].

The variation in surface condition (Fig. 1) indicates that the 300-45 treatment gave rise to a surface that appeared rougher with minimal pores compared to the 300-60 treatments. As the temperature increased from 400 to 600ºC, silica was seen to form nodule-like shapes on the surface (Fig. 1). At 400ºC, the surface appeared as flakes and at 500ºC, the silica burst.

Then at 600°C, the flakes re-appeared on the surface.

As reported by Singh et al. [25], at 400ºC, manure-based (poultry litter and cow manure) mineralize faster than 550ºC plant-based (Eucalyptus saligna wood and leaves). From this study, plant-based rice straw mineralize at 300ºC, was much lower than the temperature stated by Singh et al. [25].

SEM images of the Rsd biochar clearly show the presence of pores. Based on the size of the pores, they can be categorized as macro-pores. In biochar from wood, large macro-pores are often observed of about 10 µm or more, compared to biochars derived from cellulosic straws, where the size is often between 1 and 10 µm [26]. The presence of pores on the surface indicates that retention of nutrients and moisture are possible. Macro-pores account for most of the pore volume in biochars. These macro-pores may adsorb and retain water and nutrients. As a result, root hairs (in the rhizosphere) are more accessible to water and nutrients to support plant growth [8].

The SEM images at 50µm showed that the greatest pore size was found for the 300-60 treatment, followed by the 400-60 treatment. Pore size of ±50 µm noted in the SEM images (Fig. 2) indicates potential microsites for microbial propagation. Pore availability in the biochar can provide habitats for symbiotic microorganisms such as bacteria, fungi, and protozoa [26].

Table 1. Yield, ash contents, elemental composition and ratios, and BET-N$_2$ surface area of Rsd biochars pyrolyzed at different temperatures and residence times

Sample ID	Yield[a] (%)	Component (% dry basis)					Aromatic ratio		BET-N$_2$ surface area[b] (m² g^{-1})
		Ash	C	H	N	O[b]	H/C	O/C	
300-45	48.0±1.22	19.6	56.0d	7.05	2.32	34.6	1.51	0.46ab	N/A
300-60	46.7±1.56	18.9	58.5cd	3.97	2.21	35.3	0.81	0.45b	2.36
300-120	45.0±0.38	19.8	58.6cd	3.93	2.54	34.9	0.80	0.45b	N/A
400-45	36.1±0.60	24.5	61.0abc	2.77	2.37	33.9	0.54	0.42c	N/A
400-60	34.0±0.76	24.7	62.7a	2.31	2.19	32.8	0.44	0.39c	5.33
400-120	35.7±1.04	22.7	61.6ab	2.53	2.25	33.6	0.49	0.41c	N/A
500-45	33.1±0.94	22.2	62.1ab	2.25	2.24	33.4	0.44	0.40c	N/A
500-60	32.5±0.17	24.5	62.5a	2.17	2.17	33.2	0.42	0.40c	6.26
500-120	32.9±0.90	25.3	62.0ab	2.37	2.31	33.3	0.46	0.40c	N/A
600-45	32.2±0.24	24.2	60.1abc	1.84	2.03	36.0	0.37	0.45b	N/A
600-60	32.9±0.32	24.8	59.5bc	1.95	1.26	37.3	0.40	0.47ab	4.32
600-120	31.1±2.35	24.5	58.4dc	1.65	1.91	38.0	0.34	0.49a	N/A

[a]*mean value of duplicate measurements ± standard deviations;* [b]*estimated by difference; N/A: Not analyzed; Means within each lines followed by the same letter are not significantly different at p<0.001 as determined by Tukey test*
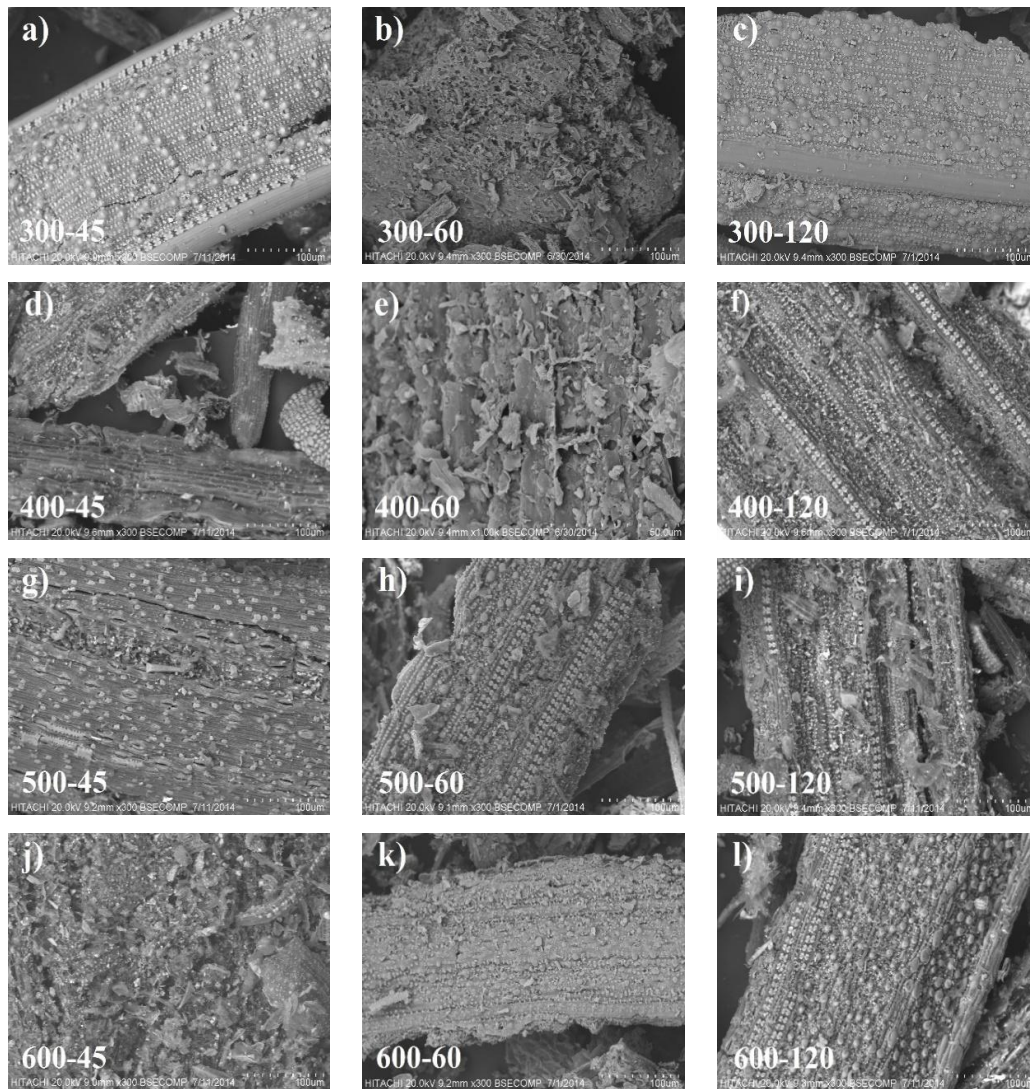
Fig. 1. Scanning electron micrographs of Rsd biochar at different temperatures and residence times (Scaled at 100 µM). Nodules form observed in the surface represent silica presence
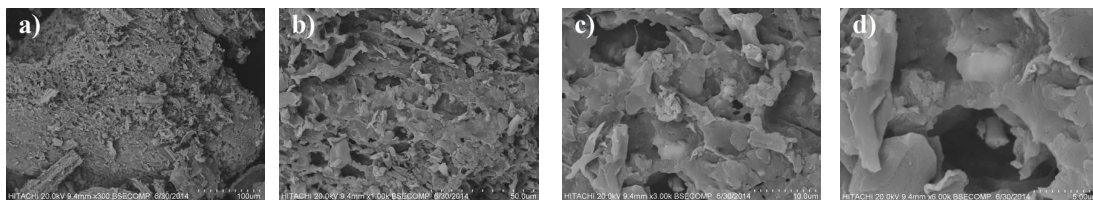

Fig. 2. Rsd biochar magnification of treatment 300-60 at (a) x300, (b) x1000, (c) x3000 and (d) x6000 by SEM; macro-porous sites of the biochar

3.2 Chemical Composition of Rsd Biochar

The ash contents in Rsd biochar increase slightly from 300ºC to 400ºC, and stabilize at about 20% at higher temperatures (Table 1), which is similar to those from grass char that stabilize at 19%

[18]. A comprehensive review on the composition of biomass ash presented by Vassilev et al. [27] shows that the main components are oxides (biomass ash) in the form of SiO_2, CaO and K_2O. This study noted presence of Si in the Rsd biochars in the form of silica nodules through

SEM images (Fig. 1), whereas Ca and K were also high as shown in Table 2.

As the pyrolysis temperature increase, biochar releases more ash (Table 1) (rich in silica), and can become an additional source of fertilizer. Ash is also known to release labile P to soil systems [28], thus higher amount of ash can potentially supply P to plants.

In elemental composition, water molecule normally are volatilized completely during pyrolysis, in contrast to ash that largely remains in the solid phase. Thus, it is important to know the ash content of the biochar [29], because the amount and type of inorganics can determine their possible applications. The ash content are often observed to increase with increment in pyrolysis temperature. This pattern have been well recorded [18,19,29,30].

Elemental analysis indicated that the C content increased with the peak at 400 and 500ºC and then declined when the temperature reached 600ºC (Table 1). In contrast, the H and O decreased with increasing charring temperatures as shown also by Keiluweit et al. [18] and Wu et al. [19]. But when the temperature reached 600ºC the O started to increase again resulting in the decrease of H/C and O/C ratio of the Rsd biochar.

Nitrogen content remained consistent with the temperature from 300 to 500°C then started to decline when the temperature reach 600°C (Table 1). The change of N shows that N is first enriched and then lost via volatilization during pyrolysis with increasing temperature [31].

The CEC of the Rsd biochar decreased with the increase of the pyrolysis temperature. With respect to the residence time, between 300 and 400ºC, the CEC increased as residence time increased from 45min to 60min and then declined when the residence time reached 120min. There was no apparent effect of residence time at temperatures of 500 and 600ºC (Table 2).

The cation adsorptive capacity (CEC) for soil-plant interactions follows this order: $Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ = NH^{4+} > Na^+$ [32]. Extractable K is within the range of 70-90 $cmol_c$ kg^{-1} in Rsd biochar and is higher than for other nutrients (Ca, Mg and Na) and therefore should be available for release to the soil system upon application as soil amendment. Rsd biochar is alkaline in nature, thus cation K^+ should be less tightly bound in an alkaline system. However, this principle is only applicable for soil-plant interactions. Thus high K in biochar may follow a different pathway as stated by Limwikran et al. [33] and, can potentially serve as slow release source of plant nutrient.

Higher temperature pyrolysis may limit the capacity of biochar to retain nutrients or even moisture, due to the collapse of the rice straw cellular structure with pyrolysis at 300-400°C as observed by Yang et al. [34], due to greater loss of cellulose and hemicellulose compared to lignin. A major portion of rice straw is in the form of cellulose and hemicellulose.

The $P_{(avail)}$ decreases (Table 2) with the increase of the pyrolysis temperatures [35]. Likely due to condensation of phosphates to pyrophosphates. This can be observed with increment in ester (-O-) in FTIR spectra at the region of 1200-300 cm^{-1}. The reaction and/or condensation of ester group is often associated with P condensation in non-labile P pool with the formation of stable complexes. A similar finding has been stated by Xu et al. [35] that, during pyrolysis process, more stable P was formed at a higher pyrolysis temperature.

The pH of Rsd biochar ranged from 8.69 to 10.18, and increased with the increment of pyrolysis temperature with the peak at 600-45. A similar finding was reported by Wu et al. [19]. The increase was probably due to the relative concentration of non-paralyzed inorganic elements already present in the original feedstocks [36]. According to Abrishamkesh et al. [37], pH values of biochar from bamboo were about 9.2, and this is similar to that of biochar produced from rice straw. The pH after pyrolysis shifts towards alkaline value as stated above, potentially may suitable to be applied into acid soils for agricultural activity such as paddy cultivation [30].

According to the results from this study, residence time has less effect on the characteristics of Rsd biochar than the temperature. A similar conclusion was reached by Wu et al. [19]. Nevertheless, another study on biochar from bamboo and rice straw indicated that residence time was the second most significant factor affecting the physiochemical, morphological and spectral properties of biochar, and that the effects of residence time on biochar characteristics were similar to the effect of temperature [24,38,39].

6

Table 2. pH, cation exchange capacity (CEC) and extractable cation in Rsd biochar

Sample ID	pH (H_2O)[a]	CEC $(cmol_c\ kg^{-1})$	Available P $(mg\ kg^{-1})$	Extractable cations $(cmol_c\ kg^{-1})$			
				K	Ca	Mg	Na
300-45	8.69±0.01	55.3	46.1	91.5	10.5	5.6	0.6
300-60	8.95±0.02	61.0	50.7	88.3	11.9	5.1	0.5
300-120	9.43±0.04	39.3	43.0	71.4	14.7	5.3	0.7
400-45	9.49±0.01	35.5	15.2	79.8	9.8	4.0	0.7
400-60	9.98±0.04	46.0	12.3	88.3	8.9	3.6	0.9
400-120	9.95±0.04	28.1	11.0	93.6	10.8	3.8	0.8
500-45	9.89±0.02	26.5	8.05	98.4	10.3	2.6	0.9
500-60	9.75±0.06	28.4	10.1	85.1	9.2	3.6	1.1
500-120	9.75±0.10	32.0	7.26	71.5	11.6	3.5	0.8
600-45	10.18±0.11	27.7	5.47	84.8	14.3	3.2	0.8
600-60	9.86±0.27	22.7	5.94	80.0	12.5	3.6	1.3
600-120	9.78±0.46	26.2	5.80	91.2	10.2	2.8	1.2

[a] *mean value of triplicate measurements ± standard deviations*

The BET surface area (S_{BET}) of Rsd biochar at 60 min residence time increased from 2.36 m² g⁻¹ to 5.33 m² g⁻¹ at 400ºC and then peak at 6.26 m² g⁻¹ when the temperatures reached 500ºC, finally falling to 4.32 m² g⁻¹ at 600ºC (Table 1). The S_{BET} values in this study are considerably higher than the results reported by Muter et al. [40] using (i) wood chips and (ii) straw pellets to produce biochar pyrolyzed at 725ºC for 60 min. Surface area is one of the most important factors that control a material's ability to adsorb chemical compounds, as larger surface area means more porous structures within the biochar [41].

3.3 FTIR of Rsd Biochar

The effects of pyrolysis temperatures and residences time of Rsd biochars on the properties of FTIR spectral band are shown in (Fig. 4). The FTIR spectra of rice straw was comparable to that of cellulose [42]. Biochar derived from biomass potentially can undergo dehydration, carbon condensation, loss of H_2, CO, CO_2, and increase in aromaticity and etc. [18,31,43,44] and the Rsd biochar from this study followed a similar trend.

At 300ºC, the loss of aliphatic C–H stretching (2950 and 2850 cm⁻¹) and C–O stretching (1110-1030 cm⁻¹) and lower H/C and O/C ratios compared with rice straw obviously indicated that rice straw experienced progressive dehydration and depolymerization.

The main components of rice straw are hemicellulose and cellulose. Therefore it is much easier to be decomposed than that of lignin during the pyrolysis process [34], it would probably be the main reason why weight loss

and a decrease of H/C and O/C (Table 1) of Rsd biochar was consistent with an increase in pyrolysis temperature. However, at 600ºC, O/C ratio increase about 10% compared to 500ºC as observed in the Van Krevelen (Fig. 3), indicative of polymerization, supported with FTIR spectra band that becomes broad and wider (Fig. 4); monomer molecules forms chemical reaction to form polymer chains. The spectral band results from this study followed a similar trend of that reported by Wu et al. [19].
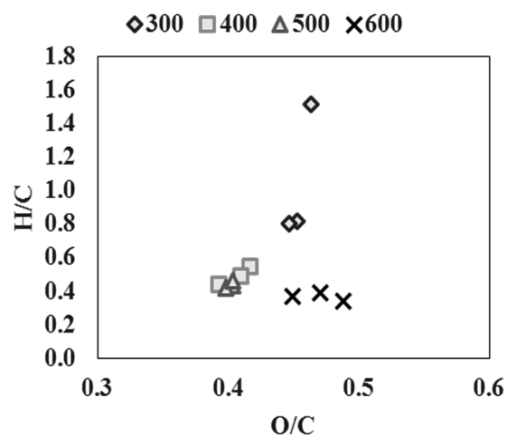

Fig. 3. Van Krevelen plot of elemental ratios of Rsd biochar

In the process of spectral identification, wave numbers from FTIR spectra were assigned accordingly: 3600-3200 cm⁻¹ to O–H stretching of hydroxyl groups; 2950-2850 cm⁻¹ to C–H stretching of aliphatic CH_x, 1740-1700 cm⁻¹ to C=O stretching of carboxyl and ketones, 1630-1600 cm⁻¹ to C=C stretching of aromatic components and to a smaller extent to C=O
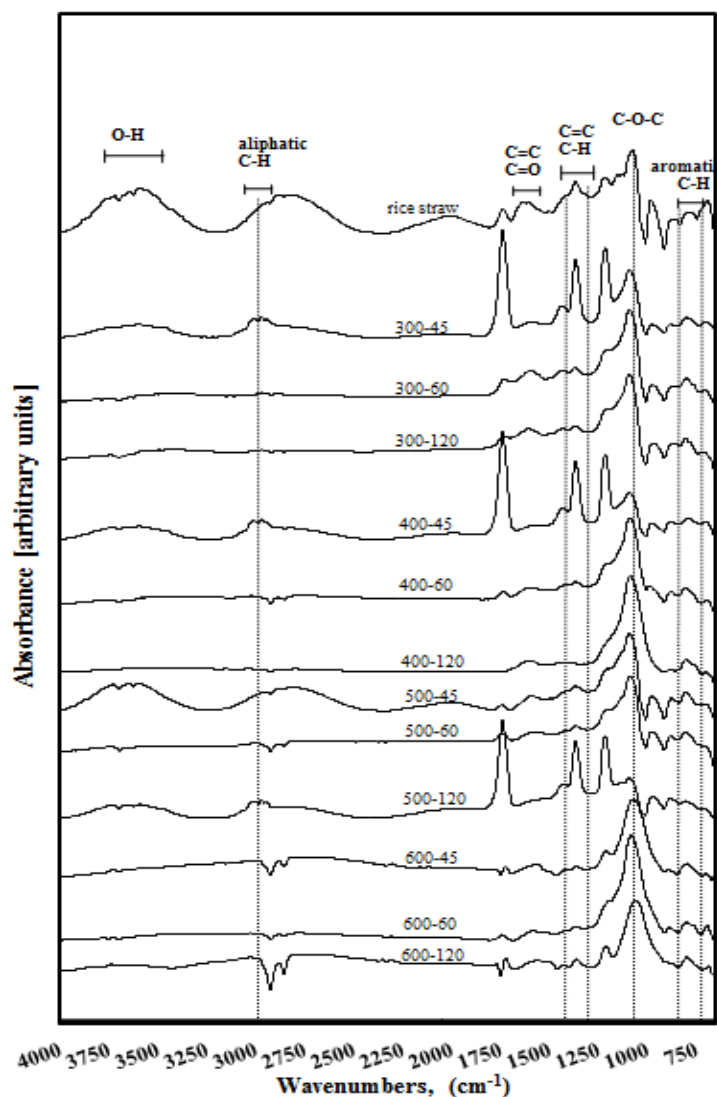
Fig. 4. Stacked ATR FT-IR spectra of Rsd biochar pyrolyzed at temperatures ranging from 300 to 600ºC and different residences time

stretching in quinones and ketonic acids, 1440 cm^{-1} to C=C stretching of aromatic C, 1375 cm^{-1} to aliphatic deformation of CH_2 or CH_3 groups or O–H bending of phenolic-OH, and 1110-1030 cm^{-1} to C-O–C stretching vibrations in cellulose and hemicellulose; 900-750 cm^{-1} to C–H bending aromatic CH out-of-plane deformation [19].

4. CONCLUSION

Rice straw-derived (Rsd) biochar yield decreases with increment in pyrolysis temperature, due to carbon condensation through dehydration and depolymerization. The residence time of the process, however, does not show any significant effect in term of biochar characteristics. S_{BET} showed macro-porosity between 2-5 µM, was noted to be well visible at 300-60 pyrolysis. The H/C and O/C ratio decrease with temperature, indicative of a shift in the functional group from single chain monomer to the aromatic functional group. Meanwhile, P_{avail} decrease as pyrolysis temperature range between 500-600°C, potentially due to Ca-P binding. Rsd biochar at 300-60 and 400-60 showed potential use as a soil amendment on agricultural soil with respect to (i) cation exchange capacity (CEC) of 61 and 46 $cmol_c$ kg^{-1}, respectively, (ii) pores size distribution. Further field studies on Rsd biochar to soil-plant interaction must be addressed to

8

understand the function of biochar in the farm-scale application.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Department of Statistics Malaysia. Malaysia Statistics Yearbook 2016; Putrajaya: Department of Statistics, Malaysia; 2017.
2. MOA (Ministry of Agriculture and Agro-Based Industry) Bulletin. No.1; 2004.
3. Tipayarom D, Oanh NTK. Effects from open rice straw burning emission on air quality in the Bangkok metropolitan region. Science Asia. 2007;33:339–345.
4. Zhang H, Hu D, Chen J, Ye X, Wang SX, Hao JM, Wang L, Zhang R, An Z. Particle size distribution and polycyclic aromatic hydrocarbons emissions from agricultural crop residue burning. Environmental Science and Technology. 2011;45:5477–5482.
5. Smith P, Martino D, Cai Z, Gwary D, Janzen H, Kumar P, McCarl B, Ogle S, O'Mara F, Rice C, Scholes B, Sirotenko O. Agriculture. In: Metz B, Davidson OR, Bosch PR, Dave R, Meyer LA, editors. Climate Change 2007: Mitigation of Climate Change. Contribution of working group III to the fourth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA. 2007;497–540.
6. Shang Q, Yang X, Gao C, Wu P, Liu J, Xu Y, Shen Q, Zou J, Guo S. Net annual global warming potential and greenhouse gas intensity in Chinese double rice-cropping systems: A 3-year field measure-ment in long-term fertilizer experiments. Global Change Biology. 2011;17:2196–2210.
7. Mosier AR, Halvorson AD, Reule CA, Liu XJ. Net global warming potential and greenhouse gas intensity in irrigated cropping systems in northeastern Colorado. Journal of Environmental Quality. 2006;35:1584–98.
8. Lehmann J. Bio-energy in the black. Frontiers in Ecology and the Environment. 2007;5:381–387.
9. Beesley L, Moreno-Jiménez E, Gomez-Eyles JL, Harris E, Robinson B, Sizmur T. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. Environmental Pollution. 2011;159:3269–3282.
10. Lehmann J, Joseph S. Biochar for environmental management: Science. Technology and Implementation; 2nd ed. Earthscan, London, UK; 2015.
11. Vaccari FP, Baronti S, Lugato E, Genesio L, Castaldi S, Fornasier F, Miglietta F. Biochar as a strategy to sequester carbon and increase yield in durum wheat. European Journal of Agronomy. 2011; 34:231–238.
12. Bell MJ, Worrall F. Charcoal addition to soils in NE England: A carbon sink with environmental co-benefits? Science of the Total Environment. 2011;409:1704–1714.
13. Silber A, Levkovitch I, Graber ER. pH-dependent mineral release and surface properties of cornstraw biochar: agronomic implications. Environmental Science and Technology. 2010;44:9318–9323.
14. Zhao X, Wang J, Wang S, Xing G. Successive straw biochar application as a strategy to sequester carbon and improve fertility: A pot experiment with two rice/wheat rotations in paddy soil. Plant and Soil. 2014;378:279–294.
15. Liu Y, Yang M, Wu Y, Wang H, Chen Y, Wu W. Reducing CH_4 and CO_2 emissions from waterlogged paddy soil with biochar. Journal of Soils and Sediments. 2011; 11:930–939.
16. Li F, Cao X, Zhao L, Yang F, Wang J, Wang S. Short-term effects of raw rice straw and its derived biochar on greenhouse gas emission in five typical soils in China. Soil Science and Plant Nutrition. 2013;59:800–811.
17. Lehmann J, Joseph S. Biochar for environmental management: Science and technology. First. Earthscan, London, UK; 2009.
18. Keiluweit M, Nico PS, Johnson MG, Kleber M. Dynamic molecular structure of plant

biomass-derived black carbon (Biochar). Environmental Science and Technology. 2010;44:1247–1253.

19. Wu W, Yang M, Feng Q, Mc Grouther K, Wang H, Lu H, Chen Y. Chemical characterization of rice straw-derived biochar for soil amendment. Biomass and Bioenergy. 2012;47:268–276.

20. Cheng CH, Lehmann J, Thies JE, Burton SD, Engelhard MH. Oxidation of black carbon by biotic and abiotic processes. Organic Geochemistry. 2006;37:1477–1488.

21. Samsuri AW, Sadegh-Zadeh F, Seh-Bardan BJ. Adsorption of As(III) and As(V) by Fe coated biochars and biochars produced from empty fruit bunch and rice husk. Journal of Environmental Chemical Engineering. 2013;1:981–988.

22. Rayment GE, Higginson FR. Australian laboratory handbook of soil and water chemical methods. Inkata: Melbourne; 1992.

23. Bray RH, Krutz LT. Determination of total, organic and available forms of phosphorus in soils. Soil Science. 1945;59:39–45.

24. Peng X, Ye LL, Wang CH, Zhou H, Sun B. Temperature- and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China. Soil and Tillage Research. 2011;112:159–166.

25. Singh BP, Cowie AL, Smernik RJ. Biochar carbon stability in a clayey soil as a function of feedstock and pyrolysis temperature. Environmental Science and Technology. 2012;46:11770–11778.

26. Thies JE, Rillig MC. Characteristics of biochar: biological properties. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science and Technology. Earthscan, London, UK. 2009; 85–105.

27. Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the composition and application of biomass ash. Part 1. Phase – mineral and chemical composition and classification. Fuel. 2013; 105:40–76.

28. Romanyà J, Khanna PK, Raison RJ. Effects of slash burning on soil phosphorus fractions and sorption and desorption of phosphorus. Forest Ecology and Management. 1994;65:89–103.

29. Weber K, Quicker P. Properties of biochar. Fuel. 2018;217:240–261.

30. Shen J, Tang H, Liu J, Wang C, Li Y, Ge T, Jones DL, Wu J. Contrasting effects of straw and straw-derived biochar amendments on greenhouse gas emissions within double rice cropping systems. Agriculture, Ecosystems and Environment. 2014;188: 264–274.

31. Gai X, Wang H, Liu J, Zhai L, Liu S, Ren T, Liu H. Effects of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate. PLoS One. 2014; 9:1–19.

32. Brady NC, Weil R. The nature and properties of soils. 15th ed. Pearson Education; 2016.

33. Limwikran T, Kheoruenromne I, Suddhiprakarn A, Prakongkep N, Gilkes RJ. Dissolution of K, Ca, and P from biochar grains in tropical soils. Geoderma. 2018;312:139–150.

34. Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel. 2007:86:1781–1788.

35. Xu G, Zhang Y. Shao H, Sun J. Pyrolysis temperature affects phosphorus transformation in biochar: Chemical fractionation and 31P NMR analysis. Science of the Total Environment. 2016; 569–570:65–72.

36. Novak JM, Lima I, Xing B, Gaskin JW, Steiner C, Das KC, Ahmedna M, Rehrah D, Watts DW, Busscher WJ, Schomberg H. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Annals of Environmental Science. 2009;3:195–206.

37. Abrishamkesh S, Gorji M, Asadi H, Bagheri-Marandi GH, Pourbabaee AA. Effects of rice husk biochar application on the properties of alkaline soil and lentil growth. Plant, Soil and Environment. 2015; 61:475–482.

38. Mui ELK, Cheung WH, Valix M, Mc Kay G. Dye adsorption onto char from bamboo. Journal of Hazardous Materials. 2010;177: 1001–1005.

39. Kuo LJ, Louchouarn P, Herbert BE. Influence of combustion conditions on yields of solvent-extractable anhydrosugars and lignin phenols in chars: Implications for characterizations of biomass combustion residues. Chemosphere. 2011;85:797–805.

40. Muter O, Berzins A, Strikauska S, Pugajeva I, Bartkevics V, Dobele G, Truu J, Truu M, Steiner C. The effects of

woodchip- and straw-derived biochars on the persistence of the herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA) in soils. Ecotoxicology and Environmental Safety. 2014;109:93–100.

41. Yao Y, Guo B, Inyang M, Zimmerman AR, Cao X, Pullammanappallil P, Yang L. Biochar derived from anaerobically digested sugar beet tailings: Characterization and phosphate removal potential. Bioresource Technology. 2011;102:6273–6278.

42. Pastorova I, Botto RE, Arisz PW, Boon JJ. Cellulose char structure: A combined analytical Py-GC-MS, FTIR, and NMR study. Carbohydrate Research. 1994;262: 27–47.

43. Paris O, Zollfrank C, Zickler GA. Decomposition and carbonisation of wood biopolymers - A microstructural study of softwood pyrolysis. Carbon. 2005;43:53–66.

44. Qayyum MF, Steffens D, Reisenauer HP, Schubert S. Biochars influence differential distribution and chemical composition of soil organic matter. Plant, Soil and Environment. 2014;60:337–343.