

Physicochemical Performance of Wood Chips Char and Wheat Husk Char for Utilisation as an Alternate Source of Energy



Swapan Suman, Shalini Gautam

ABSTRACT: *This paper explores the characteristics of biomass waste (wood chips and wheat husk) experimentally. Wood has been the primary and cheap fuel for cooking in many households of different countries because it is easily accessible whereas wheat husk is also produced parallelly in huge amount but its handling and proper utilisation also needs to be considered and energy generation. This study aims at providing an alternative to wood chips and wheat husk converted to be biochar for more energy generation. This biomass waste remains unutilised and consumes a lot of effort on its disposal; causes environmental problems such as air pollution from partially combust suspended particles and unwanted addition of gases and heat to the atmosphere along with health hazard. This study takes an attempt to reduce the requirements of fossils fuels reserves using biochar. On the basis of Gross Calorific Value (GCV) and percentage of Carbon, biochar is compared with coal. The biochar derived from biomass were analysed by proximate analysis, ultimate analysis, Heating Value, pH, BET surface area, yield percentage, functional group analysis through FT-IR and microscopic analysis by FE-SEM. The outcomes indicate a quantitative change in the volatile matter, carbon percentage, BET surface area, pH and their functional groups with increase in pyrolysis temperature. The moisture content and yield percentage decrease with increase in temperature.*

Keywords: Biomass; Pyrolysis; Biochar; Physicochemical properties; Gross Calorific Value.

I. INTRODUCTION

Energy consumption pattern of any country indicates the state of socio-economic development. The primary energy sources likes, natural gas, oil, coal are considered as the main source in all over the world. From the recent data the production of primary energy source has reached up to 75-79% compared to other energy sources [1] and the consumption of total primary energy source in the world was 12476.76 million tons in 2012 [2].

Though, renewable energy promotes only 13-18% of total primary energy consumption. Therefore, prominence has been given to utilize the renewable energy as alternative energy source to avoid the depletion of fossil fuels inputs (primary energy sources) [3]. India produces nearly about 350 million tons of solid biomass every year [4], which contains straw, bagasse, husks, shell and agricultural related wastes such as wooden chips, sawdust and wood bark etc.

Biomass is one of the most favourable and cheapest renewable energy resources on earth which is used as a biofuel in form of solid, liquid and gaseous [5]. Agricultural by-products (like, wood dust, wheat husk, rice husk, etc) are used for cooking as a fuel and also utilized in paper and pulp industries as raw material. A large amount of these wastes creates a sharp disposal problem, because if we burn these wastes than its affects the environment directly. Hence it is major challenge for us to utilize these wastes as a green fuel. Pyrolysis is a green and advanced technology, for the conversion of biomass into solid biochars with carbon rich materials. Pyrolysis has shown the potential of recovering hydrocarbons and converting them into useful products in the form of energy [6].

As biochar is a highly carbonaceous product, its high energy content comparable and equivalent with high rank coals [7]. Biochar also has a large microscopic surface area during the pyrolysis process, and it can be used for enhancement of soil fertility and the purification and adsorption of contaminants in water treatment process [8].

This study investigates the performance evolution of biochar with their properties by slow pyrolysis [9] of Wood Chips (WC) and Wheat Husk (WH). Different temperature at 400, 600, 800 and 1000°C were selected for pyrolysis study. Properties of obtained biochars of the studied samples were compared with their mass yield, physical and elemental composition, BET surface area, pH, ash content, morphological structure and their functional group.

II. MATERIALS AND METHODS

A. Biomass materials

For this study we collect two biomass wastes samples such as, wood chips (WC) and wheat husk (WH), all are obtained from different areas of Dhanbad, Jharkhand. The crop residues used varied widely in properties and representative samples of each feedstock was chosen for characterisation. The pyrolysis was carried out at varying temperature (400, 600, 800 and 1000°C) for one hour, after attaining these temperatures on heating rate @ 5-15°C/min.

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B. Characterization methodology

Proximate and Ultimate analysis

Proximate analysis was performed on studied biomass samples (WC and WH) for determination of ash, moisture and volatile matter content with following ASTM standards: E871-82, E1755-01, and E872-82 respectively [10]. And the fixed carbon content was calculated by difference.

And the proximate analysis for wooden chips char (WCC) and wheat husk char (WHC) were determined according to ASTM D1762-84 standard method [11].

Ultimate analysis was performed to obtain the elemental composition of the studied biomass samples for measuring carbon%, hydrogen%, nitrogen% and sulphur% by using the (Vario EL III) CHNS analyser. Oxygen% was calculated by the difference

Heating Values, BET Surface Area and pH

The heating values of the samples were determined by bomb calorimeter. A bomb calorimeter was used according to the (ASTM D4809-00) standard test method. Surface area was determined on dry biochar samples via N₂ adsorption on a Surface Area Analyzer [7]. Brunauer, Emmett and Teller (BET) were generated to determine the single-point surface area.

For the measurement of pH, 5 g biochar sample were soaked in (1:20, w/v ratio) slurry in distilled water [7]. For pH analysis PCS Testr[™] 35 pH meter was used. The pH meter was calibrated with standard pH buffers.

Thermo-gravimetric analysis (TGA) and Differential thermal gravimetric analysis (DTG)

Thermogravimetry analysis was employed to find out the weight loss in biomass and its bio-char generated. A computerised NETZSCH SAT 449F3 thermogravimetry analyser was working at a Nitrogen gas at the flow rate of 20 ml/min and following the ASTM E1131-03 standard.

20 milligrams of sample was taken at room temperature and heated up to a final temperature of 1000°C with a residence time of 1 minute at heating rate of 20°C/min. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of studied samples takes place.

Fourier-transform infrared (FT-IR) spectroscopy and FE-SEM (Field Emission Scanning Electron Microscope)

FT-IR spectroscopy was analysed by a (Perkin Elmer Spectra 2, USA) using the pellet technique by mixing 1 mg of biochar with 200 mg of pulverized spectroscopic-grade KBr (Potassium Bromide).

FESEM was analysed by (SUPRA'55 MonoCL4) Variable Pressure Field Emission Scanning Electron Microscope (FE-SEM). Samples were first coated with silver/gold coating in order to minimize sample charging. SEM images were taken at different points of sample surface with several magnifications ranging from 50X to 15000X. The collected images are imported into the software which converts them into equivalent binary forms based on the Gray-level Threshold values (T). The micro porous sections in the binary images are distinguished by segmenting the image into black and white regions representing solid surfaces and void spaces, respectively [12].

III. RESULTS AND DISCUSSIONS

A. Proximate & Ultimate analysis and GCV of WC and WH samples

The proximate & ultimate analysis and GCV of the WC and WH are shown in Table I. From Table, it was observed that the WC has relatively less ash (1.70%); higher content of VM (78.98%), FC (17.76%), and GCV 15.40 MJ/Kg (3870 kcal/kg) comparison with WH.

The carbon, oxygen and hydrogen content in studied feedstocks are (C, 38.70-48.11%; O, 44.79-54.73%; H, 5.50-6.40%. Further the lower content of hetero elements (N, 0.64-0.66% and S, 0.06-0.41%) in WC and WH is advantageous for environmental concerns.

Table-I Proximate and Ultimate analysis (as received basis) of agricultural biomass

AW Samples	Proximate Analysis				Ultimate Analysis					GCV (MJ/kg)
	M %	VM %	Ash %	FC %	C %	H %	S %	N %	O %	
Wood Chips (WC)	1.56	78.98	1.70	17.76	48.11	6.40	0.06	0.66	44.73	15.40
Wheat Husk (WH)	3.37	72.78	12.14	13.70	38.70	5.50	0.41	0.64	54.73	13.64

B. Yield, pH, GCV, and surface area of the biochars

Physical and chemical characteristics like, Yield%, pH, GCV, and surface area of the biochars derived from WD and WH are shown in Table II. From this table it is observed that at 400°C of pyrolysis relatively higher yield of char, which further decreases progressively with increase in temperature up to 1000°C. At high temperature may surpass the bond cessation energy of agricultural biomass, through which release the volatile components and resulting we get solid char with less yield [8].

The pH values of WCC and WHC varies from (5.65-10.41) and (7.47-11.21) respectively are increase with increase in pyrolysis temperature. Similarly, from Table II it has been clear that gross calorific value of biochar samples increasing at increase in pyrolysis temperatures because of heat promoting components (like FC, C, and H). GCV value for WCC and WHC varies in the range 19.25-24.08 MJ/kg and 16.33-21.05 MJ/kg respectively.

Also BET surface area varies along with pyrolysis temperature for both the biochars in the range 11.90-571.57 m²g⁻¹ for WCC and 116.70-366.90 m²g⁻¹ for WHC. Keiluweit et al., 2010 [13] also observed that surface area increases with increase with pyrolysis temperature. Biochars having higher pH with good surface area are better application in reducing the acidity of soil; refining the cation exchange capacity (CEC) of soil-attributable to its high surface area, creating an additional positive habitat for plants, and purification of contaminated water with toxic and organic pollutants [14-15].

Table-II Physical and chemical characteristics of WCC and WHC.

Biochar	Temperature (°C)	Biochar yield (%)	pH	HHV (MJ/Kg)	BET surface area (m ² g ⁻¹)
WCC	400	27.69	5.65	19.25	11.90
	600	27.20	7.80	20.74	207.28

	800	23.08	9.50	23.11	425.41
	1000	23.00	10.41	24.08	571.57
WHC	400	45.00	7.47	16.33	116.70
	600	38.33	10.88	17.51	259.10
	800	35.50	10.97	20.58	292.22
	1000	34.86	11.21	21.05	366.90

C. Proximate and Ultimate analyses of Wood Chips Char (WCC) and Wheat Husk Char (WHC)

Proximate and Ultimate analyses of WCC and WHC are presented in Table 3. When studied biomass materials subjected to muffle furnace VM content gets vaporised in form of gases and hydrocarbons, resulting we get VM content decreases according with increase in pyrolysis temperature. Because at lower temperature lignin can resist the pyrolytic decomposition but not at higher temperature [16]. The VM content of WCC and WHC varies from 45.55-5.33% and 43.70-6.58% respectively.

From Table III, the WHC showed high ash percentage at all pyrolysis temperatures, because of the partial change in the composition relation between organic and inorganic constituents [16]. It can also be observed that biochars having high ash content contains lower value of fixed carbon (FC) and conversely. Values of FC% varies from 51.12-91.04% and 27.77- 52.88% for WCC and WHC respectively.

Additionally, the ultimate analysis of WCC and WHC varies considerably in esteem of C, H, N, S, and O contents; the content (62.48-93.12%), (1.57-3.75%), (0.35-0.49%), (0.03-0.07%) and (4.78-33.35%) and (49.25-50.09%), (5.01-1.08%), (1.27-0.50%), (0.09-0.24%) and (44.38-48.09%) respectively.

Table-III Proximate and Ultimate analysis of WCC and WHC at different studied pyrolysis temperature

Biochars	Temperature (°C)	VM %	Ash %	FC %	C %	H %	N %	S %	O %
WCC	400	45.55	3.33	51.12	62.48	3.75	0.35	0.07	33.35
	600	19.12	5.77	75.11	79.33	2.76	0.36	0.03	17.52
	800	5.86	6.58	87.56	89.89	2.34	0.43	0.03	7.31
	1000	5.33	3.63	91.04	93.12	1.57	0.49	0.04	4.78
WHC	400	43.7	28.53	27.77	49.25	5.01	1.27	0.09	44.38
	600	10.14	40.25	49.61	50.91	4.51	1.08	0.08	43.46
	800	7.87	40.55	51.58	50.34	2.63	0.68	0.08	46.27

1000	6.58	40.54	52.88	50.09	1.08	0.54	0.24	48.09
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D. FT-IR Analysis of the WC, WH, WCC and WHC at different studied pyrolysis temperature

Figures 1-2 shows the FTIR spectra of WC, WH, WCC and WHC at different pyrolysis temperatures. These graphs are plotted along with wave numbers (cm⁻¹) and transmittance percentage (T%). Graphs represent the aliphatic losses in their functional group due to pyrolysis treatment. The WC and WH have common bands at 3391-3418 cm⁻¹ (Band: O-H stretching), 2920-2925 cm⁻¹ (Band: CH, CH₂ stretching), 1620-1635 cm⁻¹ (Band: C=C stretching), 1505-1514 cm⁻¹ (Band: benzene ring), 1423-1462 cm⁻¹ (Band: aromatic skeletal vibrations combined with C-H in plane deformation; asymmetric in -CH₃ and -CH₂-), 1319-1374 cm⁻¹ (Band: Phenolic OH; aliphatic C-H deformation vibrations, 1240-1243 cm⁻¹ (Band: C-O-C stretching in alkyl aromatic), 1158-1160 cm⁻¹ (Band: C-O-C asymmetry stretching), 1033-1056 cm⁻¹ (Band: C-O stretching). Other band/peaks appeared are at 1723 cm⁻¹ (Band: carbonyl C=O stretching) in WC [17]; additionally the peak at 470 and 1050-1100 cm⁻¹ appeared in WH, which are assigned to SiO₂ [18].

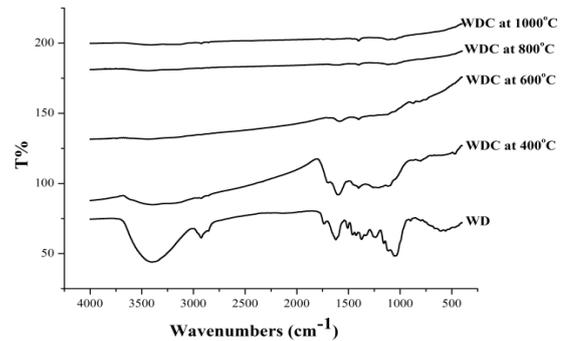


Fig.1. FT-IR Analysis of the WC and WCC at different temperature

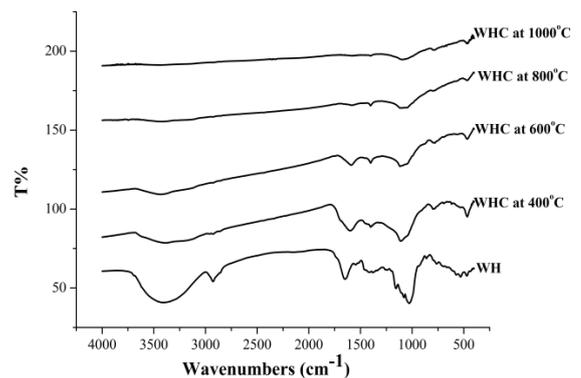


Fig.2. FT-IR Analysis of the WH and WHC at different temperature

From the FTIR spectra of the biochars (Figure 1 and 2), it is seen that the aliphatic loss process is represented by the aliphatic C-H stretching at band (Band: 2950-2850 cm⁻¹) with increasing in pyrolysis temperature from 400 to 1000°C [19].

The representative peaks appeared for aromatic carbon include C–H stretching (Band: 750–900 and 3040–3010 cm^{-1}), C=C (Band: 1380–1452 cm^{-1}), C–C, and C–O stretching (Band: 1578–1700 cm^{-1}) [20–21]. This is perceptibly because of the carbonisation temperature modifies the functional group and aliphatic-C group decreases but aromatic-C group increases [20]. But, when the carbonisation temperature range is 800–1000°C, the bands of hydroxyl and aromatic groups, (Band: 3200–3400 cm^{-1}) and (Band: 1580–1600 and 3050–3000 cm^{-1}), respectively [19] are progressively contracts or diminishes.

E Thermal analysis of the WC, WH, WCC and WHC at different pyrolysis temperature

The weight loss of studied biomass materials and their biochar at different pyrolysis temperatures is shown in Figures 3 and 4, respectively. According to the TGA curves in Figure 3 and 4, 70% to 90% of the samples were decomposed at temperature below 700°C, whereas the weight loss mostly found at the temperature between 150°C to 450°C. These studied wastes are easily decomposed via thermal processing that is a good indication to be used as excellent feedstock for various applications in alternative energy sources. In particular, the weight loss found in wood chips and wheat husk was 70–90% and 40–50%, respectively of the total weight. This behaviour imitates the high mineral content in wheat husk, which acts as a barrier that avoids the diffusion of heat [16]. Similar was the observation other [22].

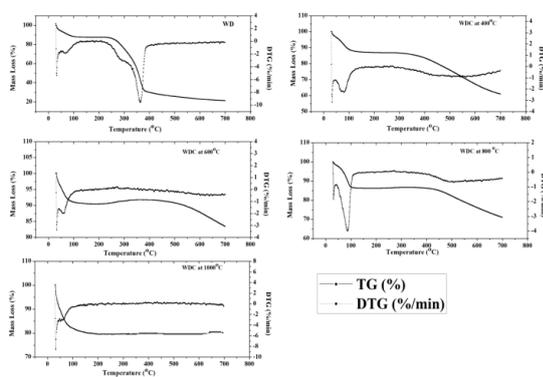


Fig.3. TG and DTA plot of WC and WCC at different temperature

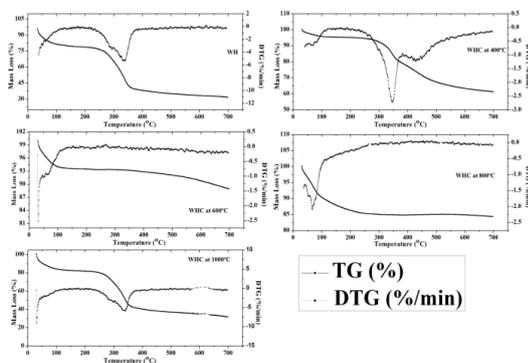


Fig.4. TG and DTA plot of WH and WHC at different temperature

From the DTG curve (Figure 3-4) of WCC, the degradation of cellulose and hemi-cellulose is accomplished at temperature 400°C and but, the degradation of lignin occurred at higher temperature at 600°C and 800°C the decomposition of lignin is almost complete, and achieves the steady state at 1000°C [23]. The DTG profile of WC and its bio-chars obtained at various temperatures is also applicable to that of the WH feedstock and its corresponding biochar at different temperatures. Thus it can be inferred that the thermal stability of the biochar enhances with increase in pyrolysis temperature.

F. FE-SEM image analysis

The FE-SEM images of the WC and WH and its biochar samples are shown in Figures 5. The pictorial inspection of taken images of FE-SEM shows the changes in microstructure among the biochar samples, with noticeable different microspores. Initially, raw biomass samples just ground, show fibrous structure with long fibres [24], which can be easily noticed in case of wood chips and wheat husk samples. The pyrolysis temperature has significant impact on the pore structure and morphology of biomass char [25]. This is because of thermal change, large amounts of VM content flows in a short period of time from the samples that changes the surface reduction and splitting of the particles. At 800°C, the release of VM completely splits the particles, which originate hole or channel like structures. Those channels might have played the role of chimneys during gas or VM release. Thermal decomposition and melting of some compounds, that can break the chemical bonds as a result creates more pores [26]. Accordingly FE-SEM analysis suggests that the BET surface area of the biochar can be enhanced with high pyrolysis temperature, and this observation is similar with others’ findings [27].

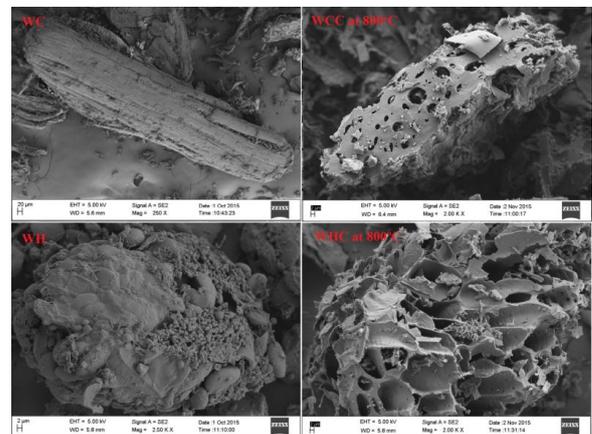


Fig.5. FE-SEM image of WC and WH and its biochar at 800°C

IV. CONCLUSION

- Biochar produced from the pyrolysis of wood chips and wheat husk samples at 400, 600, 800 and 1000°C had different physical and chemical properties.
- Biochar yield was directly influenced by the ash%, carbon% and GCV of studied biomass materials.



- Biochar from wood dust and wheat husk have better specific area at high temperature, which was favourable for soil application. While biochar is a highly carbonaceous materials, but dominant inorganic elements widely varied in both studied feedstocks (WC and WH).
- These obtained results can be used to establish ideal utilization of biomass as energy source and for biochar production.
- The prepared biochar can be a potentially utilised in various sustainable purposes like as a substitute for fossil fuel inputs; enhancement of soil fertility, C-sequestration, and also in waste water treatment.

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REFERENCES

1. Nasir N.F., Daud W.R.W., Kamarudin S.K., Yaakob Z. Process system engineering in biodiesel production: a review. *Renew Sustainable Energy Rev* 2013; 22:631–9.
2. British Petroleum (BP). BP Statistical Review of World Energy, British: BP Plc, 2013. (<http://www.bp.com/en/global/corporate/about-bp/energy-economics/statistical-review-of-world-energy-2013.html>) (accessed October 2013).
3. Halder P.K., Paul N., Beg M.R.A., Assessment of biomass energy resources and related technologies practice in Bangladesh, *Renewable and Sustainable Energy Reviews* 39 (2014) 444–460.
4. Pallavi H.V., Swamy S.S., Kiran B.M., Vyshnavi D.R., Ashwin C.A. Briquetting Agricultural Wastes as an Energy source, *J. of Engg. Sc., Comp. Sc. and Engg. & Tech.* 2014; 2:160-172.
5. Saratale G.D., Saratale R.G., Banu J.R., Chang J.S. Chapter 10 - Biohydrogen Production from Renewable Biomass Resources. *Biohydrogen (Second Edition)*, Biomass, Biofuels, Biochemicals, 2019, Pages 247-277.
6. Swapan Suman & Shalini Gautam (2017) Effect of pyrolysis time and temperature on the characterization of biochars derived from biomass, *Energy Sources, Part A*, 39:9, 933-940, DOI: 10.1080/15567036.2016.1276650.
7. Swapan Suman & Shalini Gautam (2017) Pyrolysis of coconut husk biomass: Analysis of its biochar properties, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 39:8, 761-767.
8. Swapan Suman & Shalini Gautam. (2108) Biochar: Substitute of renewable energy sources for fossil-derived fuel inputs. "(Chapter 12) *Energy Systems and Environment*" page 207-220, *InTech Open Book Progress*.
9. Maggi R, Delmon B. Comparison between 'slow' and 'fast' pyrolysis oils from biomass. *Fuel* 1994; 73(5): 671–677.
10. Demirbas A. Combustion Characteristics of different biomass fuels. *Prog. in En. and Comb. Sci.* 2004; 30: 219–230.
11. Demirbas A. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. *J. Ana. and App. Pyro.* 2004; 72:243–248.
12. Yargicoglu E.N., Sadasivam B.Y., Reddy K.R., Spokas K. Physical and chemical characterization of waste wood derived biochars, *Waste Management* 2014; 36:256-268.
13. Keiluweit M., Nico P.S., Johnson M.G., Kleber M. Dynamic molecular structure of plant biomass-derived black carbon (Biochar). *Environmental Science & Technology* 2010; 44:1247–1253.
14. Zhao S.X., Ta N., Wang X.D., Effect of Temperature on the Structural and Physicochemical Properties of Biochar with Apple Tree Branches as Feedstock Material, *Energies* 2017, 10, 1293.
15. B. Liang, J. Lehmann,* D. Solomon, J. Kinyangi, J. Grossman, B. O'Neill, J. O. Skjemstad, J. Thies, F. J. Luizã o, J. Petersen, and E. G. Neves. Black Carbon Increases Cation Exchange Capacity in Soils, *Soil Science Society of America Journal*, 70:1719–1730 (2006).

16. Jindo K, Mizumoto H, Sawada Y, Sanchez-Monedero MA, Sonoki T. Physical and chemical characterization of biochars derived from different agricultural residues. *Biogeosciences* 2014; 11: 6613–6621.
17. Qian Y, Chengji Zuo, Jian Tan, Jianhui He. Structural analysis of bio-oils from sub and supercritical water liquefaction of woody biomass, *Energy* 2007; 32:196-202.
18. Guo J, Chen B. Insights on the molecular mechanism for the recalcitrance of biochar: interactive effects of carbon and silicon components. *Environ. Sci. Technol.* 2014; 48:9103–9101.
19. Haslinawati M.M., Matori K.A., Wahab Z.A., Sidek H.A.A., Zainal A.T. Effects of temperature on the ceramic from rice husk ash, *Int. J. Basic Appl. Sci.* 2009; 9:111–116.
20. Chen B., Chen Z. Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures, *Chemosphere*, 2009; 76:127-133.
21. Ghani, W.A.W.A.K. Sawdust-derived Biochar: Characterization and CO₂ adsorption/desorption study. *J. of App. Sci.* 2014; 14(13): 1450-1454.
22. Kim WK, Kim YS, Hyun S, Ryu C, Park YK, Jung J. Characterization of cadmium removal from aqueous solution by biochar produced from a giant Miscanthus at different pyrolytic temperatures. *Bioresour. Technol.* 2013; 138: 266–270.
23. Gasparovic L, Korenova Z, Jelemensky L. Kinetic study of wood chips decomposition by TGA, *Chemical Papers* 2010; 64(2):174–181. DOI: 10.2478/s11696-009-0109-4.
24. Fernandez RG, Garcia CP, Lavin AG, de las Heras JLB. Study of main combustion characteristics for biomass fuels used in boilers, *Fuel Processing Technology* 2012; 103: 16-26.
25. Liang H, Chen L, Liu G, Zheng H. Surface morphology properties of biochars produced from different feedstocks, *International Conference on Civil, Transportation and Environment (ICCTE 2016)*, Published by Atlantis Press.
26. Fu P, Hu S, Xiang J, Sun L, Su S, Wang J. Evaluation of the porous structure development of chars from pyrolysis of rice straw: effects of pyrolysis temperature and heating rate. *J Anal Appl Pyrolysis* 2012; 98:177–83.
27. Brodowski S, Amelung W, Haumaier L, Abetz C, Zech W. Morphological and chemical properties of black carbon in physical soil fractions as revealed by scanning electron microscopy and energy-dispersive x-ray spectroscopy. *Geoderma* 2005; 128:116–129.

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