

PHYSICO-CHEMICAL CHARACTERIZATIONS OF SAWDUST-DERIVED BIOCHAR AS POTENTIAL SOLID FUELS

(Pencirian Fizikal-Kimia bagi Biochar Diperoleh daripada Debu Kayu Sebagai Potensi Bahan Bakar Pepejal)

Wan Azlina Wan Ab Karim Ghani^{1,2*}, Gabriel da Silva², Azil Bahari Alias^{2,3}

¹*Department of Chemical Engineering and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia*

²*Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia*

³*Faculty of Chemical Engineering, University Teknologi MARA Malaysia, 40450 Shah Alam, Selangor, Malaysia*

*Corresponding author: wanazlina@upm.edu.my

Abstract

Characterization Malaysian rubber-wood sawdust derived biochar (MRWSB) produced in the fixed bed pyrolysis under different temperatures (450 to 850°C) were studied for its applicability as a solid fuel. A range of analyses were carried out, including biochar oxidation reactivity, inorganic species, oxygen and hydrogen contents in the biochars, release of heteroatoms in biochar as the gaseous product, and biochar structural evolution during pyrolysis process. The results show that the optimum temperature for carbonization to obtain a char having moderately high yield was found as 450 °C. Thermogravimetric analyses (TG) shows that temperatures induces a progressively more ordered carbonaceous structure and leads to a significant changes in the biochar reactivity. The process is coupled with the loss of heteroatoms, released as dominantly carbon dioxide (CO₂) and carbon dioxide (CO). In addition, the elemental study of wood-derived biochar shows the higher carbon content but with low H/C and O/C ratio suggested this material was dominated by highly aromatic structures and this were revealed in the Fourier transform infra-red (FTIR). More importantly, insignificant amount of inorganic species is evidenced in the samples.

Keywords: biochar, sawdust, fixed-bed, pyrolysis, combustion, solid fuels

Abstrak

Pencirian biochar berasaskan habuk kayu getah Malaysia (MRWSB) yang dihasilkan melalui pirolisis reaktor tetap di bawah suhu yang berbeza (450 hingga 850 °C) telah dikaji untuk kesesuaian sebagai bahan bakar. Pelbagai analisis dilakukan, termasuk kereaktifan biochar pengoksidaan, spesies bukan organik, kandungan oksigen dan hidrogen dalam biochar, pelepasan heteroatom didalam biochar sebagai produk gas, dan evolusi struktur biochar semasa proses pirolisis. Hasil kajian menunjukkan bahawa suhu optimum untuk karbonisasi untuk mendapatkan arang dengan perolehan yang tinggi didapati pada suhu 450 °C. Analisis Termogravimetri (TG) menunjukkan bahawa suhu mendorong struktur karbon semakin lebih tersusun dan membawa kepada perubahan ketara dalam kereaktifan biochar ini. Proses ini ditambah pula dengan kehilangan heteroatom, dilepaskan sebagai karbon dominan dioksida (CO₂) dan karbon dioksida (CO). Di samping itu, kajian unsur biochar kayu yang diperolehi menunjukkan kandungan karbon lebih tinggi tetapi dengan rendah H/C dan nisbah O/C menyaranakan bahan ini dikuasai oleh struktur yang sangat aromatik dan ini telah diverifikasi di dalam transformasi Fourier infra-merah (FTIR). Lebih penting lagi, jumlah spesies bukan organik yang tidak ketara terbukti dalam sampel.

Kata kunci: biochar, habuk papan, reaktor tetap, pirolisis, pembakaran, bahan api pepejal

Introduction

Biomass utilization for energy production is highly interesting possibilities for sustainable option to reduce dependency on fossil fuels. In Malaysia, major biomass resource is cheap and widely available especially in form agricultural residues namely palm oil residues, rice, forestry and others. More than 2 million tones agricultural

wastes generated annually and a primary energy equivalent of 108 PJ, are potentially an attractive feedstock for producing energy as it use contributes little or no net carbon dioxide to the atmosphere. However, their utilization is limited due to various reasons such seasonal issues, low value heating value (HV), high ash and mineral content. These issues may cause operational problem in the boiler such agglomeration, molten slag and others [1]. Biochar is a carbon rich (65 to 90%), fine-grained and porous substance obtained when biomass, such as wood, manure and leaves, is heated or natural burned under oxygen limited condition and at relatively low temperatures (<700°C) [2]. The feedstock which is favored for biochar was those with high carbon content. These may include abundant, available and low-cost agricultural by-products, including crop residues (including straw, nut shells and rice husks and rice hulls) [3], switch grass, organic wastes including distillers grain, bagasse from sugarcane industry and olive waste [4], chicken litter dairy manure [5], sewage sludge and paper sludge [6].

There are various technologies currently in use for biochar production namely pyrolysis, carbonisation and gasification. However, slow pyrolysis technology which is characterized by moderate heating rates (ca. 20- 100 °C min⁻¹ and maximum temperatures of around 600°C is the most often referred to the biochar production from various feedstock in the literatures [7-10]. Despite the range of feedstock and techniques available to produce biochar, relatively little work has reported the mechanistic understanding on correlations between biochar's physical and thermochemical properties with view to potential solid fuel in energy production. In the present work, a rubber-wood sawdust (*Hevea brasiliensis*) has been used as a feedstock. Rubber wood is one of the main plantation crops in South East Asia with an estimated plantation area of 1.82 million hectares in Malaysia alone which accounts for 20% of global plantations. To the of the authors knowledge, apart from as successful adsorbent (activated carbon precursor dye removal [11-13]), no publicly accessible reports are available to investigate the stability rubber-wood sawdust-derived biochar as solid fuel in energy production. Hence, the present work attempted to assess Rubber-wood sawdust- derived biochars properties suitability in fuel application.

Materials and Methods

Raw Material and Sample Preparation

Sawdust from rubber wood (*Hevea brasiliensis*) is used in this study, was obtained from a local (Selangor, Malaysia) furniture manufacture. Sawdust samples were dried in crucibles in an oven at 110 °C for 24 hours. The samples were then ground and sieved to 2 to 3 mm particle sizes. The main characteristics of the raw sawdust are presented in Table 1.

Table 1. Main characteristics of the raw sawdust based on ASTM method D 5373

Proximate analyses (wt% dry basis)			Ultimate analyses (wt% dry basis)					
Volatile	Fixed carbon	Ash	Carbon	Hydrogen	Oxygen*	Nitrogen	Sulfur	Calorific Value (MJ/kg)
51.39	14.29	22.67	53.4	6.7	36.8	3.1	0	18.3

*By difference

Biochar Preparation

Pyrolysis to prepare the biochars was carried out using a specially designed fixed-bed stainless steel reactor, with an internal diameter of approximately 60 mm, housed vertically in an electrically heated furnace, under well-controlled conditions. The biomass sample (30 g) loaded into reactor and was heated at a slow-heating rate of 10 K min⁻¹ to a desired temperature (450 to 850 °C) and then held for under 200 mL min⁻¹ ultrahigh-purity (UHP) nitrogen . At the end of the experiment, the reactor was lifted out of the furnace immediately to cool naturally to room temperature with a continuous flow of argon through the reactor. The biochar was then recovered for further characterization.

Instrumental analysis

Proximate and ultimate analyses were performed according to ASTM standard test method D 5373 using a CHNSO analyser (Perkin Elmer 2400 series II). The biochar oxidation reactivity was measured using a Thermogravimetric analyser (Mettler Toledo/TGA/SDRA5le) operating under isothermal conditions. The tests were conducted in an atmosphere of 5% O₂ in nitrogen at a heating rate of 30°Cmin⁻¹ for temperature range 30 to 900°C. The gas evolution the biochars during combustion were measured using evolved gas analysis (EGA) technique and Fourier transform infrared (FTIR) (Perkin-Elmer1600 series analyzer) spectroscopic for functional group analyses. Inorganic species such as Al, Ca, Fe, Mg, Si and Zn were analysed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Results and Discussion

Evolution of biochar and its reactivity

Figure 1 shows the TG (primary y-axis) and DTG (secondary y-axis) curves for the studied biochars. The thermal events of the MRWSB generally follow the basic evolution of carbonaceous residue obtained when lignocellulosic biomass is thermally degraded under different temperatures conditions such cellulose, hemicellulose and lignin at distinctive thermal decomposition [6]. Hemicellulose is the first to decompose, beginning at 250°C and substantially completed by 300°C and followed by cellulose decomposition which may begin at temperatures as low as 300°C. Although lignin begins to decompose at 160°C, it is a slow, steady process extending to 900°C which described the lower peaks heights. However, different profiles were observed for biochar produced at higher temperatures. This suggested that these biochar is stabilized no further decompositions is occurred in their chemical structure.

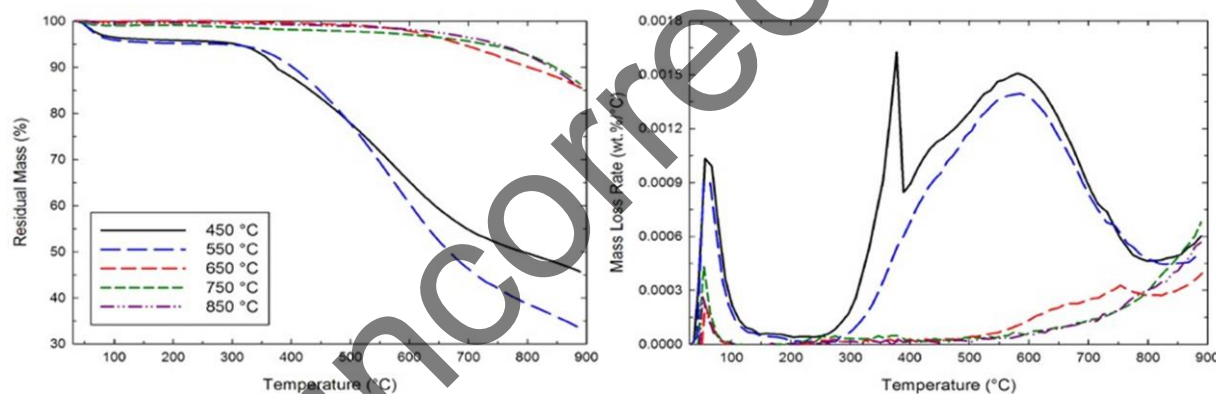


Figure 1. Thermogravimetric analysis of the pyrolysis of biochars at constant heating rate (10 °C min⁻¹) with N₂ sweep gas at 120 mL min⁻¹

Figure 2 shows the exit gas composition of raw sawdust, sawdust derived biochars samples at 450°C and 850°C, respectively. Gas evolution profiles for both samples, with the most notable difference being the releases of oxides of carbon over three distinct temperature regions compared one region to biochar samples. Raw sawdust primarily produced carbon dioxide and carbon monoxide during heating to 280, 380 and 440°C, respectively whereas for biochar samples, the gases evolved during heating between 400 and 450°C. The peaks obtained were due to decomposition of the original sawdust which suggesting that biochar has a homogeneous compound compared to raw sawdust.

This phenomenon explain the degree of aromaticity and the maturation and bonding arrangement of the biochar samples which is reflected in the FTIR spectrum analyses. This indicated that the most C is either directly bonded to a proton or connected through hydroxyl (OH) group. These information on the functionality of the biochars

suggested that the chemical characteristics can vary substantially to a significant extend by the degree of aromaticity.

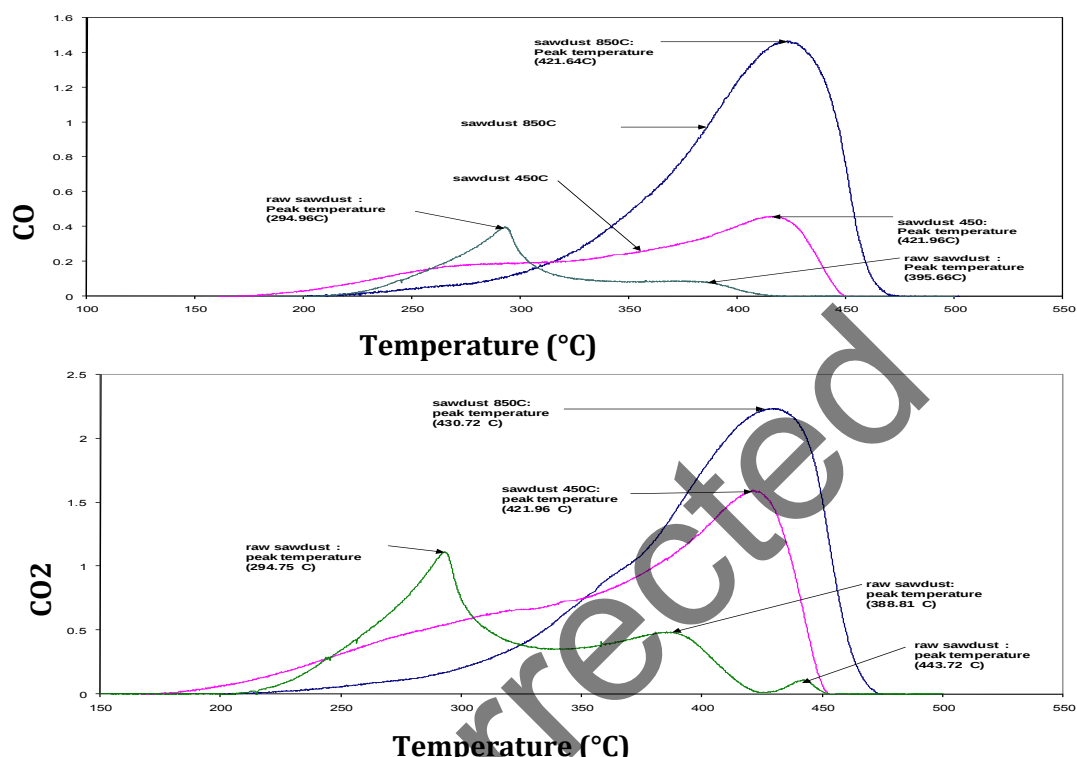


Figure 2. Gas evolution profiles during combustion runs of sawdust and sawdust-derived biochar at different temperatures

Table 2. Elemental contents of raw rubber wood sawdust and biochars. Results of elemental analysis are reported on a dry weight basis.

	Biochars				
	450 °C	550 °C	650 °C	750 °C	850 °C
H/C (mass/mass)	0.039	0.028	0.019	0.011	0.010
O/C (mass/mass)	0.17	0.073	0.067	0.012	0.005
Ash (%)	14.5	16.3	17.8	19.5	20.0
Yield (%)	41.86	37.16	32.78	30.96	28.90
Specific surface (m ² /g)	10	50	100	200	200
Heating value (MJ/kg)	27.3	27.68	27.8	29.6	30.96

BDL – below instrumental detection limit.

^a Results expressed as percentage of dry matter free of ash.

^b Calculated by difference

Effect of temperature on biochar yield, calorific value, carbon, oxygen and Hydrogen content

Table 2 shows the biochar properties for various pyrolysis temperatures between 450 and 850°C. It can be seen that the biochar yield varied according to the reaction temperature. Biochar yield decreased with increasing temperature from 41.86% at 450°C to 28.90% at 850°C. The change in the solid and gas products due to thermal decomposition of the individual components of the original biomass. This phenomenon is likely to be explained by the combined decomposition of the lignin, cellulose and hemicelluloses in the biomass since the breakdown of these components has been shown to occur between 250 and 450°C [14-15]. Above 700°C, the cellulose and hemicelluloses components of the sawdust were evolved mainly in the gas products whereas lignin was mainly responsible for the char. On the other hand, the carbon (C) content showed an increased with increasing pyrolysis temperature, from 44 wt % at 450°C to 97% at 850°C and hence calorific values. This is a result of increased oxidation at higher temperatures, and reflects the conclusion drawn by the Schmidt and Noack on the characteristics of black carbon [16].

Retention of Inorganic Species in Biochars

Table 3 shows the contents of various inorganic species in the raw sawdust and sawdust-derived biochar sample. For the raw wood, the Al and Zn species, such are dominant species but traces amount were detected in the biochar samples.

Table 3. Elemental compositions of biochar samples from sawdust

Samples	Al	Ca	Fe	Mg	Si	Zn
Raw sawdust	13.89	12.72	8.35	0.35	8.78	19.32
Biochar (450°C)	nd	4.121	6.563	nd	Nd	12.93
Biochar (550°C)	nd	6.582	7.652	nd	Nd	3.128
Biochar (650°C)	nd	10.3	6.157	nd	Nd	7.256
Biochar (750°C)	nd	1.848	0.576	nd	Nd	2.299
Biochar (850°C)	nd	5.83	1.605	nd	Nd	4.626
nd -not detected						

Conclusion

The pyrolysis of MRSWB is characterized as carbon rich and reactive where pyrolysis temperature is found greatly influenced both their thermal and chemical properties. These characterizations suggested that these biochars is suitable for fuel purposes as well after processing like briquetting and in the form of char-liquid fuel and char-water slurries. This study shows that the sawdust can be a resource for biochar production. These findings will serve as a base for future systematic research on the same issue.

Acknowledgement

The authors express their gratitude to the Ministry of Science, Technology and Innovation (MOSTI) of Malaysia, Academy Science of Malaysia and Ministry of Higher Education (MOHE) of Malaysia (FRGS 03-01-04-799FR/5523839 and RUGS 05-02-12-895RU/9346500) for financial support. Also kind acknowledgements to the Dept. of Chemical and Biomolecular, University of Melbourne, Australia for their combustion test facilities.

References

1. Werther J., Saenger M. (2000). Combustion of agricultural residues. *Progress in Energy and Combustion Science*. 26:1-27.
2. Sohi S, Lopez-Cape E, Krull E and Bol R. (2009). Biochar, Climate change and soil: A review to guide future

- research. CSIRO *Land and Water Science Report* 05/09.: 64-80.
3. Zhang T, Walawender WP, Fan T, Fan M, Daugaard D. and Brown R. C.(2004). Preparation of activate carbon from forest and agricultural residues through CO₂ activation. *Journal of Chemical Engineering* 105:53-59.
 4. Sensoz S., Demirala I. and Ferdi G. H (2006). Olive bagasse (*Olea europea* L. Pyrolysis *Bioresource Technology* 97:429-436.
 5. Das K.C., Garcia-Perez M., Bibens B., and Melear N(2008). Slow pyrolysis of poultry litter and pine woody biomass, Impact of chars and bio-oils on microbial growth. *J. of Environmental Science and Health: Part A* 43:714-724
 6. Shinogi, Y., Yoshida H., Koizumi T., Yamaoka M. and Saito, T. (2002). Basic characteristics of low-temperature carbon products from waste sludge. *Advances in Environmental Research* 7:661-665.
 7. Purevsuren B. Avid, Tesche B. and Davajaav (2003). A biochar from casein and its properties. *J. Material Science* 38:2347-2351.
 8. Sensoz S. (2003). Slow pyrolysis of wood barks from *Pinus brutia* Ten and product Compositions *Bioresource Technology* 89:307-311.
 9. Azargohar R and Dalai A. K (2008). Steam and KOH activation of biochar: Experimental and Modeling studies. *Microporous Mesoporous Material* 110: 413-421.
 10. Xinde C., Lena M., Bin G. and Willie H. (2009). Dairy-Manure derived biochar effectively sorbs lead and atrazine. *Environmental Science and Technology* 43:3285-3291.
 11. Srinivasakannan and Mohamad Zailani Abu Bakar(2004), Production of activated carbon from rubber wood sawdust. *Biomass and Bioenergy* 27:89-96.
 12. Prakash Kumar, B. G., Shivakamy, Lima Rose M. and Velan M. (2006). Preparation of steam activated carbon rubberwood sawdust (*Hevea brasiliensis*) and its adsorption kinetics. *J. of Hazardous Material* 136: 922-929.
 13. Materazzi S., Gentili A. and Curini R. (2006). Application of evolved gas analysis Part 2: EGA by mass spectrometry, *Talanta*, 69:26-35.
 14. Demirbas A. (2004). Effects of temperature and particle size on biochar yield from pyrolysis of agricultural residues. *J. of Analytical and Applied Pyrolysis* 72(2):243-248.
 15. Van de Velden M, Baeyens J, Brems A, Janssens B. and Dewil R. (2010). Fundamentals, Kinetics and endothermicity of the biomass pyrolysis reaction. *Renewable Energy*, 35: 232-242.
 16. Schmidt W. M. I and Noack A. G. (2000). Black carbon in soils and sediments: Analysis, Distribution, implications, and current challenges. *Global Biogeochemical Cycles* 14:777-793.