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Solid Biofuels from Hydrothermal Carbonization: A Comparative Study on Woody and Non-woody Biomass Material

[1] J.S. Saidatul, [2] H.R. Jonathan, [1]K.A. Tanveer, [1]S.M.F. Sharifah

[1]*Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300, Kuantan, Pahang, Malaysia.*
[2]*Department of Chemical and Process Engineering, University of Sheffield, Mappin Street, Sheffield, S1 3JD, United Kingdom.*

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ABSTRACT

The transition of energy route from fossil fuels to renewable fuels, offer an opportunity to waste material, specifically biomass, in the energy production business. Biomass is a well-known waste material that has heterogeneous nature. This complicated nature poses a barrier on the competitiveness of biomass in the energy generation market. One of the methods is through the hydrothermal carbonization process. It is also proven through various experiments that the hydrothermal carbonization process has the ability to convert different type of biomass into higher carbon products. However, the complexity of biomass in nature shows that various chemical and physical characteristics were reported. Therefore, in this study, a comparison between carbon products from woody and non-woody agricultural waste via hydrothermal carbonization was done. Wood chips (WC) were chosen for the woody type of biomass, while for the non-woody, the oil palm empty fruit bunch (EFB) was chosen. The hydrothermal carbonization process occurs in the excess water with the addition of citric acid as the catalyst. The reaction process occurs in a pressure vessel for temperature, 220°C at different operating time. The chemical (elemental analysis, proximate analysis, fourier transform infrared spectroscopy (FTIR), thermagravimetric analysis (TGA),) and physical characteristic (field emission scanning electron microscopy (FESEM) andgas pyconometer) ratio) of the carbon products were verified. The hydrothermal carbonization process converts the EFB and WC into higher percentage of carbon content solid products. The carbon conversion of EFB's carbon increased for 20% compared to the raw EFB (43.8% of carbon). Based on the FESEM pictures, the formation of globular structure on the EFB biocarbons' surface area can be seen, while, severe damages on the fibres can be observed on the morphology of WC biocarbons. In general, carbon products from hydrothermal carbonization process have the ability to produce more energy compared to their raw materials. However, the non-woody biomass product has higher carbon conversion and combustion ability compared to the woody biomass' carbon.

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INTRODUCTION

The transition of energy route from fossil fuels to renewable fuels, offer an opportunity to waste material, specifically biomass, in the energy production business. Biomass could be a possible solution to the depletion of fossil fuels as it is classified as a renewable energy source, as plants obtained energy from sunlight through photosynthesis.

Biomass is defined as any renewable organic matter. It used to be an unwanted product, which would conventionally be dumped in the landfill or burned. Nevertheless, issues such as depletion of fossil fuels and environmental problems have revolutionised the function and value of biomass, especially in the area of research and development.The ability of biomass to be converted into energy has been investigated in various areas such as the characteristics of the materials, the applicable technology and process efficiency.

The most important advantage of using biomass as a source of energy is the environmentally friendly nature of the by-products. While reducing of the amount of greenhouse gases being released into the atmosphere, because the amount of CO_2 produced from biomass is absorbed by the plants as they grow and it is always constant, so biomass does not contribute to the concentration of atmospheric carbon. Although using biomass still generates traces of sulphur and nitrogen, it does however help reduce the formation of acid rain, as the sulphur and nitrogen content from biomass is less than fossil fuel (Demirbas, A., 2005).

Corresponding Author: J.S. Saidatul, Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300, Kuantan, Pahang, Malaysia.

In Malaysia, biomass applications for generating bioenergy either directly as a fuel or first changing biomass into intermediates, such as ethaol, have taken place since 2000. The Small Renewable Energy Programme (SREP) was expedited by the Malaysian Government in 2001 (Harimi, M.Megat Ahmad, M.M. H.,Sapuan, S.M. and Idris, 2005). The objectives of this specific programme are: to set up small power producers with a maximum capacity 10 MW of electricity from renewable fuel sources, to reduce the usage of the fossil fuels as electricity resources, and to cut down the emission of greenhouse gases (GHGs).

Biomass is a well-known waste material that has heterogeneous nature. This complicated nature poses a barrier on the competitiveness of biomass in the energy generation market. For decades, several routines have been investigated and practiced to gain the optimum desired energy. One of the methods is through the hydrothermal carbonization process.

The hydrothermal carbonization process is known as an intermediate process to transform biomass into a higher carbon content product. The procedure to help the cracking process between the polymeric bonds in the biomass. The hydrothermal process is clearly a desirable process (Demirbas, A., 2005) due to its ability to process biomass in a wet condition. As the hydrothermal process involves water and heat throughout the procedure, excess water content in the beginning stage offers an advantage for this process to stimulate the formation of hydrothermal condition. The predicted reaction process can be divided into three level of process: hydrolysis, dehydration or decarboxylation, and carbonisation through polymerisation and aromatisation processes Funke, A. and Ziegler F., 2010).

This process has the ability to work with high moisture (>60%) materials and the product can be attain in short retention time. It is also proven through various experiments that the hydrothermal carbonization process has the ability to convert different type of biomass into higher carbon products (Chew, J. and Doshi, V., 2011; Kaewluan, S., Pipatmanomai, S., 2011). However, the complexity of biomass in nature shows that various chemical and physical characteristics were reported. Therefore, in this study, a comparison between carbon products from woody and non-woody agricultural waste via hydrothermal carbonization was done. The hydrothermal carbonization process converts the EFB and WC into higher percentage of carbon content solid products.

MATERIALS AND METHODS

Materials:

Wood chips (WC) were chosen for the woody type of biomass, while for the non-woody, the oil palm empty fruit bunch (EFB) was chosen.

Methods:

The hydrothermal carbonization process occurs in the excess water with the addition of citric acid as the catalyst. In this work, 3 grams of sample were added for every conditions. The reaction process occurs in a pressure vessel for temperature, 220°C for six different operating time, which are 2.5, 5, 10,14,18 and 22 hours. After that, the products were filtered to get the solid materials. The solids were dried in the oven at 105±1°C for four hours.

Characterization:

Several analysis were carried out the measure the quality of the carbon products produced. The chemical (elemental analysis, proximate analysis, fourier transform infrared spectroscopy (FTIR), thermagravimetric analysis (TGA) and physical characteristic (field emission scanning electron microscopy (FESEM) and gas pyconometer) of the carbon products were done.

RESULTS AND DISCUSSION

Raw Material Characteristics:

The raw material characteristics are an important factor, as they define, the starting point and preliminary criteria of each material chosen. The materials were analysed using proximate, elemental and thermogravimetric (TGA) analyses, and the results is shown in Table 1.

The EFB was taken directly from a palm oil mill, which resulting higher moisture content was obtained from the EFB compared to the wood shavings. However, wood shavings are dry recycling products from wood chips or wood manufacturing wastes. Consequently, high moisture content will increase the efficiency of the dehydration process during the HTC process because this method requires water during the process. The ash content was carried out to measure the quantity of the incombustible solid after the combustion process. Table 1 illustrated the amount of ash for WC were lower than EFB and confirmed by Chuah et.al (Chuah, T.G., Azlina, A.G.K.W.,Robiah Y. and Omar R., 2006), which the wood waste is 0.4 wt%, while the EFB is 8 wt% (Chuah, T.G., Azlina, A.G.K.W., Robiah Y. and Omar R., 2006).

Table 1: Chemical Compositions of Untreated EFB and WC [8].

Analysis	Characteristic	EFB	WC
Proximate	Moisture (wt%)*	63.49	11.31
	Ash (wt%)$^+$	1.00	0.17
	Volatile (wt%)$^+$	32.56	80.34
	Fixed carbon (wt%)$^+$	2.96	8.19
	Calorific value (MJ/kg)$^+$	19.98	18.23
Elemental	Carbon (wt%)$^+$	43.78	47.03
	Hydrogen (wt%)$^+$	6.06	6.51
	Nitrogen (wt%)$^+$	0.56	0.14
	Oxygen (wt%)$^+$	49.67	46.46
TGA	Cellulose (wt%)$^+$	38.50	62.08
	Hemicellulose (wt%)$^+$	20.93	9.07
	Lignin (wt%)$^+$	9.54	8.15

*Samples were measured as obtained
$^+$Dry samples were used

The procedure of investigating the volatile content was similar and a fast pyrolysis process was used. It required a high temperature process (925°C) at short residence time (7 minutes) as at this condition, the volatile matter in the sample will be fully converted into gaseous material and leave the solid. Based on the calculations the quantity of volatile matter in EFB is lower than WC.

The remaining mass of carbon found in the solid products after releasing moisture, ash and volatiles contents is known as the fixed carbon. Table 1 shows that the EFB content 5 wt% lower fixed carbon than the WC. Although, fixed carbon does not indicate the amount of carbon, it has good connection with the amount of lignin in lignocellulose due to the ability of this component to withstand a high temperature decomposition process (Demirbas, A., 2005).

Thermogravimetric (TGA) analysis was carried out to measure the lignocellulosic component of samples. High cellulose and hemicellulose content will give an advantage on the HTC process as these substance reacts well in subcritical water condition. Therefore, we expect to see conversion of the EFB and WC in chemical and physical characteristics after the HTC process.

Biocarbon Characteristics:

Solid products (noted as biocarbon) generated for every process show variation in physical and chemical characteristics. The colour of these products changes from light brown light to completely black and char like. The HTC process convert estimately 60 wt% of the sample into biocarbon.

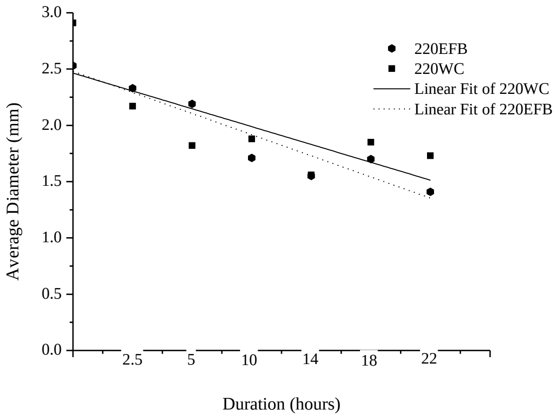


Fig. 1: Average particle diameter of the EFB biocarbons.

The average diameters of the biocarbon particles produced were calculated from the volume data obtained from a gas pyconometer. The term ‘average diameter’ was used in this calculation because the particle size of our product was not uniform.Theoretically, the particle size of the products will be smaller for higher operating temperature due to the subcritical water characteristic, such as density, ionization constant and solubility is basically reducing. These characteristics enhanced the reaction capacity of the liquid medium with the solid substance, lead to increase break-up of the material.

The average particle diameters of the EFB and WC biocarbons are plotted in Fig. 1. As seen in the graph, the mean diameters of the EFB biocarbons are smaller than the WC biocarbons. The average diameter of EFB biocarbon processed at 220°C for 22 hours is 1.41 mm while the diameter of WC biocarbon from the same condition is 1.73 mm. The results shows that the biocarbons heated at 220°C started to show the effect of different operating time as the trend of the mean diameters of biocarbons is declining.

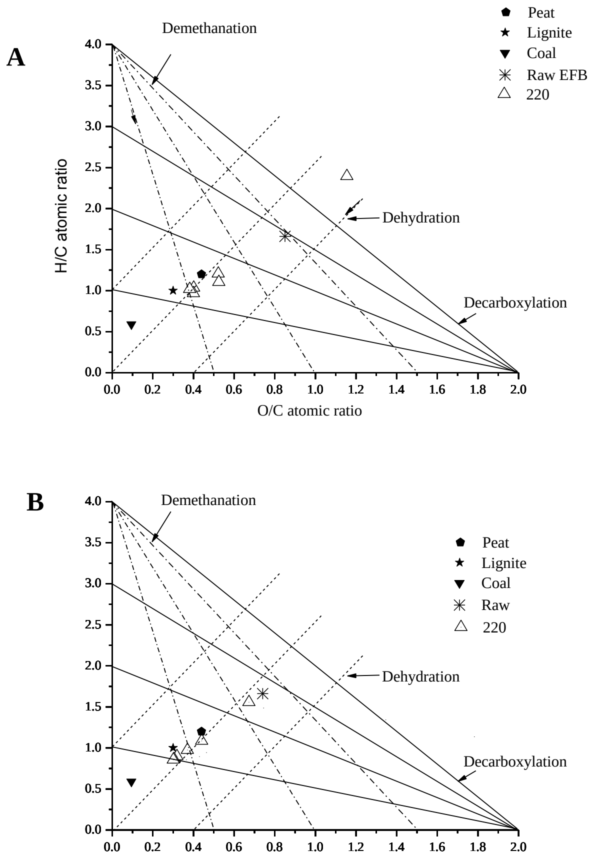


Fig. 2: Van Krevelen diagram of biocarbons (A: EFB and B:WC) at different residence time and constant temperature (220^{o}C).

A van krevelen diagram is a plot of hydrogen (H) and carbon (C) atomic mass ratio relative to oxygen (O) and carbon (C) atomic mass ratio, which gives prediction on the possible reactions occurs during the HTC process. The biocarbons and raw EFB are plotted in Fig. 2A showslower O/C and H/C ratios obtained for the EFB biocarbons in comparison with the raw EFB. The O/C ratio of raw EFB is 0.85 and the H/C ratio is 1.66. While, a reduction of 55% of O/C and 38% of H/C ratio was calculated for the biocarbon operated at 220°C and 22 hours. In addition, the H/C ratios of the biocarbons processed at 220°C are mainly located between the H/C ratios of peat and lignite.

In Fig. 2B, the O/C and H/C ratios of biocarbons from WC are plotted. The increment of operating temperature and time reduced the O/C and H/C values of the WC biocarbons. Similar to the trend observed for EFB biocarbons (Fig. 2A), the ratios of the WC biocarbons are smaller than the raw WC. Compared to the raw WC, the H/C value of WC biocarbon heated at 220°C for 22 hours decreased from 1.66 to 0.86 while the O/C ratio reduced from 0.75 to 0.30.

The H/C and O/C ratios decreased, generally, for longer time and higher temperature. In addition, the biocarbons from WC recorded smaller ratios than the EFB biocarbons. Based on the trend of the biocarbons, it can be concluded that the HTC process was dominated by dehydration process.

A comparison on the spectrum for different operating time at 220°C were illustrated in Fig. 3 as the spectrum trends for both, EFB and WC biocarbons are not affected by the operating time less than 10 hours. As shown in Fig. 3, the intensity of carbon products at 5 and 10 hours are high in range 1. It can be assumed that hydrolysis process is mainly occur for this residence time. However for longer operating time (> 10 hours), the spectrum peaks, especially OH bridge, started to diminish.

The biocarbons heated at temperature, 220°C, showed less peaks detected due to the changes of the chemical bonds during the reaction. The formation of aromatic structures and more aliphatic structures are deminishedcan be evaluated as only 2 clear peaks of C=O (range 3) and C=C (range 4) bonds and small peaks of CH (range 5) and CO (range 6) bonds were detected.

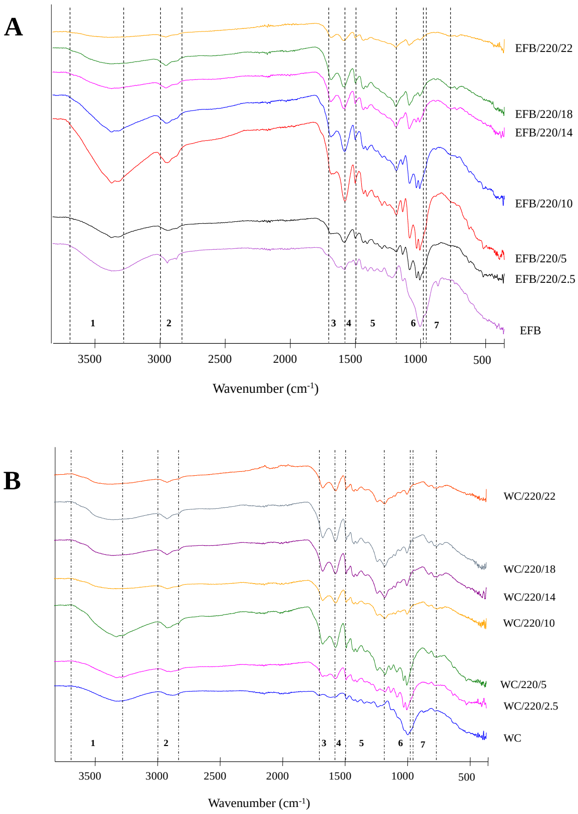
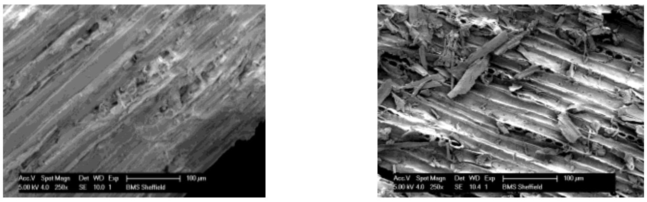
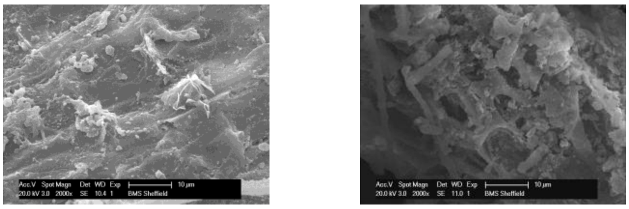


Fig. 3: FTIR spectra of biocarbons (A: EFB and B: WC) at different residence time and constant temperature (220^{o}C).



A B

Fig. 4: Morphology of WC biocarbons at 220°C and different residence time (A= 2.5, B=22 hours).



A B

Fig. 5: Morphology of EFBbiocarbons at 220°C and different residence time (A= 2.5, B=22 hours).

The morphology of WC and EFB investigated to study the structure before and after processing at several operating temperatures and times.Small holes can be seen on the morphology of biocarbons as a repetition of the pores occurs at similar distance with another pore. This can be assumed that a rupture process of fibres on the weakest spot, which is amorphous part[7,8], of the fibre polymeric bonds starts to occur at all durations for temperature 220°C. While, a major breakage can be seen on the surface morphology of the WC biocarbons process 220°C for more than 10 hours due to the formation of small fibres.

Compared to WC biocarbons, an increment of the surface area can be seen on the surface of the EFB biocarbaons due to the number of the pores detect. The EFB biocarbons show an increment on the diameter of the pores with the formation of small globules for all operating time 220°C.

Conclusion:

In general, carbon products from hydrothermal carbonization process have the ability to produce more energy compared to their raw materials. However, the non-woody biomass product has higher carbon conversion and combustion ability compared to the woody biomass' carbon. In future, the characteristics and potential of the liquids products will be furhter investigate.

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