Australian Journal of Basic and Applied Sciences, 10(17) Special 2016, Pages: 122-127

AUSTRALIAN JOURNAL OF BASIC AND APPLIED SCIENCES

ISSN:1991-8178 EISSN: 2309-8414
Journal home page: www.ajbasweb.com

Effect of Mixing towards the Production of Carbonaceous Kenaf Fiber via Hydrothermal Carbonization Process

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ARTICLE INFO

Article history:
Received 19 August 2016
Accepted 10 December 2016
Published 31 December 2016

Keywords:
Kenaf Carbonaceous Fiber Hydrothermal Carbonization Process (HTC) Biomass Biochar

ABSTRACT

Hydrothermal carbonization process (HTC) is a relatively simple method to convert biomass to carbonaceous material that involves reaction in a closed system. HTC is convenient, fast and environmentally friendly way to convert biomass into higher value of carbonaceous material. A comparison on the carbon percentage produced from HTC using Kenaf fiber is performed and the optimum HTC operating condition of Kenaf fiber is aimed. The heating process is carried out using two different conditions, with and without stirring at different time period which is 2 hours, 4 hours, 6 hours, 8 hours and 10 hours at constant temperature of 225 °C. Vario Micro CHNS Analyzer used to determine the element values in the sample shows that for sample without stirring, sample heated for 2 hour produces lowest carbon percentage which is 52.51% and sample heated for 10 hour produces the highest carbon percentage which is 60.20% similar trend was obtained for the stirring sample heated for 2 hour produces 48.43% and sample heated for 10 hour produces 56.73%. The percentage of carbon increase as the longer time period of heating. Based on the results, samples without stirring obtain the higher percentages of carbon content compared to the samples with stirring at 10 hour operating time.

INTRODUCTION

Hydrothermal carbonization process (HTC) can be defined as combined dehydration and decarboxylation of a fuel to raise its carbon content with the aim of achieving a higher calorific value (Basso et. al, 2015., Berge et.al, 2011., Funke & Ziegler, 2010). The advantage of HTC is that it can convert wet input material into carbonaceous solids at relatively high yields without the need for an energy-intensive drying before or during the process. This opens up the field of potential feedstock's to a variety of nontraditional sources: wet animal manures, human waste, sewage sludge, municipal solid waste (MSW), as well as aquaculture and algal residue (Libra et.al, 2011., Oliveira *et al*., 2013., Tekin *et al*., 2014). HTC process is an exothermal process (Berge *et al*., 2015., Parshetti *et al*., 2013) which lowers both the oxygen and hydrogen content of the feed by mainly dehydration and decarboxylation and achieved by applying temperatures of 180- 350°C in a suspension of biomass and water at saturated pressure for several hours (Funke & Zeigler, 2011., Hu et.al, 2010., Kruse et.al, 2013). HTC process can be carried out in two ways which is directly or catalyst assisted. As for direct HTC process, only water and sample are heated in the vessel while catalyst assisted process catalyst such as citric acid and metal ions are added into the process (Libra et.al, 2011., Xiao *et al*., 2012., Sabio *et al*., 2015). In this study, HTC process is carried out in the directly in which Kenaf fiber and water are heated together without any

To Cite This Article: Munirah Ezzah Binti Tuan Zakaria, Norlirabiatuladawiyah Binti Che Ani, Saidatul Shima Binti Jamari, Suriati Ghazali, Tanveer Ahmed Khan, Mohd Faizal Bin Ali., Effect of Mixing towards the Production of Carbonaceous Kenaf Fiber via Hydrothermal Carbonization Process. ***Aust. J. Basic & Appl. Sci.,*** *10(17): 122-127, 2016*

catalyst according to parameters. Natural fibers has been proved as replacement for synthetic and other non-recyclable fibers as they are abundant, cheap, renewable and easily recycled. Kenaf fiber or also known as *Hibiscus Cannabinus L* is the natural fiber used in this study. Kenaf can produce high content of cellulose in average of 44 to 63.5% and hemicellulose in average between 15 to 23% made it suitable as the raw material use for HTC process due to high contain of lignin, hemicellulose and cellulose (Zainuddin et.al, 2013). Moreover, kenaf is very suitable in tropical warm area (Falasca *et al*., 2014., Saba, Paridah, *et al*., 2015., Saba, Jawaid, *et al*., 2015) because of it is a fast growing plant and in almost four month it can be ready for harvesting (Saba, Paridah, *et al*., 2015). Hence, in one year it is possible to obtain two times fibers production.

MATERIALS AND METHODS

Kenaf fiber was obtained from Lembaga Kenaf and Tembakau Negara (LKTN), Indera Mahkota in Pahang. Kenaf fiber was processed to a small length in ranging of 10 cm to 20 cm before grinding to fine pieces approximately from 550 to 600µm. The HTC process was conducted at different time (2h, 4h, 6h, 8h and 10h) with constant temperature, 225°C by using the supercritical unit Buchiglauster model. The process is divided to two conditions which are with and without stirring. 50g of grinded Kenaf fiber was dispersed in 1L of pure water and mixed homogenously before inserted into the reactor. The reactor was sealed to avoid any pressure released and heated to 225°C. Residence time was defined when the reactor reached the desired temperature and the stirrer speed was increased to 50 rpm. When HTC process reached time, reactor was set to be cooled to room temperature for 12 hours before the product can be collected. The product was then dried at 105 °C until solid carbonaceous product known as biochar was collected. The sample without stirring was conducted with similar method without active the stirrer.

RESULTS AND DISCUSSION

Solid product generated from HTC process shows variation on the color of the product in which the color changes from dark brown to completely black. The chemical characteristic of carbonaceous Kenaf fiber produce by the hydrothermal carbonization process were determined from their elemental contents, such as carbon (C), hydrogen (H), and oxygen (O) using an elemental analyzer(Vario Macro CHNS Analyzer). The percentage of the elements and molecular formula of carbonaceous Kenaf fiber with stirring and without stirring processed at different operating time for 225°C was listed in Table 1 and Table 2.

Table 1: Percentage of carbon at different time with stirring.

Sample	Time (h)	C (wt%)	H (wt%)	N (wt%)	*O (wt%)	Molecular formula, CHxOy
Kenaf fiber	0	38.86	6.39	3.28	51.47	$CH_{1.96}O_{0.99}$
	2	48.43	5.83	5.96	39.90	$CH_{1.44}O_{0.62}$
	4	48.31	5.59	8.38	37.60	$CH_{1.38}O_{0.58}$
	6	54.91	5.25	11.27	28.57	$CH_{1.14}O_{0.39}$
	8	55.74	5.01	14.22	25.03	$CH_{1.08}O_{0.34}$
	10	56.73	5.05	18.31	19.91	$CH_{1.07}O_{0.26}$

Table 2: Percentage of carbon at different time without stirring.

Sample	Time (h)	C (wt%)	H (wt%)	N (wt%)	O* (wt%)	Molecular formula, CHxOy
Kenaf Fiber	0	38.86	6.39	3.27	51.46	$CH_{1.96}O_{0.99}$
	2	52.51	6.20	1.38	39.47	$CH_{1.46}O_{0.58}$
	4	56.25	6.17	1.45	35.90	$CH_{1.35}O_{0.49}$
	6	56.15	6.17	1.51	35.85	$CH_{1.35}O_{0.49}$
	8	59.28	6.09	1.44	33.08	$CH_{1.26}O_{0.43}$
	10	60.20	6.03	1.62	31.74	$CH_{1.23}O_{0.41}$

*O (wt%) = 100 – C (wt%) – H (wt%) – N (wt%)

Table 1 and Table 2 showed that the amount of carbon content increased as the time increased for both condition while the hydrogen and oxygen decreased due to the removal of H and O element in the HTC process. The molecular formulas for carbonaceous Kenaf fiber illustrated longer operating condition will resulted lower H and O atoms attached with one carbon atom. As showed in Table 1 and 2, the percentage of carbon produced varies between with stirring and without stirring condition. The percentage of carbon produced was higher from without stirring sample compared to with stirring sample.

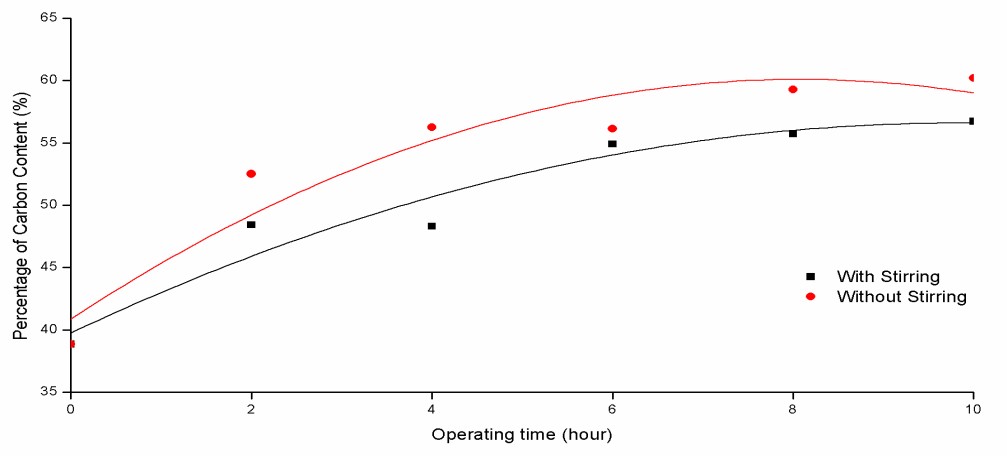

Fig. 1: Percentage of carbon content (%) vs time (h) for sample with and without stirring.

Figure 1 shows the percentage of carbon keeps on increasing as the time period increase. The carbon content increase up to 56.73% for sample with stirring and 60.20% for sample without stirring and both condition at 10 hour operating time. The HTC process generally happened in three reactions which are hydrolysis, dehydration and carboxylation process throughout the conversion of Kenaf fiber into carbonaceous Kenaf fiber (Fakkaew *et al*., 2015., Jamari and Howse, 2012., Nizamuddin *et al*., 2016). In Figure 1, there was a slight decrement of carbon value at 4 hour operating time (with stirring) and 6 hour operating time (without stirring) which predicted that HTC process promote hydrolysis reaction. These results shows that with stirring, HTC process undergo hydrolysis reaction faster than without stirring but produces lower carbon percentage and vice versa. Besides, a higher carbon yield produced at 10 hours operating time for both condition explained that the cleavage and breakage of weak oxygen and hydrogen bonds happened during HTC process. Based on Figure 1, 10 hours operating time without stirring condition giving the high yield of carbon content compared to with stirring condition.

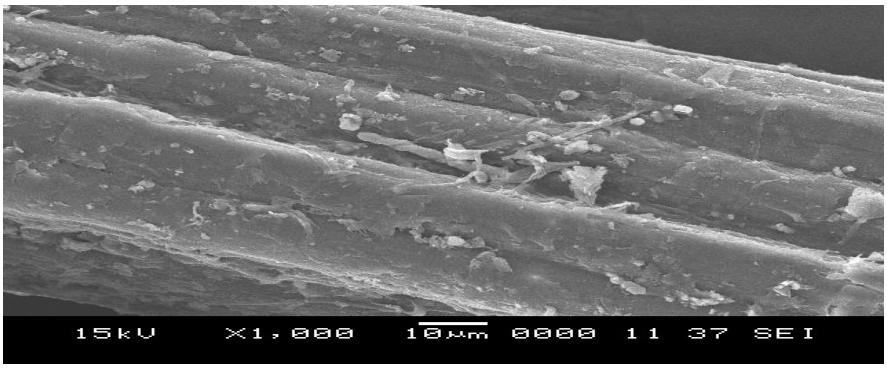

Fig. 2: SEM micrographs of raw kenaf fiber with 1,000x magnification.

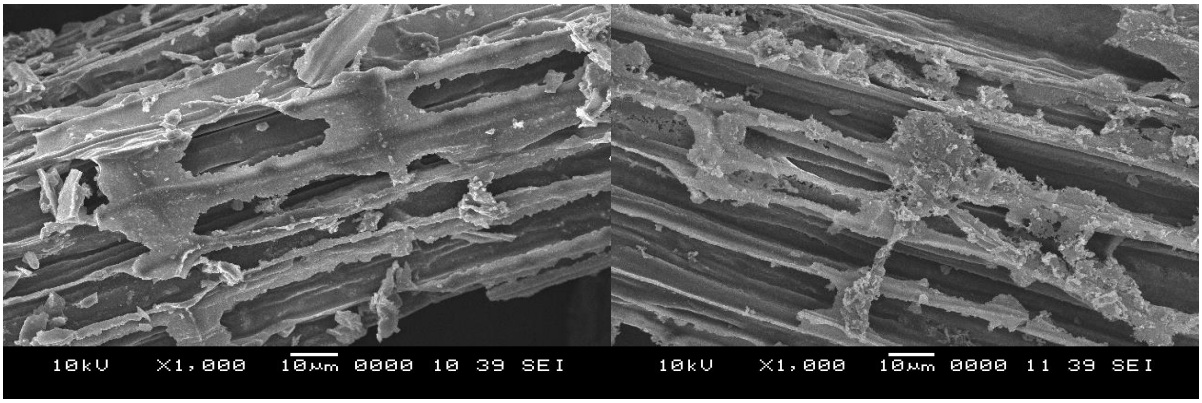

Fig. 3: SEM micrographs of 10 hours operating time for stirring and without stirring condition with 1,000x magnification.

The morphology of raw Kenaf fiber (Figure 2) and biochar for both conditions which is with stirring and without stirring (Figure 3) were investigated to study the structure before and after HTC process. Based on the Figure 2, the raw kenaf fibers illustrate cellular structure of lignocellulosic materials with even and smooth surface compared to the biochar (Figure 3). As illustrated in Figure 3, the outer layer of Kenaf fiber or lignin has broken down leaving cellulose and hemicellulose at the inner layer of the fiber. The damages on the outer layer increase as the operating time increase. Morphology of biochar without stirring shows more visible pores and ruptures on the sample than biochar with stirring condition. More severe damages on the fiber resulted on higher percentage of carbon produced as can be seen in the elemental analysis which samples without stirring produces higher percentage of carbon than sample with stirring. Generally, increment of operating time affected the transformation on the morphology of the Kenaf fiber.

Fourier Transform Infrared Spectroscopy (FTIR) was carried out to identify the component and chemical composition exists in raw Kenaf fiber and biochar for both conditions. Kenaf fiber comprises cellulose, hemicellulose and lignin. The single bonds such as O–H (3000–3700 cm^{-1}), C–H (2987.54 and 784.22 cm^{-1}), C-O (1084.11 cm^{-1}), and C–O–C (913.71 cm^{-1}) are characteristic of cellulose and hemicellulose. The peaks of C=O (1699.06 cm^{-1}) and C=C (1643.88 cm^{-1}) bonds in the FTIR spectra provide further support of the existence of cellulose, hemicellulose and also lignin in Kenaf fiber. Table 3 shows the details on the spectra group detected using FTIR. Meanwhile, Figure 4 and 5 shows the FTIR spectra for both with and without stirring sample of biochar. Based on FTIR spectra, the chemical structure does not illustrate big differences for both with stirring and without stirring condition.

Table 3: Details on the spectra group detected using FTIR, adapted from several references (Parshetti et.al,2013., Reza et.al, 2014., Stemann et.al, 2013., Xiao et.al, 2012., Jamari & Howse, 2012)

Range	Functional group	Wavelength (cm^{-1})	Description
1	O–H stretch	3700– 3000	Detect the presence of water, alcohol from cellulose or phenols from lignin.
2	C–H stretch	3000 – 2800	Vibration of aliphatic C–H bond.
3	C=O stretch	1800 – 1650	Vibration from esters, carboxylic acids or aldehydes from cellulose and lignin.
4	C–O–C stretch	1275 – 800	Vibration from ether, open ring ether and cyclic ether from cellulose.
5	C–H bend	1450 – 1200 900-750	Absorption from C–H bridge of aliphatic carbon, methylene, methyl. Deformation of C–H bond in aromatic compounds.
6	C–O stretch	1200 – 950	Vibration from esters, phenols and aliphatic alcohols.
7	C=C stretch	1650 – 1500	Vibration from aromatic ring from lignin.

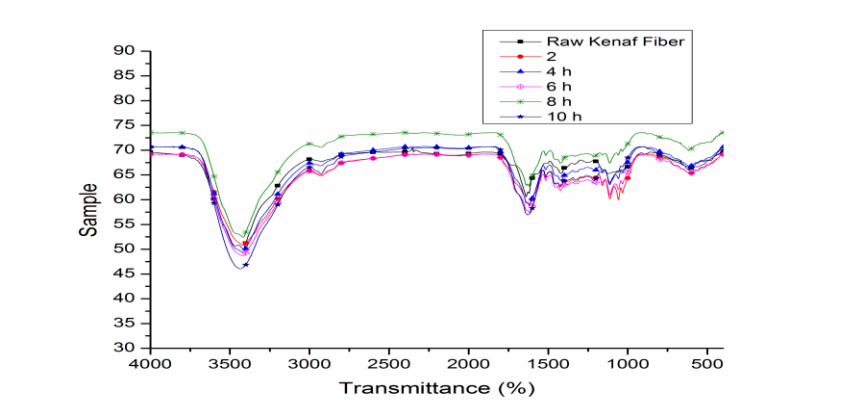

Fig. 4: FTIR Spectra for biochar without stirring condition.

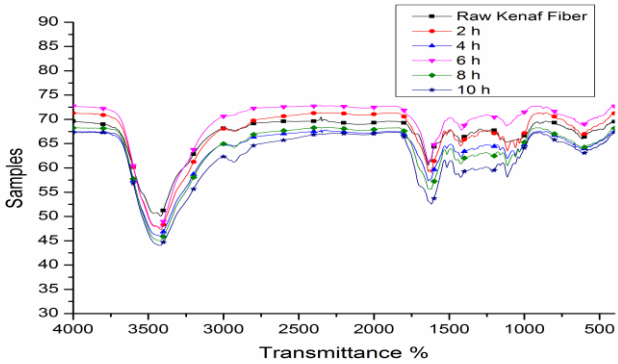

Fig. 5: FTIR Spectra for biochar with stirring condition.

Conclusions:

Hydrothermal Carbonization Process (HTC) provided 30% to 60% increment of carbon content from Kenaf fiber. The result depends on the operating time and stirring speed, which in this work the stirred and unstirred was compared. As a conclusion, HTC process promote without stirring rather than stirring condition in order to produce high carbon content, which is at 10 hours of operating time.

ACKNOWLEDGEMENTS

Special thanks to Lembaga Kenaf dan Tembakau Negara for the raw material provided and Universiti Malaysia Perlis SEM unit for helping with surface morphology analysis. Also biggest thanks to RDU140106 (FGRS Grant Scheme), and Universiti Malaysia Pahang for the financial aid during this project.

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