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Production Of Carbonaceous Kenaf Fiber Via Hydrothermal Carbonization Process

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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 52.25% 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 48.31% 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, longer time period should be conducted to determine the optimum percentage of carbon produced.

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^[1-3]. 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 feedstocks to a variety of nontraditional sources: wet animal manures, human waste, sewage sludges, municipal solid waste (MSW), as well as aquaculture and algal residues^[8]. HTC process is an exothermal process 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^[3-6]. 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^[17]. In this study, HTC process is carried out in the directly in which Kenaf fiber and water are heated together without any catalyst according to parameters. Natural fibers has been proved as replacement for synthetic and other non-recycleable fibers as they are abundant, cheap, renewable and easily recycled. Other advantages are low density, low cost, high toughness, comparable specific strength properties, easy to separate, decreased energy of fabrication, and CO₂ neutrality^[18-20]. 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%^[21] made it suitable as the raw material use for HTC process due to high contain of lignin, hemicellulose and cellulose.

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 condition 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 for with stirring sample, 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.

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 string 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, CH _x O _y
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, CH _x O _y
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}

$$*O (wt\%) = 100 - C (wt\%) - H (wt\%) - N (wt\%)$$

produced varies between with stirring and without stirring sample compared to with stirring sample.

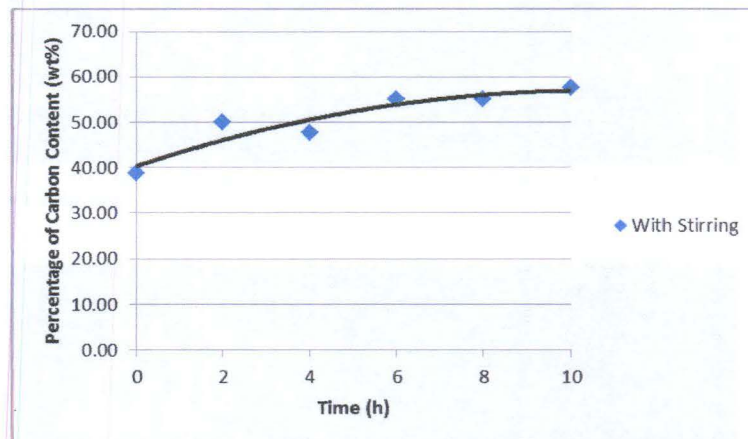


Fig. 1: Percentage of carbon content (%) vs time (h) for sample with stirring.

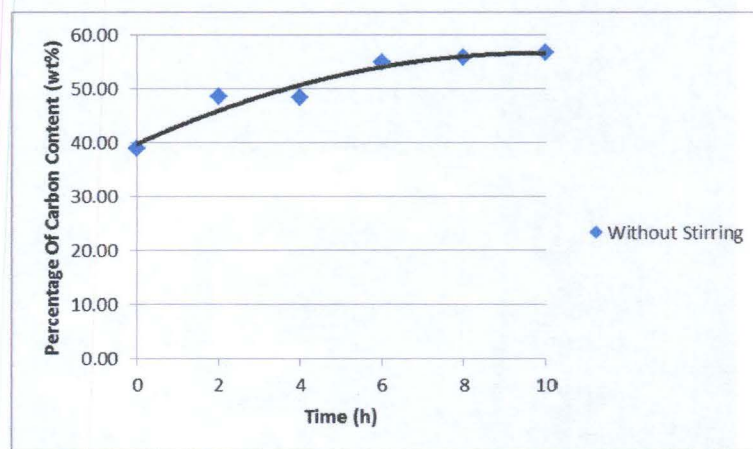


Fig. 2: Percentage of carbon content (%) vs time (h) for sample without stirring.

Figure 1 and 2 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. In figure 1, there was a slight decrement of carbon value at 4 hour operating time and as for figure 2, the slight decrement can be seen at 6 hour operating time which predicted that HTC process promote hydrolysis reaction. 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^[3]. These results shows that with stirring, HTC process undergo

hydrolysis reaction faster than without stirring but produces lower carbon percentage and vice versa.

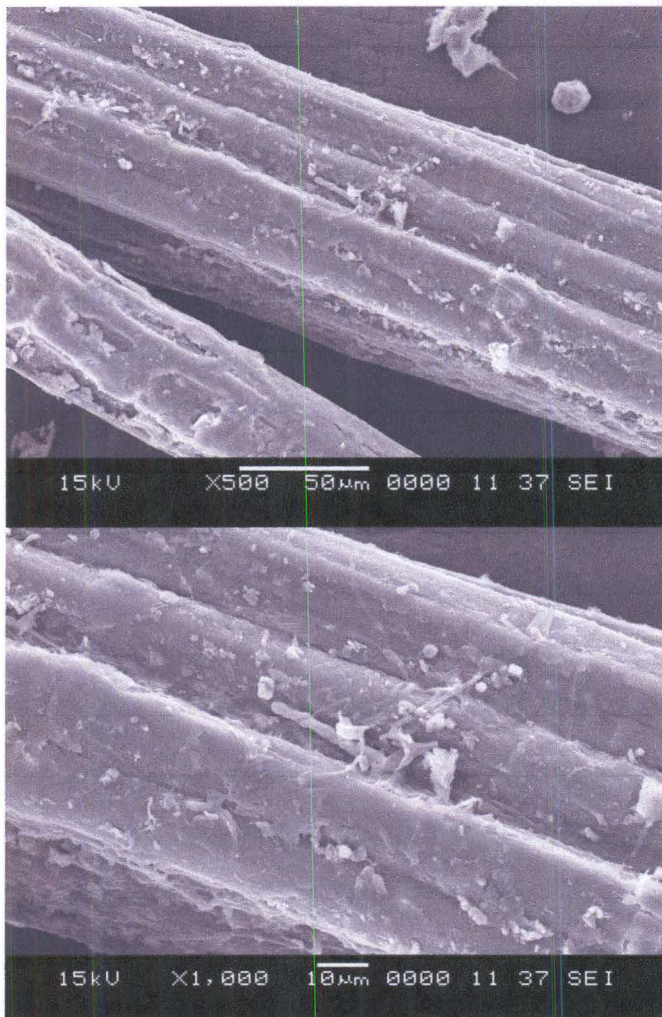


Fig. 3 : Surface morphology of raw Kenaf Fiber.

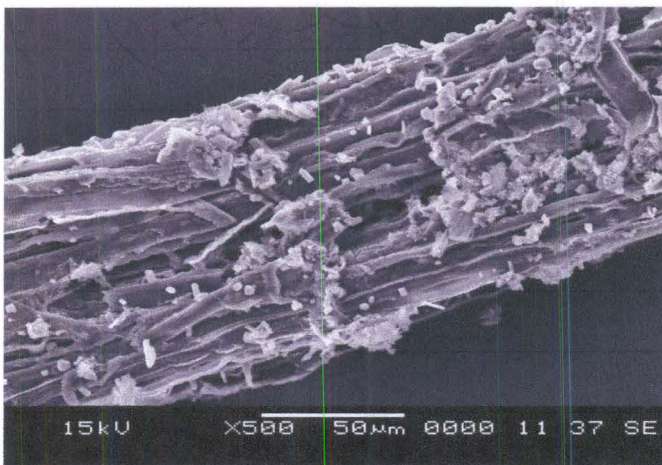


Fig 4: Surface morphology of Kenaf Fiber after HTC process at 6 h with stirring.

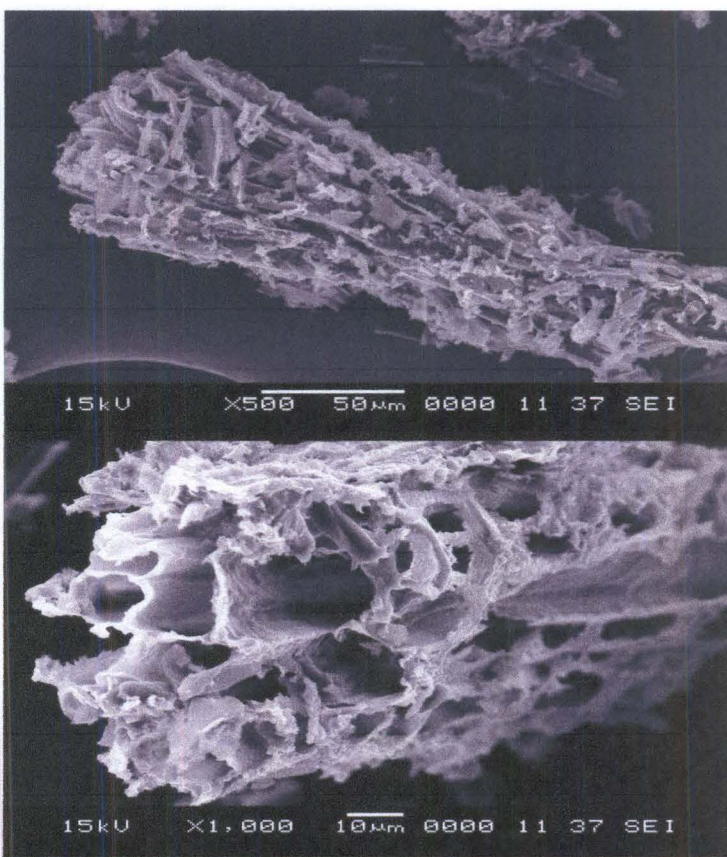


Fig 5: Surface morphology of Kenaf Fiber after HTC process at 10 h without stirring.

The morphology of raw Kenaf fiber (Figure 3) and Kenaf fiber after HTC (Figure 4 & 5) process investigated to study the structure before and after HTC process. As illustrated in figure 4 and 5, 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. Kenaf fiber that undergo HTC process without stirring shows more visible pores and ruptures on the

sample than Kenaf fiber that undergo HTC process with stirring. 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 Kenaf fiber after HTC process. Kenaf fiber comprises cellulose, hemicellulose and lignin. The single bonds such as O-H ($3000-3700\text{ cm}^{-1}$), 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 4 shows the details on the spectra group detected using FTIR. Meanwhile, figure 8 and 9 shows the FTIR spectra for both with and without stirring sample of carbonaceous kenaf fiber. The FTIR spectra trend are similar for both with and without stirring sample.

Table 3 : Details on the spectra group detected using FTIR, adapted from several references [10,13,16,17].

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.

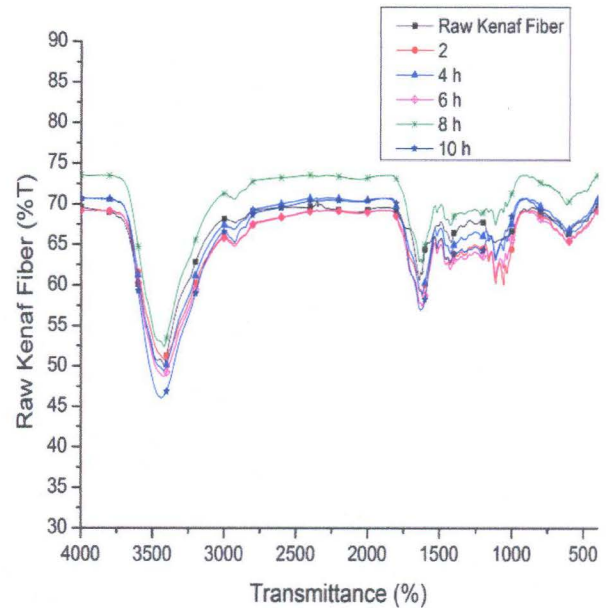


Fig. 8 : FTIR Spectra of without stirring Carbonaceous Kenaf Fiber sample

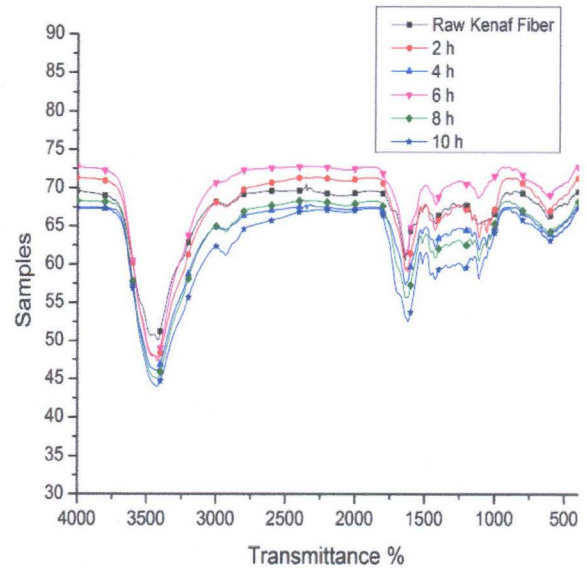


Fig. 9: FTIR Spectra of with stirring Carbonaceous Kenaf Fiber sample

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, longer operating time needed for both condition to determine the most optimum operating time for HTC process to produce optimum amount of carbon.

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