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Carbonization Process of Water Hyacinth as an Alternative Renewable Energy Material for Biomass Cook Stoves Applications

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Abstract. Water hyacinth is a source of biomass, easily found in large quantities from our environment and one of renewable energy sources. As for biomass fuel, it was prepared by carbonizing process. Carbonization of biomass (fueling) includes a process to increase the content of heating value of biomass. In this study, carbonization process was carried out for temperatures 400°C, 500°C and 600°C. Activated carbons were prepared from water hyacinth using NaOH activation (ACWH). Characterization of the ACWH were performed using Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD). Other physical parameter such as moisture content, ash content and volatile matter were measured in this article. The result of SEM-EDX showed the pore size and element carbon of the ACWH increases with increasing carbonization temperature. The ACWH was containing functional groups representing phenols, hydroxyl, carboxyl and carbonyl groups. The increases carbonization temperature seems to be increasing crystallinity and crystal size of the ACWH. The physical parameter of the ACWH showed ash content increases when increasing the carbonization temperature. Nevertheless, parameter of moisture content and volatile matter was decreased. The study concludes that the carbonization temperature of the ACWH causes changes in the characteristics of the structure and composition of chemical compounds which are different from the origin.

Keywords: Biomass energy, Water hyacinth, Carbonization process

1. Introduction

Renewable energy is one alternative to resolve energy crisis in the future. Large amount of fossil energy using causes an energy crisis now. One of the uses of fossil energy by public is as a fuel. Cooking accounts for about 90% of the contribution in household energy consumption in developing countries. A majority of rural households use biomass to meet their heating and cooking need [1]. Biomass cook stoves remain an alternative renewable energy source, which abundant and easily to find. One of biomass sources that easily found in large quantities is water hyacinth. Water hyacinth (*Eichhornia crassipes*) is one of many water plants found in rivers, lakes or swamps. In this time, water hyacinth is considered a weed because of produce rapid growth almost around 1 m² in a period of less than two months. This reduce plankton productivity, interfere significantly with light penetration into water, which seriously endangers farmland irrigation and drainage, water transportation and human health



[2,3]. However, water hyacinth contains lignocellulose (60% cellulose, 8% hemicellulose and 17% lignin) and high carbon-nitrogen ratio, so that water hyacinth can use as an alternative renewable energy directly [4,5].

Biomass can be converted into alternative fuels by carbonized methods. Carbonization is a heat treatment at 400-800 °C which converts raw materials to carbon by minimizing the content of volatile matter and increasing the carbon content of the material. Carbonization of biomass includes a process to increase the biomass heating value. In addition, activated carbon can create an initial porous structure. The activated carbon has good flame properties and produces little smoke [6,7]. The variation of carbonization temperature that used in this study is 400 °C, 500 °C and 600 °C, respectively. Activated carbons prepared from water hyacinth (ACWH) by chemical activation using 25% NaOH. The ACWH were characterized by SEM-EDX, FTIR spectroscopy and XRD. Meanwhile, the content of moisture, ash and volatile matter of the ACWH were measured in this article too. Hence, the aim of this work is to study the influence of carbonization temperature of activated carbons from water hyacinth (ACWH) based on characteristics and physical parameter so that it can be used as an alternative renewable material for biomass cook stoves applications.

2. Material and Methods

Biomass fuels for cook stoves was prepared by the heat treatment using the carbonization process carried out in the furnace with temperature variations of 400°C, 500°C and 600°C for 60 min to obtain carbons from water hyacinth (CWH). To prepare activated carbons of water hyacinth (ACWH), CWH was chemically activated using 1:3 of 25wt% NaOH activator (Merck KGaA, Darmstadt, Germany). The ACWH is continued by heating and stirring using magnetic stirrer hotplate at 80°C with a rotating speed of ~350 rpm for 4 hours. Then, ACWH was washed with 2 M HCl (Mallinckrodt Baker, Inc, Paris, Kentucky) then washed again with distilled water for several times. Furthermore, the ACWH is dried in the oven at 100°C till the mass is constant. The activated carbons are hereafter referred to as ACWH400, ACWH500, ACWH600; the prefixes “ACWH” are abbreviated form of activated carbon from water hyacinth, and the numbering following “ACWH” represents the temperature carbonization.

The morphology of the ACWH was characterized by SEM-EDX (FEI, JEOL-JSM-6510LA). FTIR spectroscopy (Routine Spectrometers) was employed to identify the functional groups on the ACWH. The XRD patterns of the ACWH were obtained using PANanalytical type E'xpert Pro operating with a Cu K α ($\lambda = 1.54060 \text{ \AA}$) radioactive source. The obtained XRD patterns were analyzed using High Score Plus software and then matched with the International Center Diffraction Database (ICDD) in Powder Diffraction File (PDF). Crystallite size (L_c) is calculated according to the Debye Scherrer equation, namely [8]:

$$L_c = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where the Scherrer constant (k) is 0.9, β is full width at half maximum (FWHM), and θ is the diffraction angle. Whereas for crystallinity is calculated by comparing the area of the crystal curve with the total area of amorphous and crystal [9].

$$\text{crystallinity} = \frac{\text{Broad crystal fraction}}{\text{Broad crystal fraction} + \text{amorphous outer fraction}} \quad (2)$$

Other physical parameter such as moisture content, ash content and volatile matter has been validated by Pusat Penelitian dan Pengembangan Hasil Hutan (P3HH)-Bogor using the SNI 06-3730-1995 method.

3. Results and Discussion

3.1. Characterization of SEM-EDX

The morphology structure and elemental of the carbons were observed by the Scanning Electron Microscopy (SEM) and the Energy Dispersive X-ray analysis (EDX), respectively. Figure 1 shows the SEM micrograph of the ACWH prepared at various carbonization temperatures (i.e 400°C, 500°C and 600°C). The SEM micrograph shows a rough and irregular area with different pore diameters distribution

over the surface of ACWH. The pore size of the activated carbons on the ACWH400, ACWH500 and ACWH600 were $0.380\ \mu\text{m}$, $0.532\ \mu\text{m}$ and $0.664\ \mu\text{m}$, respectively. According to this micrograph, it seems that the presence of wide pores resulted from chemical activation with NaOH during the carbonization process. The activation process causes more volatile matter to be released from activated carbons, which makes the remaining cellular structures open, resulting in pore formation [10]. The high pore size of ACWH400, ACWH500 and ACWH600 indicated to contribute their adsorptive effects [11].

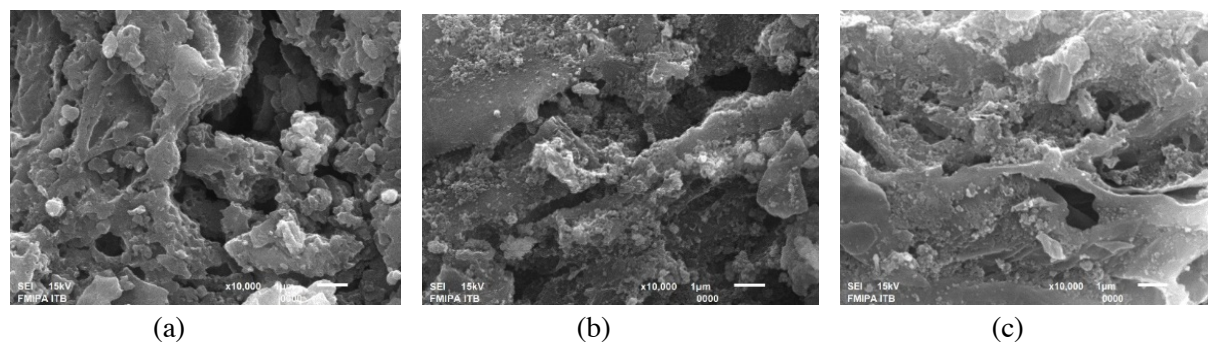


Figure 1. Scanning electron micrographs of the activated carbons from water hyacinth with carbonization temperature of (a) 400°C (ACWH400), (b) 500°C (ACWH500) and (c) 600°C (ACWH600)

Table 1. The content of ACWH at various carbonization temperature

Element	wt%		
	ACWH400	ACWH500	ACWH600
C	81.34	82.65	82.26
O	16.60	14.02	14.53
Na	-	0.74	0.47
Mg	0.52	0.90	1.24
Cl	-	0.45	-
Ca	1.54	1.24	1.50

The results obtained from EDX elemental content of ACWH at various carbonization temperature dominated by carbon elements. Based on Table 1, the percentage of carbon elements on the ACWH400, ACWH500 and ACWH600 were 81.34 wt%, 82.65 wt% and 82.26 wt%, respectively. The three samples of ACWH have met the activated carbons quality standard according to SNI 06-3730-1995 with a minimum quality of activated carbons in powder form of 65%.

The percentage value shows the carbon content produced almost uniform and does not produce a significant difference. This shows that the activation process does not help the material to increase the carbon content in activated carbons of water hyacinth. Whereas, the activation process is the treatment of carbon which aims to enlarge the pore by breaking down hydrocarbons or oxidizing surface molecules so that the activated carbons undergoes changes in properties, both physical and chemical, i.e the surface expands and affects the adsorption power.

3.2. Characterization of FTIR

Figure 2 shows the influence of carbonization temperature on the surface functional groups of ACWH. The band at around $3324\ \text{cm}^{-1}$ can assigned to the O-H stretching vibration mode of the hydroxyl functional groups, due to the existence of cellulose and lignin [12]. In general, these bands show low intensity with increasing carbonization temperatures. It assumed that the some of the surface functional groups on the surface carbon was evaporated [13]. The asymmetric ($2927\ \text{cm}^{-1}$) C-H stretching and

symmetric (1316 cm^{-1}) C-H bending bands were associated with aliphatic functional groups and were observed in ACWH400 but not in ACWH500 and ACWH600, thus indicating a decreased non-polar aliphatic fraction [11]. A strong band at 1584 cm^{-1} is ascribed to C=C stretching variation in aromatic rings. The intensity of C=C stretching decreased at higher carbonization temperature which is assumed due to the bond cleavage in aromatic rings [13]. The band at around 1413 cm^{-1} can assign to the asymmetric C-H bending. The band at around 1060 cm^{-1} could be ascribed to phenolic C-O stretching vibration. Band observed appearing at around 873 cm^{-1} for C-C stretching. In short, the functional groups observed on the ACWH included phenols, hydroxyl, carboxyl and carbonyl groups. Reducing intensity of bands may support the process of the bond cleavage of C=C stretching indicating the progressive elimination of hydrogen functional groups, thus the pore size of ACWH become enlarged because of breaking down hydrocarbons or oxidizing surface molecules.

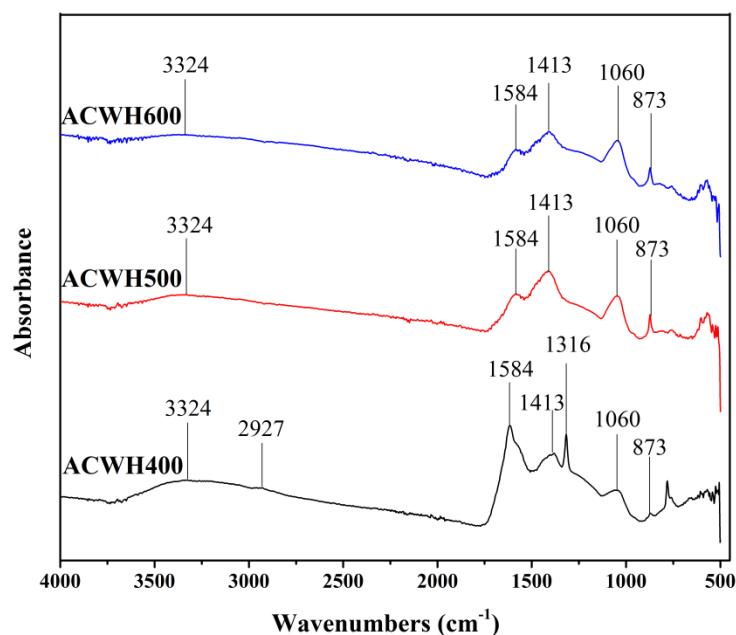


Figure 2. FTIR spectra of activated carbons from water hyacinth at various carbonization temperature

3.3. Characterization of XRD

XRD characterization obtained from a diffractogram graph showing the relationship between diffraction angle and intensity (Figure 3). Figure 3 shows that ACWH form a crystal and amorphous structure. The formation of crystal and amorphous structures due to water hyacinth contains lignin, hemicellulose, and cellulose. Lignin and hemicellulose have an amorphous structure, whereas cellulose has a crystalline structure [14].

The highest crystalline peaks of ACWH400, ACWH500 and ACWH600 at the position of diffraction angle 2θ are 24.33° , 31.68° and 29.40° , respectively. The ACWH400, ACWH500 and ACWH600 peaks are located at hkl (211), (310) and (113), respectively. The height of ACWH crystal peaks in Figure 3 with a variation of the carbonization temperature of 400°C , 500°C and 600°C shows that the increased carbonization temperature forms a higher crystalline peak.

The crystal peaks on the ACWH400, ACWH500 and ACWH600 have two phases. For ACWH400, it has a cellulose and carbon. ACWH500 has a cellobiose and carbon. Whereas, the ACWH600 has the glucose phase pentaacetate and carbon. The cellulose, cellobiose, and glucose phases pentaacetate show that the increase in carbonization temperature causes the breakdown of disaccharide compounds, namely cellulose into cellobiose and then into glucose [15]. This chemical transformation can be caused due to the microfibrils in the cell walls are formed from cellulose chain that are aligned and held together by hydrogen bonding between the hydroxyl groups on the repeating glucose units [16].

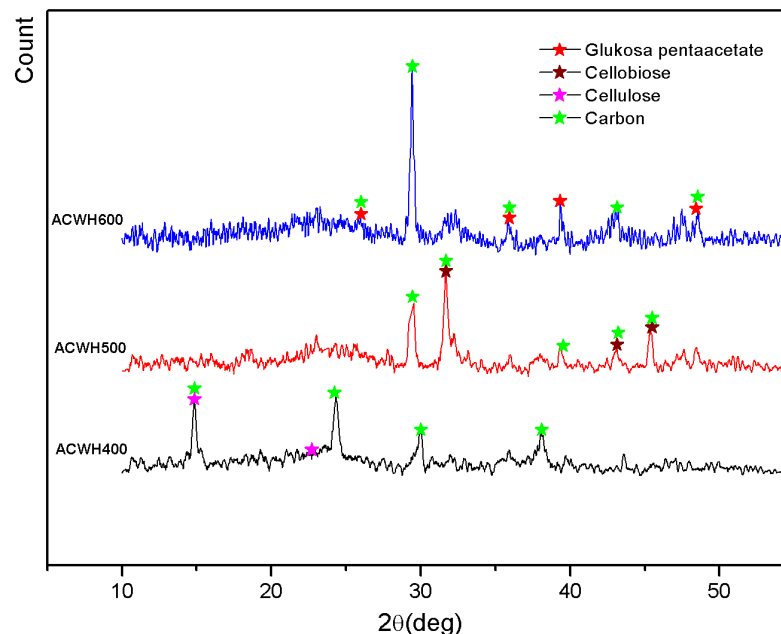


Figure 3. Diffractogram of activated carbons from water hyacinth

The size of the ACWH400, ACWH500 and ACWH600 are 17.98 nm, 28.62 nm and 78.36 nm, respectively. This shows that the increasing carbonization temperature causes a larger crystal size. Crystal size calculation is influenced by the FWHM value, if the value of FWHM gets smaller then the size of the crystal obtained will be even greater. Figure 3 shows that the increasing carbonization temperature causes an increasing crystalline peak high, sharp, and narrow so that the value of FWHM obtained is smaller which affects the size of the crystal obtained is getting larger.

Crystallinity functions to determine the number of crystals contained in a material. The crystallinity of the ACWH400, ACWH500 and ACWH600 are 33.61%, 36.04%, and 39.19%, respectively. This shows that crystallinity is increasing with increasing carbonization temperature. The increase in temperature in the carbonization process can lead to more intensive arrangement of carbon elements so that the carbon crystal structure is getting more organized [17].

3.4. Moisture Content

Level tests were carried out to determine the quality of ACWH and combustion characteristics. The higher the moisture content, the harder the material to burn [18]. The results of the moisture content are obtained as shown in Figure 4.

Based on Figure 4, it can be seen that the carbonization temperature can affect the moisture content contained on the ACWH. The moisture content of ACWH400, ACWH500 and ACWH600 are 8.03%, 5.61% and 4.98%, respectively. The increasing carbonization temperature can reduce the moisture content in activated carbons. The decreasing moisture content is due to the evaporation process of water during the carbonization process. The moisture content has obtained appropriate with SNI 06-3730-1995 standard, where the maximum moisture content in activated carbons in the form of powder based on SNI 06-3730-1995 is 15%.

3.5. Ash Content

Ash content is a percentage of the substances left over from the combustion process that have no carbon element. The higher the ash content in a material, the lower the quality because high ash content can reduce the level of calorific value [18]. The results of the ash content on the ACWH as shown in Figure 5.

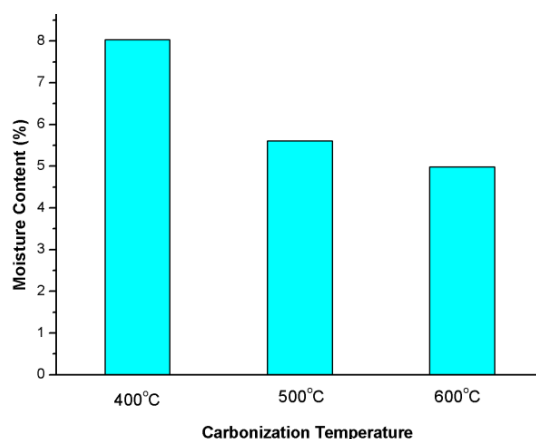


Figure 4. Moisture content of ACWH400, ACWH500 and ACWH600

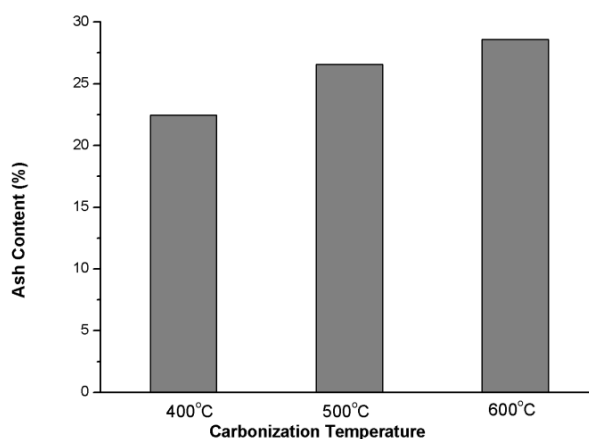


Figure 5. Ash content of ACWH400, ACWH500 and ACWH600

Figure 5 shows that the carbonization temperature affects the ash content contained on the ACWH. The ash content of ACWH400, ACWH500 and ACWH600 are 22.47%, 26.57% and 28.59%, respectively. The increase of carbonization temperature causes an increase of ash content but also provides a greater carbon content. According to Ristianingsih et al. [19], the high ash content is influenced by impurities contained in raw materials so that the mineral content is quite high and leaves ash as residual combustion. These impurities are in the form of minerals that cannot be oxidized by oxygen, such as SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , and alkali. The ash content has below SNI 06-3730-1995 standards, where the maximum ash content in activated carbons in powder form is based on SNI 06-3730-1995 is 10%.

3.6. Volatile Matter

Volatile matter is substances that can evaporate as decomposition of compounds that are still present in materials other than water. The high levels of volatile matter will cause more smoke when ignited. The levels of volatile matter contained on the ACWH can be seen in Figure 6.

In Figure 6, it can be seen that the increasing carbonization temperature can reduce the levels of volatile matter contained on the ACWH. The volatile matter of ACWH400, ACWH500 and ACWH600 are 33.91%, 22.52%, and 15.69%, respectively. The volatile matter has obtained appropriate with SNI 06-3730-1995 standard, where the volatile matter in activated carbons powder based on a maximum SNI 06-3730-1995 is 25%.

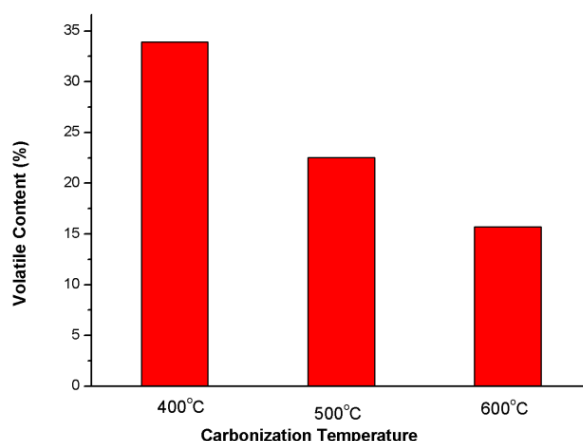


Figure 6. Volatile matter of ACWH400, ACWH500 and ACWH600

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