

## **ANALYSIS OF POROSITY IN CARBON FROM ALKALINE (KOH) TREATED SELF-ADHESIVE CARBON GRAIN FROM OIL PALM BUNCH**

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### **ABSTRACT**

Self-adhesive carbon grain (SACG) was prepared from oil palm empty fruit bunch by a low carbonization temperature. Green pellets (GP), with a dimension of 9.4 mm in diameter and 1.3 mm in thickness, made from the SACG added with 0.0% to 7.0% KOH by weight were carbonized up to 700 °C in a nitrogen atmosphere using a multi-steps heating profile. It was found that carbon pellets from GP of 1.0% KOH have the BET surface area (Y1), pore area (Y2), pore volume (Y3), and average pore diameter (Y4) of 290 m<sup>2</sup>/g, 280 m<sup>2</sup>/g, 0.112 m<sup>3</sup>/g and 19 Å respectively. Further increased in the KOH content did not significantly change these values. These values, Y1 to Y3, and Y4 are approximately 9.1, 9.1, 9.3 times higher, and 1.5 times lower than those of the carbon pellet from the GP without KOH respectively. This result shows the advantage of the SACG since significant change in the porosity characteristic can be made by using only a very small quantity of activating agent (KOH) compared to the quantity normally required by the non-precarbonized precursor. The result also shows that the mesopore volume is higher than that of the micropore and macropore. Without KOH, carbon pellets do not have micropores and with 0.5% KOH the micropores are formed and its volume decreases with increasing KOH content. Maximum volume of mesopores occurs at the KOH content approximately in between 4% - 5% and it decreases beyond this range. Macropores do not significantly change with the KOH content.

### **INTRODUCTION**

Porous carbon has been used extensively as adsorbents, catalysts, and catalyst supports for the removal of pollutant from gases or liquids and for purification or recovery of chemicals [1,2]. Although a wide range of carbonaceous materials can be converted into carbon porous, coal and polymeric substances are the most commonly used as starting materials. Recently, agricultural by-products have been a focus for the production of this carbon porous due its economically low cost [3-7]. Oil palm empty fruit bunches (EFB) is an agriculture by-product generated in very large quantities by palm oil mills. It is estimated about 18.7 million tons of EFB (or equivalent to ≈ 80 tons fresh fruit bunch) would be produced by the year 2006 [8,9].

Studies on producing carbon pellets from EFB fibers have been initiated in early 90's [10-14]. Recently, studies on the porosity of the carbon pellet have shown that certain chemical activation applied on the pre-carbonized gives different characteristics of the carbon pellets [15-19]. Generally, high adsorptive capacities of carbon are associated with their internal porosity and are related to properties such as surface area, pore volume and pore distribution. Based on the average pore width(w) defined by IUPAC(International Union of Pure and Applied Chemistry ), the porosity of carbon can be classified into micropore(w ≤ 20 Å (2 nm)), mesopore(20 Å ≤ w ≤ 500 Å (2 nm ≤ w ≤ 50 nm)) and macropore(w ≥ 500 Å (50 nm)).

Porous properties of carbon can be tailor made by means of chemical and physical activation [1]. Activation using alkaline metal compound, KOH had been studied extensively on coal precursors or chars [20-23]. The effect of chemical activation on carbon depends on parameters such as carbonization temperature, chemical use, concentration and temperature of the chemical treatments and even the effect of the leaching process [24]. Studies of reactions of KOH towards the cellulose, hemicellulose and lignin components inside lignocellulosic materials had been widely reported. KOH acts as swelling agent for the crystalline cellulose and simultaneously as dissolving agent for lignin [25,26]. In the work reported in the present paper, KOH with different concentration was used to treat the milled pre-carbonized EFB(SACG). It was expected that such a treatment would change the porosity characteristic of carbon pellet prepared by carbonizing the SACG pellets up to 700 °C.

## **MATERIALS AND METHODS**

### ***Pre-carbonization of EFB***

EFB fibers obtained from SABUTEK SDN. BHD., Perak, was pre-carbonized at temperature of 280 °C for 3 hours in nitrogen environment. This process can minimize the low molecular weight and volatiles components in the fibers, hence improve the weight loss, shrinkage and density of carbon pellets after carbonization [27]. The pre-carbonized fibers were then ball milled for 20 hours to obtain the self-adhesive carbon grains(SACG) which can pass through a 53 µm sieve.

### ***Chemical activation***

Chemical activation process was done by mixing the SACG with KOH with the proportion of 0.0% to 7.0% KOH(weight basis to the SACG). The SACG mixture was added with water and stirred by a magnetic stirrer for 1 hour at room temperature. The sample was left for 24 hours before it was dried in an oven at 70 °C for 24 hours. The dried mixture was ball milled again for 6 hours and sieved through a 53 microns sieve. The label for each sample is shown in Table 1.

### ***Thermogravimetry Analysis (TGA)***

Shimadzu Thermal Analyzer 501 was used to obtain the thermograms of the SACG and treated SACG in the temperature range up to 600°C in an inert atmosphere at the heating rate of 20°C/min.

### ***Carbon pellet preparation***

The green pellets were prepared by applying 2 metric tones of compression force on 0.3 g of the SACG and treated SACG. These green pellet with the approximate dimension of 9.4mm in diameter and 1.3 mm in thickness, were carbonized up to the temperature of 700°C using a box furnace (Vulcan 3-1750) filled with a flow of nitrogen gas at the rate of 1.0–1.5 x10<sup>-3</sup> m<sup>3</sup>/min. The carbonization started from room temperature up to 375 °C at the rate of 3.0 °C/min and continue heating up to 700°C at the rate of 5.0°C/min [28-30]. Subsequently, the samples were cooled down under nitrogen flow and the carbonized pellets were washed several times with 0.1 N solution of HCl, and finally with distilled water to remove residual chemicals. The washed samples were dried in an oven at 70°C to obtain the final carbon pellets.

### **Porosity analysis**

The porosity of the carbon pellet was measured by physical adsorption of nitrogen gas at 77K using an automated adsorption apparatus (Micromeritics, ASAP 2000). The specific surface area of the samples was determined from nitrogen adsorption isotherms by the standard BET method [31]. The cross sectional area for nitrogen molecule was assumed to be 0.162 m<sup>2</sup>. The micropore volume was calculated using a micropore analysis based on the *t*-plot method. The micropore surface area was then determined from the value obtained for the micropore volume [32,33]. The total pore volume was found from the amount of nitrogen adsorbed at a relative pressure of about 0.99. The mesopore size distribution was calculated using BJH model [31,34].

### **Scanning Electron Microscopy Analysis**

The micrographs of the carbon pellets(S0020 and S1020) were recorded at the magnification of 5000X and 10000X using the Scanning Electron Microscope (SEM: Phillip XL 30).

## **RESULTS AND DISCUSSION**

The TGA plots shows that the treated SACG gives a higher carbon yield compared to that of the untreated SACG (Figure 1). This figure also shows that the KOH treatment causes the peak height and position of the rate of weight loss to decrease and slightly shift to the higher temperature region respectively. It is possible that the presence of more water in the micropores may provide a strong interaction with the surface of the substrate, which cause the slow release of water during carbonization. Therefore, the lower peak height and peak shift of the rate of weight loss reflects the interaction strength between the water and the adsorbent [35]. During carbonization, the impregnated KOH dehydrates the SACG, resulting in charring and carbonizing the carbon skeleton with creation of porous structure. The activation agent KOH, influences the decomposition process and inhibits the formation of tar, resulting in a decrease in the formation of compounds like acetic acid and ethanol and thus enhancing the carbon yield [1].

The results on the weight, bulk density, weight loss of the pellets before and after carbonization for all the samples investigated are shown in Table 1. This data shows that the carbon pellet from the SACG treated with 1.0%(w/w) KOH has the highest weight loss and the lowest density. It also shows that the weight loss of all the treated pellets are slightly lower than that from the untreated pellets, which indicates that reaction with KOH produced some complexes that would not volatiles during the carbonization.

The density loss of the acid washed pellets is inconsistent for each samples, but the weight loss due to the acid washing is increasing with the increased of the KOH concentration (Table 1). It is expected that the acid washed of the carbon pellet would increase the weight loss and hence decrease the density of the pellet. The acid will neutralized the remaining KOH or reacts with the complexes form from the KOH with component in SACG. The removing of these components will consequently form pores in the carbon pellet.

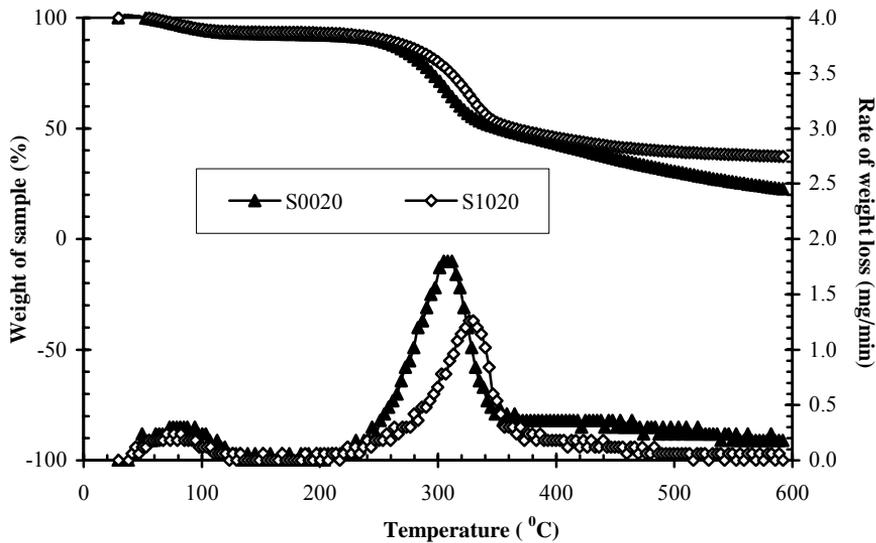


Figure 1 . TGA-DTA profiles of S0020 and S1020 samples of SACG.

Table 1. W(weight),  $\rho$ (density) and WL(weight loss) of pellets from the SACG treated with different concentration of KOH by weight percentage(Con.). \*Data before washed.

Sample ID	Before Carbonization			After Carbonization		
	Con.(%)	W(g)	$\rho(\text{gcm}^{-3})$	W(g)	$\rho(\text{gcm}^{-3})$	WL(%)
S0020	0.0	0.299	1.256	0.109*(0.100)	1.047*(1.073)	63.5*
S0520	0.5	0.271	1.111	0.110*(0.100)	1.101*(1.083)	59.4*
S1020	1.0	0.289	1.202	0.111*(0.098)	1.052*(1.056)	61.6*
S3020	3.0	0.294	1.265	0.117*(0.099)	1.157*(1.067)	60.2*
S5020	5.0	0.293	1.294	0.117*(0.096)	1.392*(1.196)	60.2*
S7020	7.0	0.290	1.320	0.119*(0.088)	1.428*(1.119)	59.0*

Figure 2 shows the  $\text{N}_2$  adsorption isotherms at 77K of acid washed carbon pellet from the GP treated with different concentration of KOH. All samples present Type 1 isotherms according to the IUPAC classification [31] on characteristic of microporous solids. The isotherms of KOH treated samples show a rounded knee indicating a wider pore size distribution and the amount adsorbed increased significantly as compared with that of the untreated sample. The maximum amount adsorbed was by S1020 at  $88 \text{ cm}^3(\text{STP})/\text{g}$ , suggesting that the pore volume increases significantly due to KOH treatment. However, for the S3020 and S7020, the nitrogen adsorption capacity decreases due to the more aggressive activation conditions [36].

Table 2 shows the summary of BET analysis of the carbon pellet from GP treated at different concentration of KOH. This table clearly shows that the BET surface area have significantly increased with the treatment of KOH and the carbon pellet(1.0%KOH) has the highest BET surface area. Similar behaviors are shown by the porosity area and

volume of carbon pellet. However, the average pore diameter does not seem to change significantly with increasing KOH concentrations.

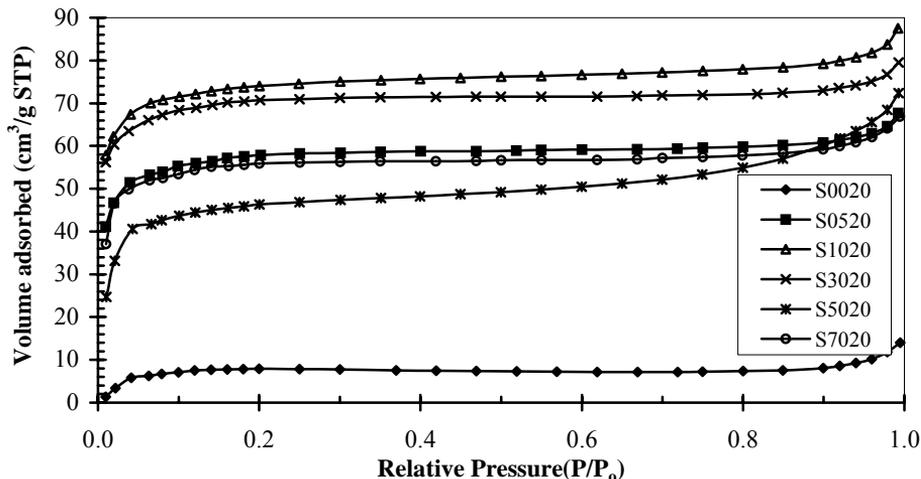


Figure 2. Nitrogen adsorption isotherms at 77K of carbon pellet prepared from SACG treated with different KOH concentration.

Table 2. Porosity properties of carbon pellet prepared from KOH treated SACG.

Parameters	KOH concentration (% <sub>w/w</sub> )					
	0	0.5	1.0	3.0	5.0	7.0
BET surface area (m <sup>2</sup> /g)	32	223	290	274	187	218
Pore area, (m <sup>2</sup> /g)	31	219	280	272	167	214
Pore volume (m <sup>3</sup> /g) x 10 <sup>-3</sup>	12	89	112	110	64	85
Average pore diameter (Å)	27	19	19	13	24	19

Figure 3 shows the pore size distribution (PSD) of the carbon pellets from the treated SACG. It was found that the carbon pellets S0020 showed (not plotted in this figure) the dominance of meso- and macropores with no peak for pore diameter below 100 Å. However the PSD of the carbon pellet from the treated SACG show a sharp increase of the pore size distribution curves for pore diameters less than 20 Å. This indicate that the treatment contribute to the formation of micropores, particularly for the carbon pellets S0520, where higher peaks appear in the region less the 50 Å. In the region of pore diameter higher than 100 Å, similar broad and lower PSD curves are observed for all carbons pellets. This result demonstrates that a very small quantity of activating agent applied on the SACG can significantly promote the development of micropores in carbon pellets prepared from the SACG.

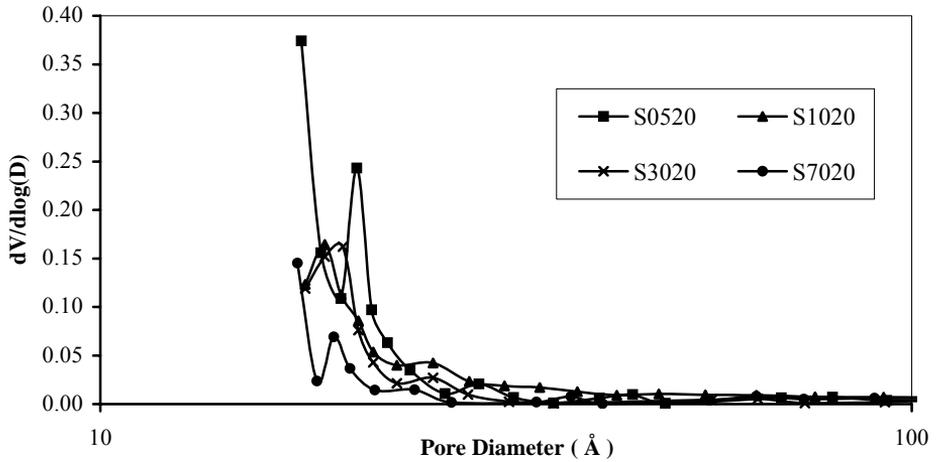
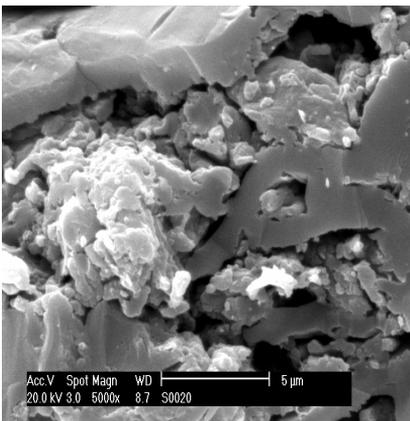
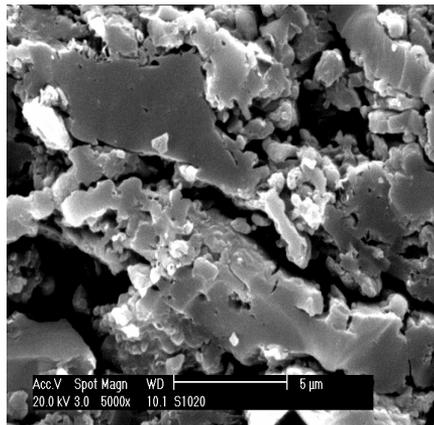


Figure 3. Pore size distribution of carbon pellets from the treated SACG determined from BJH model.

SEM micrographs of the longitudinal section surfaces of the S0020 and S1020 carbon pellet are compared in Figures 4. It can be seen in these micrographs that both of these samples have almost the same shaped and sizes of macropores. This indicates that the treatment only affects the development of the micropore and mesopore in the carbon pellets.



(a)



(b)

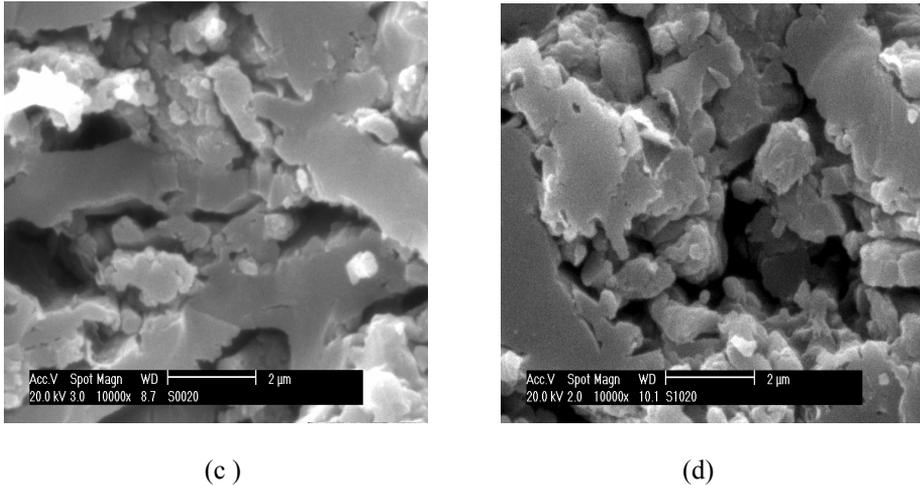


Figure 4. SEM micrographs of carbon pellets S0020 and S1020 for the magnification of 5000x (a and b) and 10000x (c and d).

#### ACKNOWLEDGEMENT

IRPA grant (Codes 09-02-02-0070/09-02-02-0022-EA077) from Ministry of Science, Technology and Environment, Malaysia and the assistance of Mr. Saini Sain, Mr. Zailan Mohd Yusof and Mr. Mohd Halidin Das are gratefully acknowledged.

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