

MESOPORES AND MICROPORES OF CARBON PELLET PREPARED FROM H₂SO₄ TREATED SELF-ADHESIVE CARBON GRAINS FROM OIL PALM EMPTY FRUIT BUNCHES

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ABSTRACT

Self-adhesive carbon grains (SACG) from oil palm empty fruit bunches (EFB) was treated with 0.0, 0.2, 0.4 and 0.6 M of H₂SO₄ before drying. Green pellets prepared from the treated SACG were carbonized at 600 °C in nitrogen atmosphere using multi-steps heating profile to produce carbon pellets (CP). Elemental (CHNO) analysis of the treated SACG shows a reduction of carbon content from 49.3 % to 42.9%, whereas thermogravimetric analysis (TGA) shows an increase of carbon yield at 600 °C from 39.5% to 45.3%. Treatment with 0.0 M to 0.2 M H₂SO₄ increased the BET surface area (S_{BET}) of the CP from 56.2 up to 354.4 m²/g STP respectively, and the maximum S_{BET} is 386.5 m²/g STP at 0.6 M treatment. Similar trend was observed on the CP micropore area (S_{MIC}) whereby the maximum S_{MIC} is 360.54 m²/g STP at 0.6 M. Mesopore area (S_{MES}) of the CP increased to 81.9 m²/g STP at 0.2 M. However, further increase of acid concentration was found to reduce the S_{MES} of the CP. Maximum total pore volume (V_{TOT}) and micropore volume (V_{MIC}) of the CP treated with 0.6 M H₂SO₄ were 0.193 and 0.146 cc/g STP respectively. Maximum mesopore volume (V_{MES}) of the CP was 0.065 cc/g STP and was achieved when treated with at 0.2 M H₂SO₄. Further increasing acid concentration was found to reduce the V_{MES} of the CP. Increase of H₂SO₄ concentration up to 0.4 M was found to reduce the mesoporosity (V_{MES}/V_{TOT}) as well as the average pore diameter of the carbon pellets, but these values increased slightly at 0.6M.

INTRODUCTION

Oil palm empty fruit bunches (EFB) is a by product extracted in a large quantity from the palm oil mills. From the 370 oil palm mills operating in year 2003, it was estimated an average of 19 tonnes / hectares of fresh fruit bunches was produced [1]. Based on 23% extraction, around 4.4 tonnes of EFB was produced per hectares in that year throughout Malaysia. List of the uses of EFB at commercial and research levels can be found elsewhere [2]. Studies on the preparation of solid carbon products from EFB were initiated in 1990's [3-8], which followed by several treatments to improve the

characteristics of the solid carbon. Preparation of self-adhesive carbon grains (SACG) from the pre-carbonization of the EFB [9] was found to exhibit a good binding property during the preparation of the green pellets. Studies also showed it improve the physical and mechanical properties of the carbon pellet. A number of chemical treatments of the SACG have also shown improved those properties of the carbon pellet [10-15], and recent development found that chemical treatments could also improve the porosity of the carbon pellets [16-17].

The use of acids for the activation of the lignocellulosic materials to prepare high surface area porous carbon has been known [18-19]. Basically, acids are an oxidation agent, which promotes the dehydration and redistribution of biopolymers in the lignocellulosic materials. It involves in the cleavage of the ether bonds between the lignin and the cellulose, followed by recombination reactions in which larger structural units are formed, with the end result of a rigid cross linked solid [18]. Sulfuric acid (H_2SO_4) treatment of the SACG was found to increase some of the physical and mechanical properties of the carbon pellets prepared at higher carbonization temperatures 900 – 1000 °C [12,15]. However, at lower carbonization temperatures 500 – 700 °C, the recombination and cross-linking of the hydrolysed biopolymers is insufficient or incomplete and therefore higher surface area of the porous carbon is expected [20].

According to the International Union of Pure and Applied Chemistry (IUPAC), the pores of a porous material are classified in three groups: micropores (width $d < 2$ nm), mesopores ($2\text{nm} < d < 50$ nm) and macropores ($d > 50$ nm) [21]. The main objective of this work is to study the effect of H_2SO_4 treatment on SACG at different concentrations towards the porosity properties of the carbon pellets prepared at carbonization temperature of 600 °C. The results would include the mesopores and micropores distribution, and will be discussed in relating to the initial properties of the untreated precursors.

MATERIALS AND METHODS

The pre-carbonized fibers were ground and ball milled for 24 hours to obtained self-adhesive carbon grains (SACG) which can pass through a 53 μm sieve [8,9]. One hundred grams of SACG was dissolved in 500 mL of H_2SO_4 at different concentrations of 0.0, 0.2, 0.4 and 0.6 M. The 0.0 M was using distilled water. The mixture was then heated at 100 °C for 5 minutes before drying in oven. The dried treated SACG was then again ball milled for another 24 hours and passed through a 53 μm sieve. Two grams of the treated SACG was then used to produce green pellet at the size of diameter 27.205 ± 0.003 mm and thickness 3.118 ± 0.003 . The green pellets were then carbonized at the temperature of 600 °C using a box furnace (Vulcan 3-1750) in nitrogen atmosphere. The multi-steps heating profile involves heating up to 320 °C with the rate of 1.0 °C/min and holding period of 60 minutes. Further increase of temperature was up to 600 °C at the rate of 3.0 °C/min and holding time of 5 minutes. The total carbonization period carried out was 6 hours.

The dimensions of the pellets before and after carbonization were measured using a micrometer and the density was determined by dividing the weight of the sample with its volume.

Shimadzu Thermal analyzer 501 was used to obtain the thermograms of the SACG in the temperature range up to 600 °C in the inert atmosphere at the heating rate of 20 °C/min. The elemental analysis for carbon (CHNO) analysis was carried out using Eager 300 ThermoFinnigan pyrolysis instrument. The chemical bonding of the treated SACG were analyze using Fourier transformed infrared spectroscopy (FTIR-2000 Perkin Elmer). The spectra were recorded from 650 to 4000 cm⁻¹.

The porosity of the carbon pellet was measured by physical adsorption of nitrogen gas at 77K using an automated adsorption apparatus, Micromeritics, ASAP 2000. Surface areas and micropores volume of the carbon pellets were determined from the application of the Brunauer-Emmett-Teller (BET) and Dubinin-Radushkevich (D-R) equations, respectively, to the adsorption isotherms at relative pressure, P/P₀, values between 0.01 to 0.5. The t-plot method was applied to calculate the micropore volume and external surface area (mesopore surface area). The total pore volumes were estimated to be the liquid volume adsorbate (N₂) at a relative pressure of 0.98 [21]. The mesopore volume was calculated by subtracting micropore volume from the total pore volume.

RESULTS AND DISCUSSION

The thermograms or the weight loss (%) and the pyrolysis rate of H₂SO₄ treated SACG are shown in Figure 1. Each treated SACG shows different pattern of weight loss (%) during the pyrolysis of up to 600 °C, where such pattern becomes more linear for higher concentration of H₂SO₄ treatment. This indicates that higher H₂SO₄ concentration hydrolyze the lignocellulosic complex component of the SACG into lower molecular weight biopolymers. At the pyrolysis temperature of 600 °C, the increase of H₂SO₄ concentration increased the final weight of the sample from 39.48 to 45.33 % (Figure 2). These results suggest that higher yield of sample could be obtained from the sample treated with higher concentration of H₂SO₄. This is due to the increase of low molecular biopolymers in the treated SACG and hence enhancing the polymerization process at elevated temperature. Furthermore, H₂SO₄ hydrolysis/oxidation of lignocellulosic material causes the hydrogen and oxygen atoms to be stripped away as water during the pyrolysis (as shown in the first peak of the rate of weight loss thermograms, Figure 1) rather than a hydrocarbons or oxygenated organic compounds. As a result, the carbon yield is much higher with the increase of H₂SO₄ activation [22,23].

Figure 2 also shows the relationship between the TGA characteristic (second peak of the thermograms) and the carbon content of the treated SACG. The second peak temperature of each treated SACG shows a decreased with the increase of H₂SO₄ concentration, which further explained the formation of low molecular weight biopolymers from the hydrolysis. Whereas, the peak height (rate of weight loss, g/min) shows almost constant, except at 0.4 M. The effect of these pyrolysis characteristic will be discussed in relation with the porosity properties of the carbon pellets.

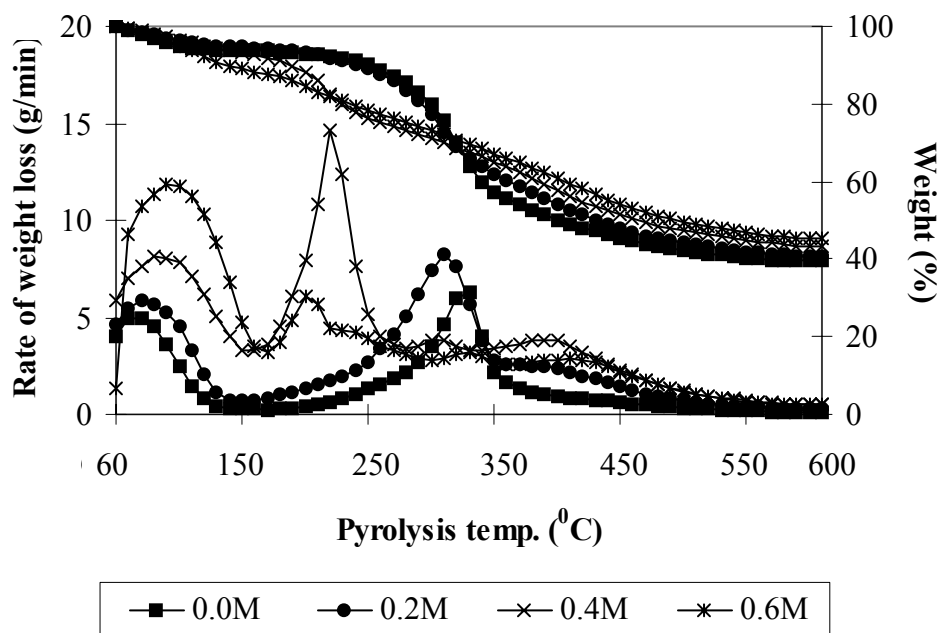


Figure 1: The weight loss and rate of pyrolysis of the H₂SO₄ treated SACG from the TGA analysis.

The FTIR spectra of the H₂SO₄ treated SACG are shown in Figure 3, displaying the following bands; 3340 cm⁻¹: O-H stretching in alcohols, 2925 cm⁻¹: C-H stretching in methyl and methylene groups 1702 cm⁻¹: C=O stretching in unconjugated ketones, carbonyls and ester groups (frequently carbohydrate origin), 1510 cm⁻¹: C=C stretching in aromatic rings, 1161 cm⁻¹: C=O stretching from ester groups of lignin, 1035 cm⁻¹: aromatic C-H and finally the 849 cm⁻¹: C-H out-of-plane from aromatic groups (lignin). The main oxygen groups were suggested to be carbonyl groups, ethers and phenols, which corresponds to the carbohydrate and lignin component of the SACG. The spectra show an increase of lignin characteristics, indicating the hydrolysis of carbohydrate (cellulose part) and hence exposing more lignin [24].

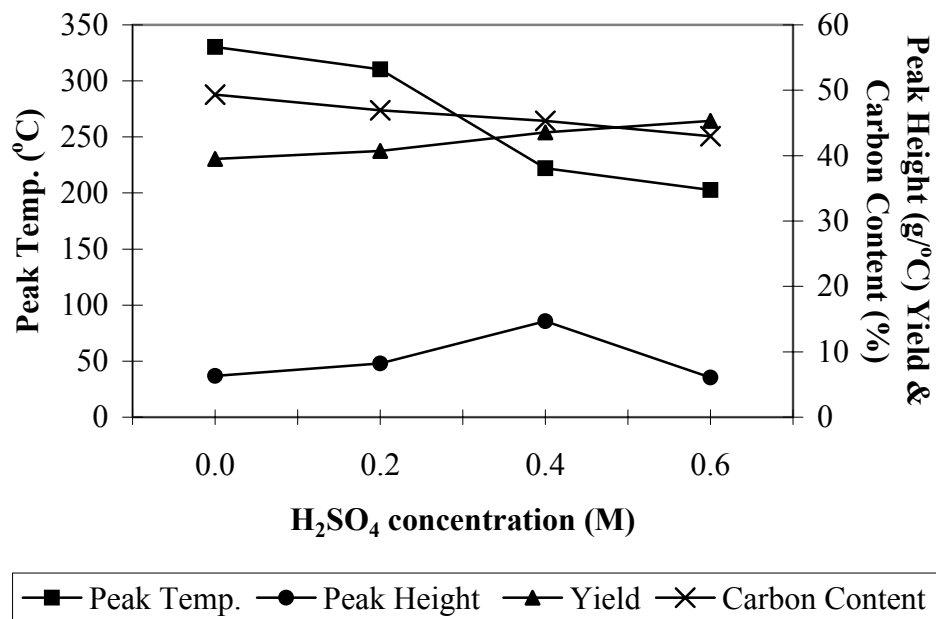


Figure 2. The relationship between the TGA characteristics towards the carbon content of the SACGs treated with different concentration of H₂SO₄.

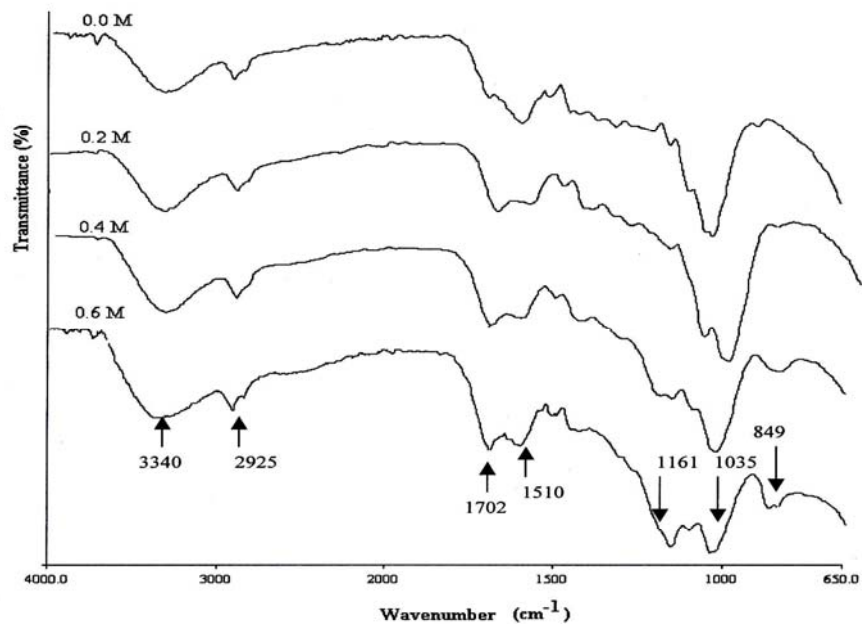


Figure 3: FTIR spectrum of H₂SO₄ treated SACG from EFB

Figure 4 shows the nitrogen adsorption desorption isotherms of the carbon pellets as a function of H₂SO₄ concentration. All isotherms show Type I and the majority of uptake are at a low relative pressure ($P/P_0 < 0.2$), indicating a microporosity. Unlike the rest, 0.0 M (water) shows an open loop of adsorption desorption isotherms, which may be due to the micro-cracks of pellet during the desorption of the N₂ during the analysis. The pore area and volume details as the function of H₂SO₄ are tabulated in Table 1. These results show that H₂SO₄ treatment had enhanced the porosity of the carbon pellets, where at the concentration of 0.2 M the BET surface area (S_{BET}) and the total volume (V_{TOT}) were increased as much as 5.3 and 4.5 times respectively, and further increased of treatment gradually increased the porosity. Treatment with 0.4 M gave the highest results of the S_{BET} and V_{TOT} of the carbon pellet up to 386.5 m²/g and 0.171 m³/g respectively. These figures are still low compared with other molecular sieve carbon pellet for the purpose of methane storage of at least 1790 m²/g (S_{BET}) and 0.74 m³/g (V_{TOT}), Table 1 [25, 26].

The above results also show that the microporosity of the carbon pellet increase with H₂SO₄ concentration, and the formation of mesopores increased on treatment with 0.2 M but decrease at higher concentration. This different from the results obtained from phosphoric acid treatments on some lignocellulosic materials, where the increase of acid concentration enhanced the formation of mesopores [27]. In carbons, mesopores can be formed by enlargement of micropores [28]. The possible explanation for this is that the excessive milling process applied on the SACG before and after acid treatment has severely reduce the particle sizes of the treated SACG, hence resulted the formation of micropores after the carbonization process [12].

Figure 5 shows the pore size distribution of the carbon pellets as the function of H₂SO₄ concentrations. This figure shows that carbon sample from untreated SACG consist of almost equal volume of mesopores, micropores and macropores. However, such a trend has systematically and significantly changed for the treated SACG samples, particularly in the region of micropore. Increased in H₂SO₄ concentration causes an increase of pore volume of micropores, mesopore and macropore volumes moderately.

Table 1: Effect of different H₂SO₄ concentrations treatments of the SACG and the effects toward the porosity of the carbon pellets.

Sample	S_{BET} (m ² /g)	S_{MIC} (m ² /g)	S_{MES} (m ² /g)	V_{TOT} (m ³ /g)	V_{MIC} (m ³ /g)	V_{MES} (m ³ /g)	Average pore diameter (Å)
A	55.28	56.17	0.89	0.031	0.018	0.013	22.30
B	354.40	272.47	80.93	0.171	0.106	0.065	19.35
C	371.25	348.60	22.64	0.182	0.141	0.041	19.63
D	386.51	360.54	25.97	0.193	0.146	0.047	19.99
K	1790	n.a.	n.a.	0.740	0.700	0.040	16.00

Notes: A,B,C and D: Carbon pellet prepared from SACG treated with H₂SO₄ at 0.0, 0.2, 0.4 and 0.6 M respectively, where K: Carbon pellet prepared from cellulose micro-crystals [25].

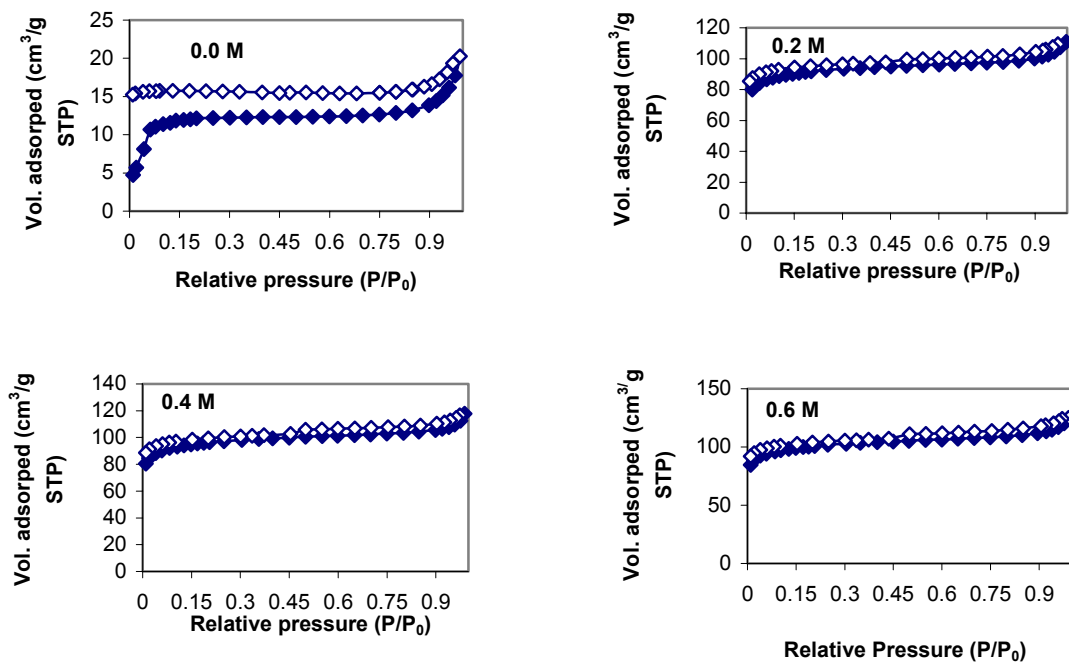


Figure 4: The adsorption (solid mark) and desorption (empty mark) isotherms of SACGs treated with different concentrations of H_2SO_4 .

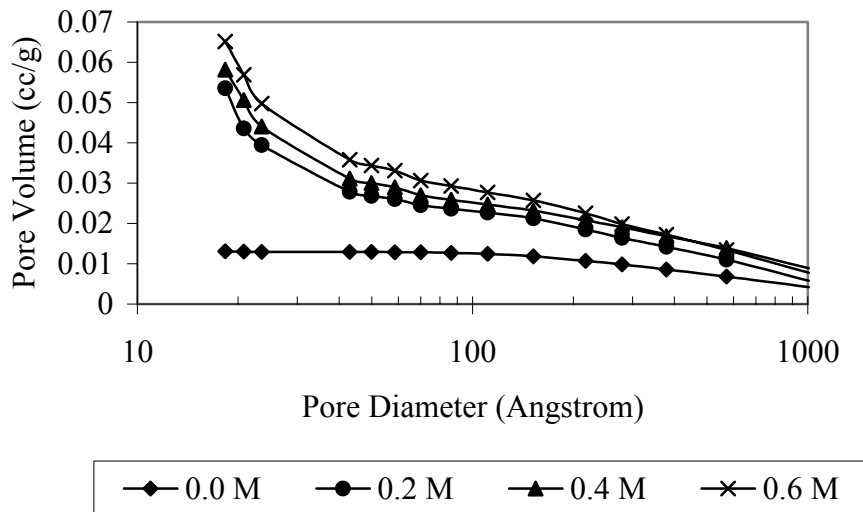


Figure 5: The pore size distribution of the carbon pellet prepared from different H_2SO_4 concentrations treatment of the SACGs.

CONCLUSION

A method has been developed to obtain a carbon pellet with high microporosity, which can be tailored by adjusting the concentration of the H₂SO₄ during the treatment of the SACG. The results from the porosity analysis show that pellet carbon from EFB has a good potential for the gas storage and separation purposes. Increased of H₂SO₄ concentration has reduced the mesopore surface area and volume, however it increases that of the micropore. Still, the results are lower as compared to the commercial carbon pellet. By further studying of the heating profile during the carbonization process, it is possible to prepare a higher adsorption capacity carbon pellet as well as carbon molecular sieve pellet with a controlled micropore size.

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