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ADVANCED CARBON PRODUCTS FROM OIL PALM BIOMASS

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ABSTRACT

A method was developed to produce advanced carbon products from oil palm biomass. Oil palm empty fruit bunch (EFB) contains polymeric lignocellulosic components such as hemicellulose, cellulose and lignin, and is therefore a potential raw material for producing advanced materials such as carbon electrode and molecular sieve carbon. Carbon precursors were prepared by slow pyrolysis of EFB under vacuum at 280°C. Powder obtained from grinding and ball milling the semi-pyrolysed EFB was then treated with 0.2, 0.4 and 0.6 M H_2SO_4 *and dried at 100°C. The chemical changes of the treated EFB carbon precursors are discussed by their Thermogravimetric (TGA) results. Green body pellets were then prepared by molding of the carbon precursors powder at 10 t of compression force and then carbonized at 600°C, 800°C and 1000°C using multiple heating profiles under nitrogen gas flow. The carbon pellets prepared from 0.4 M* H_2SO_4 *gave the highest density (*ρ*), Young's modulus (E), Rockwell hardness (H) and electrical conductivity (*σ*). These indicated that the treatment had increased the crystallinity of the carbon as also evidenced by the XRD analysis results. BET surface area analysis was carried out and it was found that the carbon precursors treated with 0.6 M* H_2SO_4 *produced the activated carbon with the highest porosity. The carbon pellets produced from the treatment with 0.6 M* H_2SO_4 *and carbonized at different temperatures were further activated with* CO_2 *to further increase their porosity, and the effects of different carbonization temperature on the pore structure and adsorptive properties for oxygen and nitrogen were investigated. This study has identified oil palm EFB as a potentially suitable raw material for the preparation of carbon electrode and molecular sieve carbon.*

Keywords: advanced carbon products, EFB, carbon electrode, molecular sieve carbon, biomass.

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INTRODUCTION

There are many carbon products in the market, for example, coke, graphite, carbon and graphite fibres, carbon fibre-carbon matrix composites, adsorbent carbons and monoliths, glassy carbon, engineering carbon, carbon black, carbon film, carbon nanocone and multilewall carbon spheres. The traditional raw materials for making them are petroleum, triglyceride and coal, but with the soaring fuel prices, alternative raw materials are being sought. Thus, there have been attempts to produce highly activated carbon (for adsorbents and electrodes) from rice husk (Daifullah *et al*., 2004), Eucalyptus waste wood (Tancredi *et al*., 2004), coconut shell (Dandekar *et al*., 2005) and peanut husk (Dincer *et al*., 2007).

Malaysia is one of the world leading producers of palm oil with the oil palm plantations with the hectarage of 4.305 million hectares in 2007 (MPOB, 2008). The average of fresh fruit bunch yield is estimated around 20.08 t ha^{-1} and considering 22% of yield, it is estimated around 19.03 million tonnes (wet weight basis) of empty fruit bunch (EFB) has been produced in 2007. The EFB fibre contains 77.7% holocellulose, 44.2% α-cellulose and 33.5% hemicellulose and, additionally, 20.4% lignin (Basiron and Husin, 1996). These components contribute to the carbon content of EFB fibres which has been reported to be 42%-43% (wet basis) (Gurmit *et al*., 1990). EFB has been found suitable for

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conversion (by pre-carbonization) into self-adhesive carbon grains (SACG) that can be palletized without any binding agent (Deraman *et al*., 1998). A number of attempts have been made to improve thermal and chemical characteristics of the SACG produced from EFB (Deraman *et al*., 2000; 2002; Abdul Aziz *et al*., 2003).

The use of acids to activate lignocellulosic materials for producing porous carbon with a high surface area is well-known (Mochida *et al.,* 1985; Guo and Lua, 1999; Guo *et al.,* 2005; Legrouri *et al.,* 2004). Basically, strong acids are oxidizing agents, and would dehydrate and redistribute the biopolymers in lignocellulosic materials (Song and Lee, 1984). The ether bonds between the lignin and cellulose are cleaved, followed by recombination of the cleaved units into larger structural units as a rigid cross-linked solid (Helm and Young, 1989; Sabio *et al.,* 1995; El-Hendawy, 2003). Based on this action, using sulphuric acid (H_2SO_4) to treat SACG (from EFB) will modify the thermal and chemical properties of the SACG, hence, would increase the physical and mechanical properties of the carbon pellets.

By the norms of the International Union of Pure and Applied Chemistry (IUPAC), there are three classes of pores in a porous material - micropores (width $d < 2$ nm), mesopores (2 nm $< d <$ 50 nm) and macropores ($d >$ 50 nm) (Gregg and Singh, 1982). Previous authors claimed that CO_2 activation of activated carbon was found to increase the micropores by partially oxidizing the tar, produces an opening of mesopores and macropores into micropores, simultaneously followed by widening of the narrower micropores (RodriGuez-Reinoso *et al.,* 1995; 2000; Sanhez *et al.,* 2001).

Gas separation by adsorption is widely used in the petrochemicals, biochemical, environmental, oil and gas industries. A material very useful to these industries is molecular sieve carbon, a special activated carbon with a discrete pore structure that allows it to discriminate between molecules on the basis of their size. It can separate molecules based on their rates of adsorption rather than on the differences in their adsorption capacity. It is a kinetic adsorbent that, for example, separates N_2 from air by the faster sorption of O_2 (Hu and Vasant, 1995). The most important application of a carbon molecular sieve (CMS) is the separation of nitrogen from air by pressure swing adsorption (PSA) (Foley, 1995). Various types of molecular sieve carbon have been prepared from carbonaceous sources, such as coal (Miura and Hayashi, 1991), lignocellulosic materials and biomass (Hu and Vansant, 1995; Nguyen and Do, 1995; Hayashi, 1999; Farris and Coe, 1992) and oil palm wastes (Guo and Lua, 1999; Tan and Ani, 2004). Generally, there are two major methods of preparation - controlled pyrolysis of the carbon precursor or modification of the existing porosity of an activated carbon by carbon deposition.

However, there has been little work on preparing carbon adsorbents in pellet form except for Inomata *et al.* (2002) who prepared high porosity pellets for methane transport. It is thus the objective of this article to study the effects of H_2SO_4 treatment of EFB carbon precursor and different carbonization temperatures (600°C, 800°C and 1000°C) use to prepare the activated carbon on the physical and mechanical properties, as well as the pore structure of the carbon pellets. Subsequently, an attempt will be made to increase the porosity of the carbon pellets by partial oxidation activation using CO_2 gas. It is anticipated that it would be possible to increase the BET surface area (S_{BET}), following which the O_2/N_2 separation capacity will be investigated.

MATERIALS AND METHOD

Chips of dried oil palm EFB were used. The EFB carbon precursor was prepared by pre-carbonizing the EFB chips, followed by grinding and sieving through a 53-micron sieve (Deraman *et al*., 1998). The carbon precursor was then treated with 0.2, 0.4 and 0.6 M H_2SO_4 at 100°C for 5 min before drying overnight at room temperature. Green pellets were produced by mold compacting 2 g of the treated carbon precursor to a compression of 10 t. The effects of the different H_2SO_4 concentrations on the thermal characteristics of the carbon precursor were studied using Thermogravimetric analysis (TGA) and Fourier Transformed Infra-red Spectroscopy (FTIR).

The green pellets were then carbonized under a flow of nitrogen gas at 600°C, 800°C and 1000°C in a Vulcan Box Furnace 3-1750. The temperature of the furnace was raised to 280°C at 1.0°C min^{-1} and left at that temperature for 60 min before finally raising it to 600°C at 3.0°C min^{-1}, then kept constant for 5 min before allowing it to cool down. For the carbonization at 800°C and 1000°C, the same heating profile was used to reach the temperature of 600°C and then the heating was proceeded after 5 min at 5°C min^{-1} until the respective temperatures and kept there for another 5 min before cooling. On cooling to ambient temperature, the pellets were taken from the furnace and washed with distilled water until the pH of the wash was neutral. This was to ensure that the activated carbon was free from ash and oxides that could have invalidated the BET analysis.

The pellet dimensions were measured using a micrometer and their bulk density obtained by dividing the weight of a sample by its volume. Their electrical conductivity was measured using the four-point-probe technique (Keithley Micro-Ohmeter). A micro-hardness tester (Wilson-Rockwell Series 2000) was used to measure the Rockwell hardness of the pellets using loads from 10 kg (minimum) to 50 kg (maximum). Young's modulus of the pellets was measured using the ultrasonic-mechanical-characterization (UMC) of materials instrument. The signal from the ultrasonic pulser (Panametrik 500PR) was transferred to a computer via the PICO ADC 200 software for calculation of the longitudinal ultrasonic velocity in the sample (Deraman *et al.*, 2002).

The diffraction intensity of the carbon pellets was measured using an X-ray diffractometer (Bruker Advanced X-Ray Solution AXS, D8), which employed Cu Kα radiation, scanning with a step size of 0.04° in the range 2.3° to 60°. The X-ray diffraction patterns showed a disordered graphitic structure which assigned two broad peaks at the 002 plane and 10 plane (overlapped 100 and 101) (Ryu *et al.*, 2002). From the peaks can be obtained the interlayer spacing (d_{002}) of the carbon stacks. The activated carbon pellet sample had a different full-width half maximum of the 002 peak, indicating a different micropore wall structure. From the position of the 002 peak can be estimated the interlayer spacing, d_{002}, by direct application of Bragg's Law:

$$d_{002} = n\lambda \ / \ \sin\theta_{002} \qquad (1)$$

Estimates of the mean crystallite dimensions can generally be made from the XRD data by application of the Debye-Scherrer equation. When applied to carbon materials, the equation takes the form where β equals the peak width at half height, corrected for instrumental broadening. The L_c and L_a are not exactly equal to the height and width of the crystallites, but can be used as convenient relative estimates of them (Carrot *et al.*, 2001).

$$L_c = 0.90\lambda / \beta \cos\theta_{002} \qquad (2)$$

$$L_a = 1.84\lambda / \beta \cos\theta_{10} \qquad (3)$$

The BET surface area (S_{BET}) and O_2/N_2 separation analyses, and measurements of the micropore surface area (S_{MIC}), pore volume (V_{MIC}) and pore diameter were done using a unit of Micromeritics ASAP 2010 from Micromeritics, Inc. Norcross, GA, USA. The porosity of the pellets was determined using N_2 adsorption at 77 K (static volumetric method) measured using mass balance equations, appropriate gas equations of state, and measured pressures to obtain all the adsorption isotherms of the molecular sieve carbon (Webb and Orr, 1997). The micropore volume was calculated using the Dubinin-Radushkevish (D-R) equation (Gregg and Sing, 1982). The O_2/N_2 separation rate was calculated using software to provide the adsorbed amounts of the adsorbates or system pressure changes as a function of the time. To evaluate the kinetic separation efficiency for oxygen and nitrogen, the adsorption rates for O_2 and N_2 were taken separately at 298°K and constant starting pressure within 1 min of each other. Finally, the overall kinetic separation efficiency was calculated by dividing the adsorption capacity for oxygen and nitrogen at approximately 1 min intervals (Tan and Ani, 2004).

RESULTS AND DISCUSSION

The typical TGA curves of the treated EFB carbon precursors (*Figure 1*) clearly show that the H_2SO_4 treatment had changed the thermal characteristics of the samples. Basically, the initial weight loss occurring from 25°C to 150°C was the loss of adsorbed water. The increased molarity of H_2SO_4 used increased the hygroscopic characteristic of the treated EFB carbon precursors as shown by the increase in the first peak rate of weight loss. The treatment with H_2SO_4 also broke down the lignocellulose in the EFB carbon precursors as shown by the shift in the second peak (between 200°C to 300°C) of the carbon precursors treated with 0.4 M and 0.6 M H_2SO_4. Normally, the decomposition of cellulose and lignin occurs at about 300°C (Bryne and Nagle, 1997), and the EFB carbon precursors treated with 0.2 Molar H_2SO_4 behaved the same way. However, hydrolysis by the H_2SO_4 converted the high molecular weight cellulose and lignin to smaller oxidized and hydrolyzed components, thus, limiting the weight loss by the EFB carbon precursors. Increasing the H_2SO_4 concentration increased the solid carbon yield at 600°C as shown in the weight loss curve in *Figure 1.*

The H_2SO_4 treatment also enhanced the binding of the of EFB carbon precursors and increased the possibility of further recombination and cross-linking during the carbonization as indicated by the increases in ρ, *E* and *H* of the carbon pellets (*Figure 2*). Their values were much higher than those from carbon pellets made from EFB fibre without the slow pyrolysis process (Deraman, 1993). This was because the EFB carbon precursors had less volatiles and their lower evaporation caused less restructuring of the carbon pellets during the carbonization. However, using the more concentrated H_2SO_4 (0.6 M) produced lower figures, possibly due to burn off of the EFB carbon polymers by this strong oxidizing agent which enabled less recombination and cross-linking subsequently. The highest ρ, *E* and *H* were obtained from the EFB carbon precursors treated with 0.4 M and carbonized at 1000°C at 1.25 g cm^{-3}, 14.06 GPa and 91.06 HRF (equivalent to 110.06 kg mm^{-2}) respectively. These values are lower as compared to the commercial glassy carbon pellet SIGRADUR K, which has those values of 1.25 g cm^{-3}, 35 GPa and 334 kg mm^{-2} respectively. Meanwhile, the σ for all the carbon pellets was only detected at the carbonization temperature of 800°C, as at the lower temperature the recombination and cross-linking of the hydrolyzed carbon precursors were insufficient or incomplete to create an optimum networking for the electrical conductivity occurs. As the carbonization temperature increases, so would the σ as the cross-linking of the carbon precursors increases with the carbonization temperature (Jenkins and Kawamura, 1976). The highest σ was also obtained from the EFB carbon precursors treated with 0.4 M and carbonized at 1000°C at 64.39 $(\Omega\text{cm})^{-1}$, and this value is in the range of the values currently observed in commercial graphite and non-graphitizing carbons (Coutinho *et al*., 2000).

In addition, the carbon microstructure also contributed to the electrical conductivity of the carbon pellets, as evidenced by the X-ray diffraction results obtained. The interlayer spacing (d_{002}) of the carbon pellets was calculated from the peak at $2\theta = 25^\circ$ and the effect of H_2SO_4 concentration shown in *Figure 3*. The X-ray diffraction patterns for all the carbon pellets over the angular range 20° to 70° had two broad 002 and 100 peaks lying at 23.4° to 25.2° and 44.5° to 45.5°, respectively. This indicated that the samples had a turbostratic structure (Short and Walker, 1963). It is obvious from *Figure 3* that as the carbonization temperature rose, there was higher growth of crystallites in the carbon pellets from all the H_2SO_4 treatments as shown by the fall in d_{002}. Meanwhile, d_{002} of the carbon pellets treated with 0.2-0.4 M H_2SO_4 moved towards that of graphite (d_{002} graphite = 0.3355), which explained the increased electrical conductivity as was also found by others (Kuga *et al*., 2004; Sevilla and Fuertes, 2006). In general, H_2SO_4 treatment increased d_{002} although at the highest concentration used (0.6 M), it was reduced. This shows that the microstructure of carbon pellets also influences their electrical conductivity.

The nitrogen adsorption isotherms of all the carbon pellets are shown in *Figure 3*. All the isotherms for the pellets prepared using 0.6 M H_2SO_4

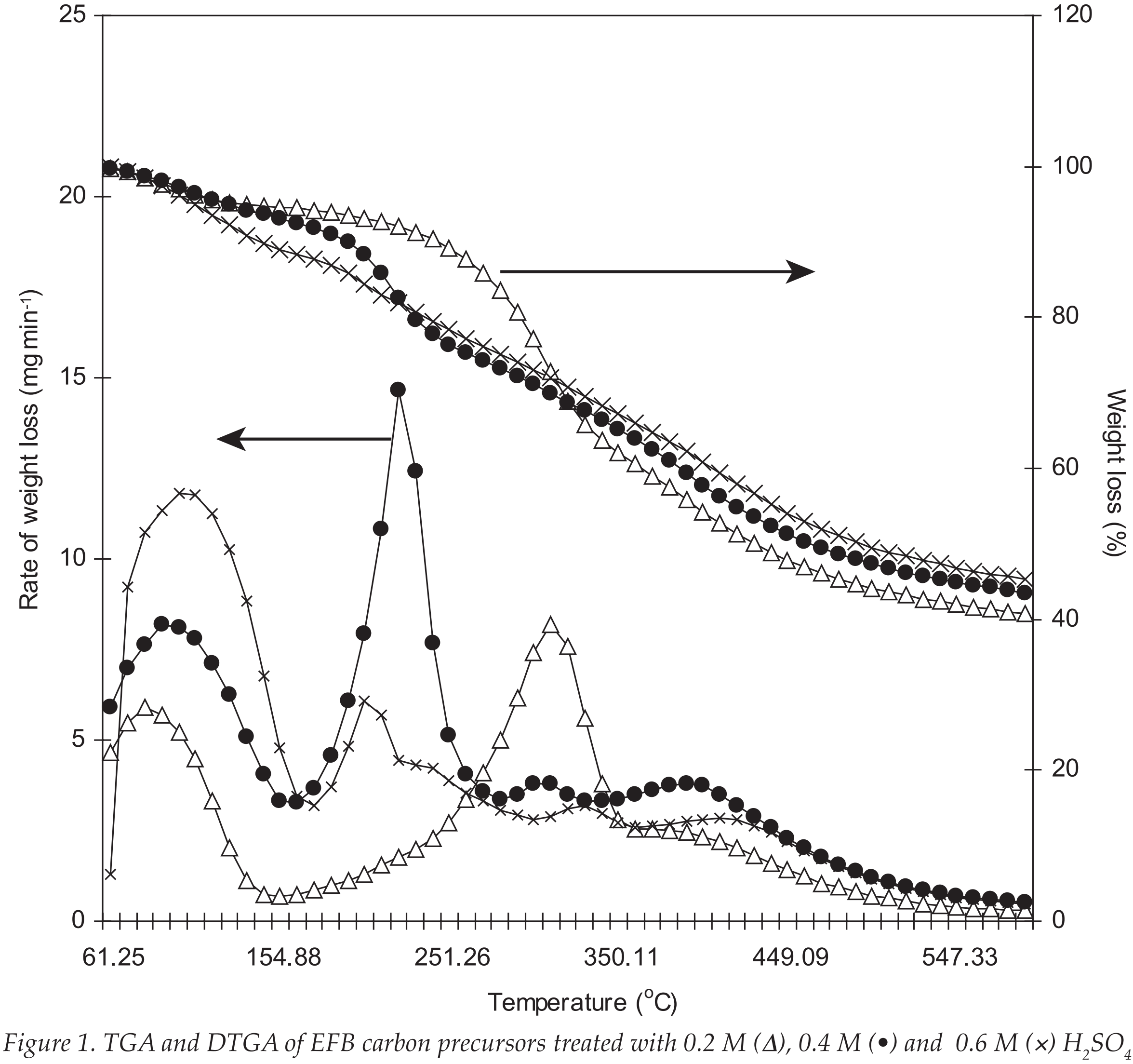

Figure 1. TGA and DTGA of EFB carbon precursors treated with 0.2 M (Δ), 0.4 M (•) and 0.6 M (×) H_2SO_4.

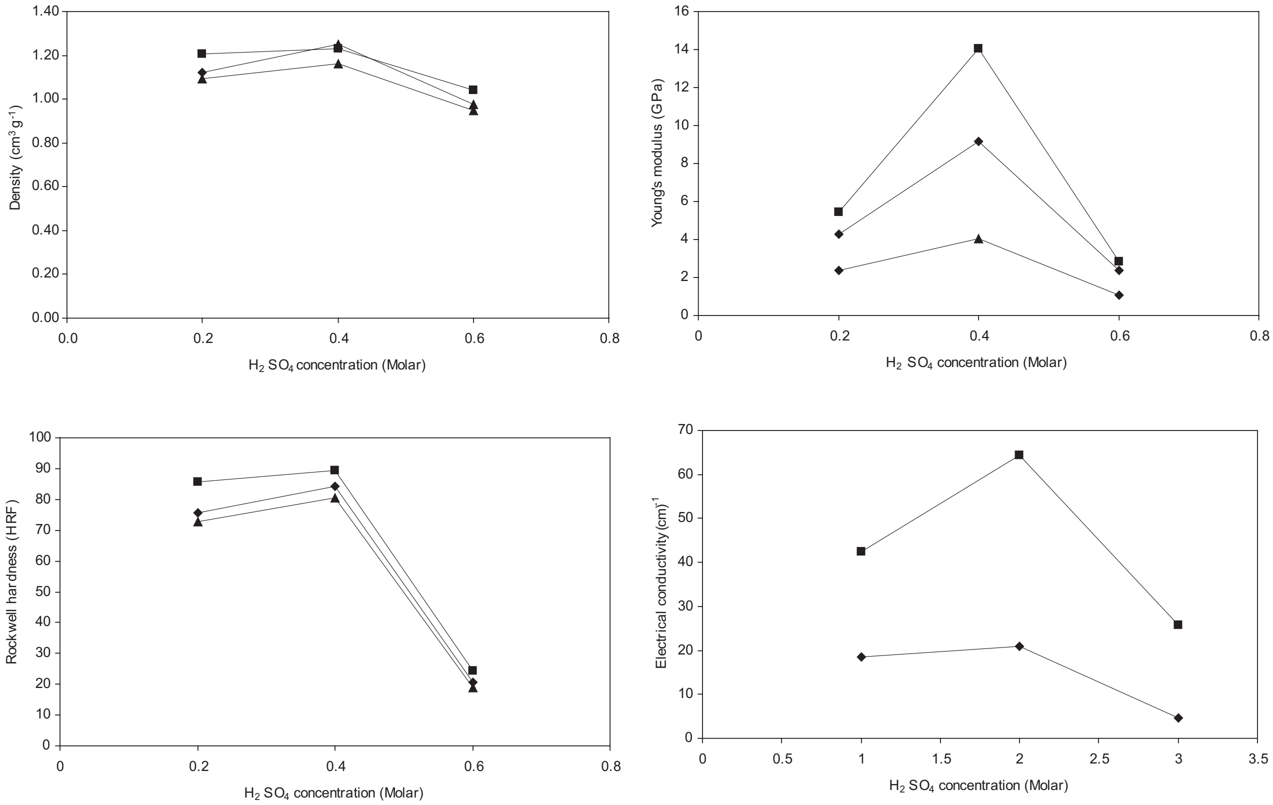

Figure 2. The ρ, E, H and σ for carbon pellets prepared using different concentrations of H_2SO_4 as a function of carbonization temperature (▲ = 600°C; ◆ = 800°C; ■ = 1000°C).

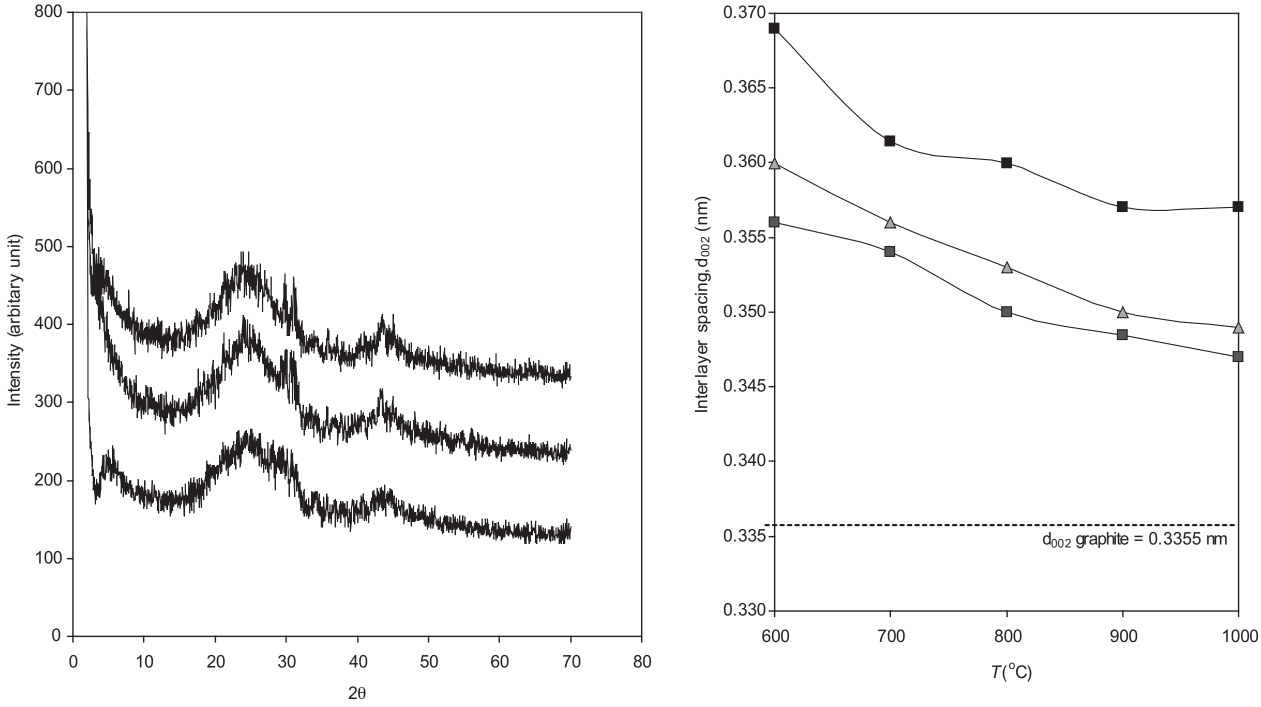

Figure 3. The X-ray diffraction and calculated d_{002} for the carbon pellets prepared at T = 1000°C as a function of the H_2SO_4 concentration.

show Type I by BDDT classification (Barrett *et al.*, 1951) with adsorption increasing fairly rapidly at low relative pressure in a range of 0.0 – 0.2, followed by a slow uptake of adsorbent at a relative pressure of >0.2, indicating predominant microporosity. The samples made from 0.2 M and 0.4 M H_2SO_4 show a Type II curve, indicating a predominance of mesopores or macropores (with the micropores ruptured) as indicated by their larger average pore diameter (*Table 1*). The pore area and volume details of the carbon pellets prepared at different carbonization temperature and as a function of the H_2SO_4 concentration are also tabulated in *Table 1*. Overall, S_{BET} and S_{MICRO} of the pellets fell with increased carbonization temperature. Some of these results and observations have been discussed in detail elsewhere (Abdul Aziz *et al.*, 2005). The highest S_{BET} and S_{MICRO} were from the carbon pellets prepared with 0.6 M H_2SO_4 and carbonized at 600°C at 386.51 $m^2 g^{-1}$ and 360.54 $m^2 g^{-1}$, respectively.

The carbon pellets made with 0.6 M H_2SO_4 and at different carbonization temperature were selected for further activation with CO_2, and the N_2 adsorption isotherm for all the pellets are shown in *Figure 4* to *6*. All the pellets show Type I isotherm curves, indicating their highly micro-porous characteristics. The maximum adsorption of N_2 occurred at a very slight relative pressure (P/P_o < 0.05), indicating that CO_2 produces an opening, followed by widening of the narrow microporosity (RodriGuez-Reinoso *et al.*, 1995; Sanchez *et al.*, 2001; Rodriguez-Valero *et al.*, 2000). Obviously, the carbon pellets prepared at higher carbonization temperature showed an increased effect of CO_2 as indicated by their increased S_{BET} and S_{MICRO} (*Table 2*). This observation contradicts earlier results in which carbonization temperature decreased S_{BET} and S_{MICRO}. The CO_2 activation of the carbon pellets increased both their surface area and pore volume. Activation of the 0.6 M H_2SO_4 treated carbon pellets carbonized at 1000°C produced the highest pore surface area (S_{BET} = 793.97 $m^2 g^{-1}$) and total pore volume (V_{TOTAL} = 0.35 $cm^3 g^{-1}$). This can be related to the surface chemistry of the carbon pellets prior to CO_2 activation. The H_2SO_4 acted on lignocellulose to produce more acidic functional groups linked to the carbon atoms, such as phenols and carboxylic acids (Guo and Lua, 1999). These acidic functional groups adsorbed and reacted

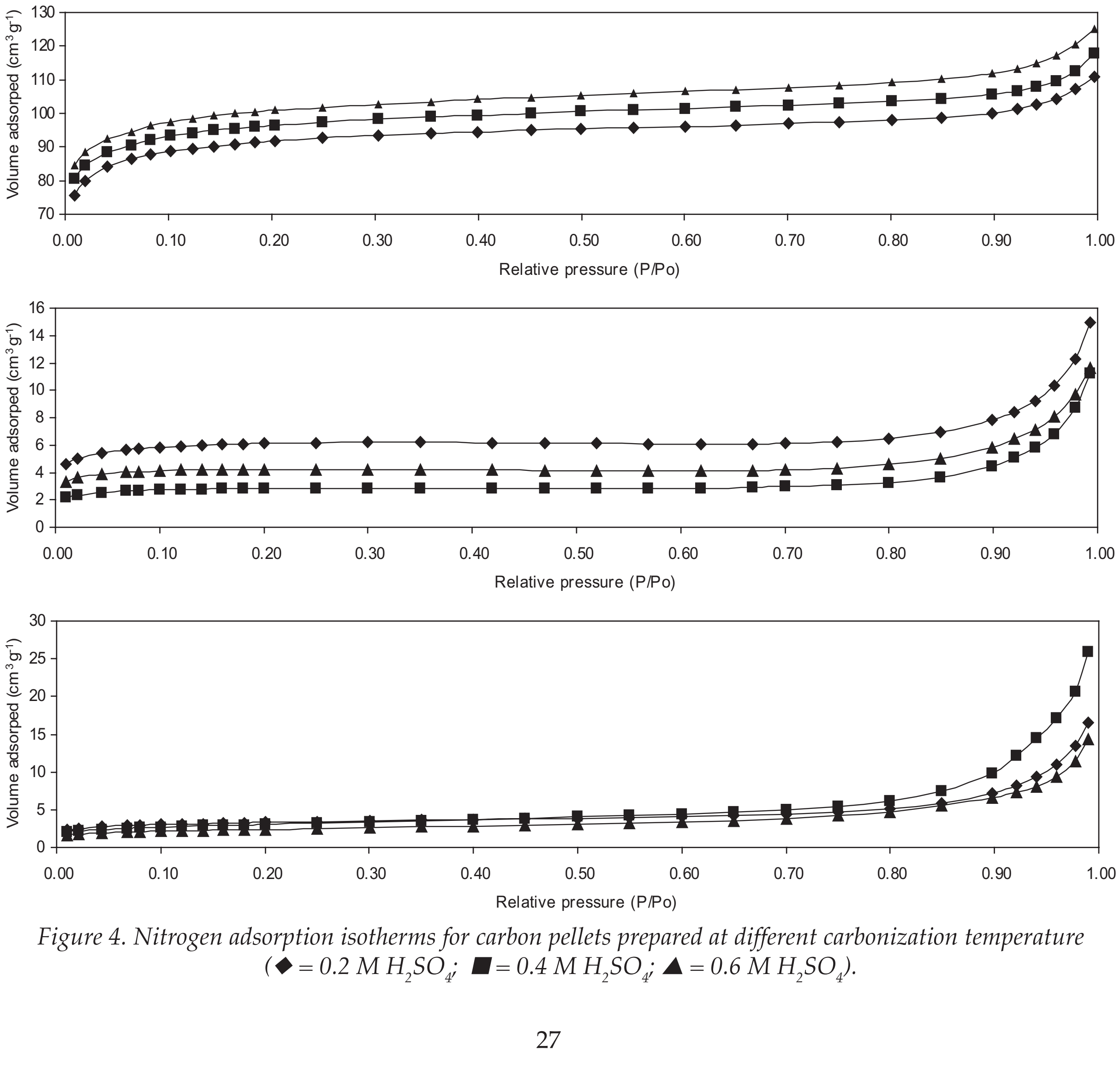

Figure 4. Nitrogen adsorption isotherms for carbon pellets prepared at different carbonization temperature (◆ = 0.2 M H_2SO_4; ■ = 0.4 M H_2SO_4; ▲ = 0.6 M H_2SO_4).

TABLE 1. BET ANALYSIS RESULTS OF THE CARBON PELLETS

T (°C)	[H_2SO_4] (M)	S_{BET} (m^2 g^{-1})	S_{MICRO} (m^2 g^{-1})	S_{MESO} (m^2 g^{-1})	V_{TOTAL} (cm^3 g^{-1})	V_{MICRO} (cm^3 g^{-1})	D (Å)
600	0.2	354.40	272.42	81.98	0.1715	0.1062	19.35
	0.4	371.25	348.6	22.65	0.1822	0.1407	19.63
	0.6	386.51	360.54	25.97	0.1932	0.1461	19.99
800	0.2	23.42	15.71	7.71	0.0231	0.0061	39.51
	0.4	10.94	10.85	0.09	0.0174	0.0043	63.60
	0.6	16.64	13.07	3.57	0.0179	0.0050	43.13
1 000	0.2	12.04	8.17	3.87	0.0256	0.0035	85.21
	0.4	10.76	3.80	6.96	0.0402	0.0017	149.25
	0.6	8.57	3.76	4.81	0.0221	0.0017	103.10

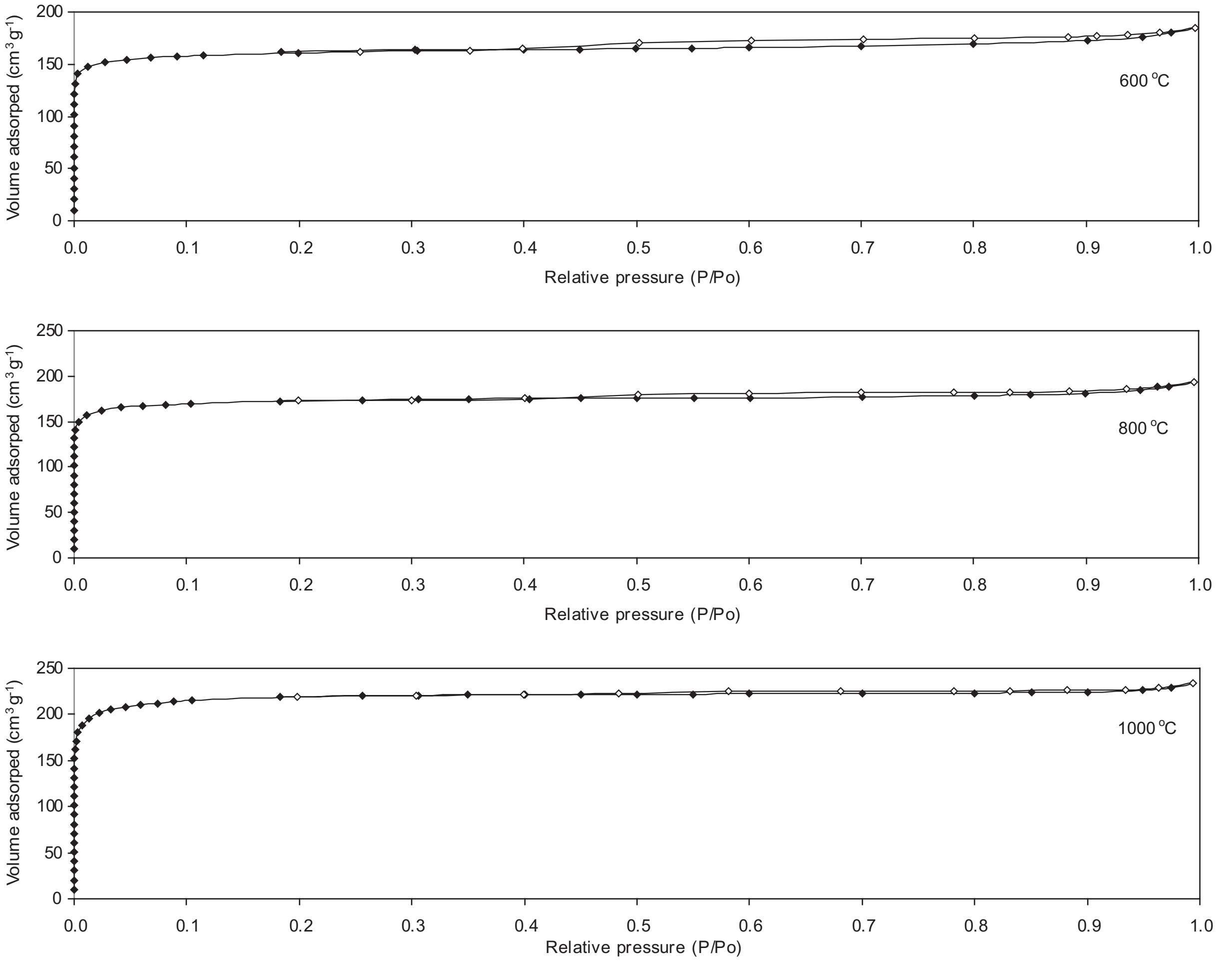

Figure 5. Nitrogen adsorption of CO_2 activated carbon pellets produced from 0.6 M H_2SO_4 treated EFB carbon precursors.

with CO_2, whereby the CO_2 probably function as a cross-linker or functionalization agent in the present of residual acid. It therefore enhanced the activation to form more micropores (Encinar *et al.*, 1998; Mohamad *et al*., 2005). However, the carbon pellet porosity properties are still quite lower as compared to the commercial carbon, for example Filtrasorb 100 powder as had been studied by Hu and Srinivasan as shown in *Table 2* (Hu and Srinivasan, 2001). However, based on the knowledge that almost all the commercial carbon adsorbent are in the powder or granule forms, this comparison is being made between two different physical properties of porous carbon. The lower porosity of the carbon pellets as compared to the commercial carbon powder is anticipated due to the compression effect during the

TABLE 2. BET ANALYSIS RESULTS OF CARBON PELLETS PRODUCED FROM 0.6 M H_2SO_4 TREATED EFB CARBON PRECURSORS AND ACTIVATED WITH CO_2

T (°C)	S_{BET} ($m^2 g^{-1}$)	S_{MICRO} ($m^2 g^{-1}$)	S_{MESO} ($m^2 g^{-1}$)	V_{TOTAL} ($cm^3 g^{-1}$)	V_{MICRO} ($cm^3 g^{-1}$)	D (Å)
600	671.97	548.84	69.13	0.2969	0.2635	7.10
800	622.86	559.11	63.75	0.2909	0.2666	7.20
1 000	793.97	710.39	83.58	0.3544	0.4008	7.60
Filtrasorb 100*	937.00	863.00	74.00	0.494	-	-

Note: *The data source for Filtrasorb 100, a commercial porous carbon is from reference (Hu and Srinivasan, 2001).

preparation of the carbon pellet that has compressed the total porosity. One study found that compression pressure affects the porosity of carbon disk prepared from micro-crystalline cellulose powder, in which higher compression pressure reduces the pore surface area as well as the total pore volume (Inomata *et al.*, 2002).

The suitability of these porous carbons as molecular sieve carbon in O_2 and N_2 separation was studied. The S_{BET} and S_{MICRO} increased with their O_2/N_2 kinetic selectivity. *Figure 6* shows the O_2 and N_2 uptake by each type of pellets with their calculated O_2/N_2 kinetic selectivity given in *Table 3.*

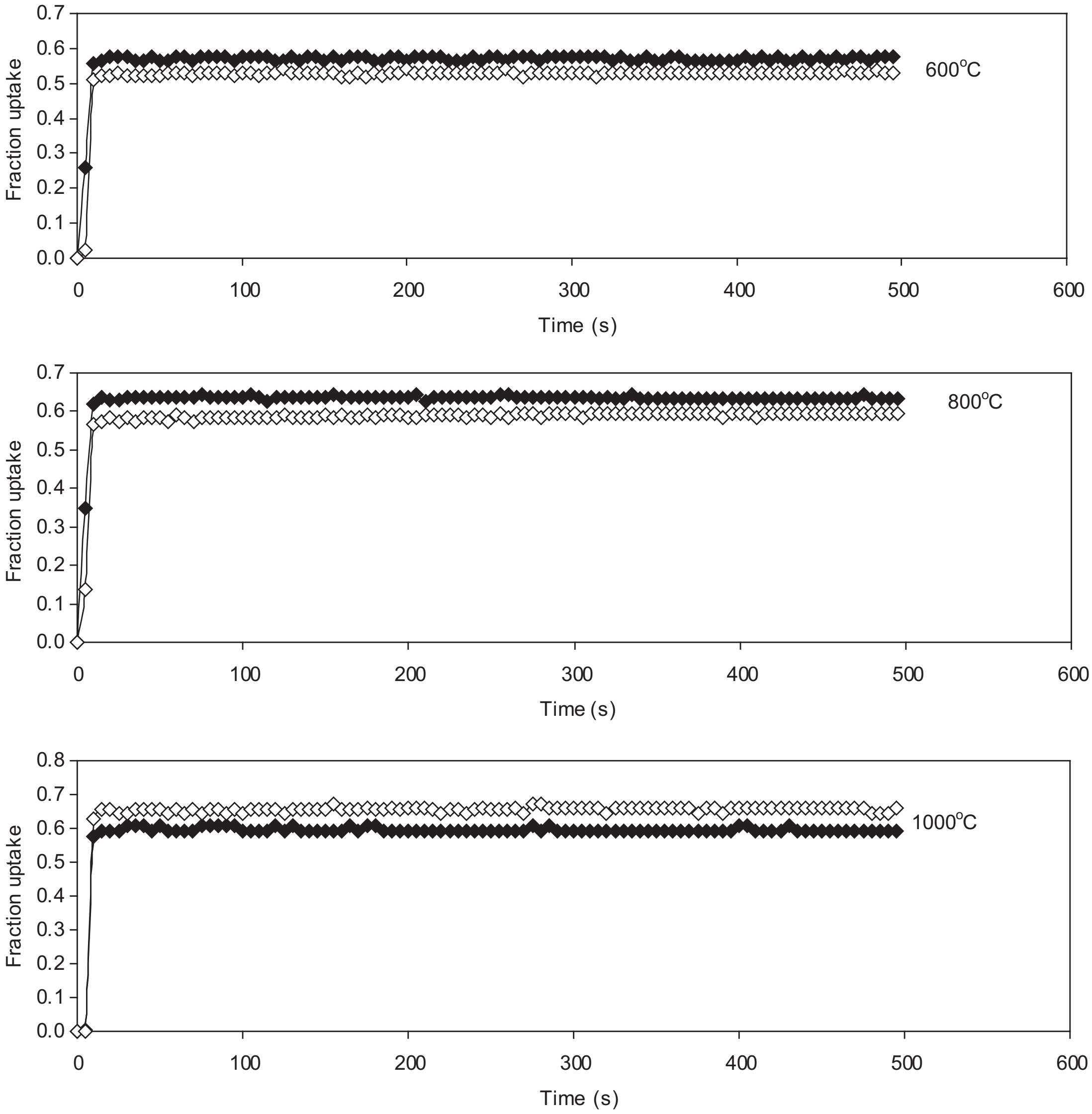

Figure 6. The O_2/N_2 separation by CO_2 activated carbon pellets prepared from 0.6 M H_2SO_4 at different carbonization temperatures.

The carbonization temperature of the carbon pellets also influenced their O_2/N_2 kinetic selectivity. As with the effects of *T* on CO_2 activation, the surface chemistry also played a role in the O_2/N_2 kinetic selectivity. The same observation had been made on other raw materials, such as xylan, cellulose and Kraft lignin (Guo and Rockstraw, 2006). This is due to the decomposition of the acidic surface groups when subject to high temperature, contributing to the increased oxygen uptake by the carbon pellets (Phillips *et al*., 1998). The maximum O_2/N_2 kinetic selectivity was exhibited by the carbon pellets prepared from EFB carbon precursors treated with 0.6 M H_2SO_4, carbonized at 1000ºC and activated with CO_2 at 1.42.

TABLE 3. THE O_2 AND N_2 ADSORPTION CAPACITY AND SELECTIVITY OF CO_2 ACTIVATED CARBON PELLETS PREPARED FROM 0.6 M H_2SO_4 AT DIFFERENT CARBONIZATION TEMPERATURES

Temperature	Oxygen uptake (ml g^{-1})	Nitrogen uptake (ml g^{-1})	O_2/N_2 kinetic selectivity
600°C	4.36	4.40	0.73
800°C	4.88	5.18	0.80
1 000°C	5.62	4.73	1.42

CONCLUSION

This article discussed the potential for preparing advanced carbon products, such as carbon electrodes and molecular sieve carbon from EFB chips. An innovative process of slow pyrolysis of EFB chips was used to produce self-adhesive carbon precursors. Then, treatment with H_2SO_4 enhanced their cross-linking during carbonization of the green body pellets. This increased ρ, *E*, *H* and σ of the carbon pellets, with H_2SO_4 at 0.4 M giving the highest values, comparable to those for commercial carbon electrodes. However, higher H_2SO_4 concentration (0.6 M) severely oxidized and hydrolyzed the lignocellulose, reducing the values. On the other hand, the concentration produced the highest S_{BET} and S_{MICRO}, possibly due to the altered surface chemistry of the pellets. Further activation with CO_2 greatly increased the porosity of the carbon pellets (0.6 M H_2SO_4 and T = 600ºC) which, in turn, increased their O_2/N_2 kinetic selectivity.

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