

**BULK DENSITY, MICROCRYSTALLITE AND POROSITY OF CARBON PELLET FROM NITRIC ACID TREATED SELF-ADHESIVE CARBON GRAIN FROM OIL PALM EMPTY FRUIT BUNCH**

Masliana Muslimin, Mohamad Deraman, Mohd. Hafizuddin Jumali, Ramli Omar.  
Izan Roshawaty Mustapa\*, Mazliza Mohtar, Astimar Abdul Aziz, Rus Mahayuni Abd.  
Rahman and AbuBakar Elshiekh Abdelrahman

*School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan  
Malaysia, 43600 Bangi, Selangor, Malaysia*

*\*Department of Physics, Faculty of Science and Technology, Universiti Pendidikan Sultan  
Idris, 35900 Tanjung Malim, Perak, Malaysia*

**ABSTRACT**

Self-adhesive carbon grain (SACG) prepared from oil palm empty fruit bunch (EFB) by a low carbonization process were treated with 1, 3, 5 and 7 Molar (M) nitric acid ( $\text{HNO}_3$ ) at  $27^\circ\text{C}$  and  $100^\circ\text{C}$ . The SACG green pellets were converted into carbon pellets by a carbonization process up to  $1000^\circ\text{C}$  in  $\text{N}_2$  environment using a multi-step heating profile. The treatment was found to increase the green pellets density from  $1.24 \text{ gcm}^{-3}$  to about  $1.35 \text{ gcm}^{-3}$ , but there was no significant change in pellet density after carbonization. X-ray diffraction analysis showed that 1 M treatment at  $27^\circ\text{C}$  caused the stacking height ( $L_c$ ) and width ( $L_a$ ) of microcrystallites of carbon pellets to increase from 0.866 to 1.339 nm and from 3.534 to 8.720 nm respectively. Above 1 M the microcrystallite dimension of carbon pellets decreased but their values are still higher than that for the untreated samples. A similar trend was observed for the treatment at  $100^\circ\text{C}$ . The BET isotherm plots show that the increase in molarity can widen the middle region of the relative pressure that has negative curves, and for molarity higher than 3 M the BET experiment is no longer able to produce such a plot. This results demonstrate that a significant change in the microcrystallite dimension or pore structure in carbon pellets due to the treatment is corresponding to a dramatic change in their adsorption capacity.

**INTRODUCTION**

Oil palm empty fruit bunch (EFB) are a by-product generated in large quantities at palm oil mills. It has traditionally been used as boiler fuel, mulching material in the oil palm plantation and organic fertilizer (after burning). However, efforts to give more value-added to its application have been made in many laboratories in Malaysia including processing EFB into chemically modified fibre [1, 2], fibreboard [3] and solid carbon [4-12]. If solid carbon can be manufactured from EFB this will reduce Malaysian import of solid carbon products, which is amounted to about RM120 million for the period from 1995 to early 2000 [12]. EFB supply is renewable and its continuous production at palm oil mills makes the EFB to have a great prospect for commercial exploitation [13].

Solid carbon products in the form of carbon pellets can be prepared from self-adhesive carbon grains (SACG) prepared from the EFB. It was found that the properties of carbon

pellets prepared from the SACG treated with HNO<sub>3</sub> at room temperature have changed with the acid concentration and reaction time, and the results for the concentrations of 1 Molar (*M*) to 5 *M* with the reaction time of 16 h [14], and 1 *M* to 7 *M* with the reaction of 1 h to 19 h [15] have been reported. In the present study, the acid treatment on the SACG was carried out at 27°C and 100°C for 16 hours in order to investigate its effect on the bulk density, microcrystallite dimension and porosity of carbon pellets. The mechanism of reaction between HNO<sub>3</sub> and carbon samples or its precursors can be found elsewhere [16,17,18,19,20,21,22,23].

## MATERIAL AND METHOD

Some of the properties of EFB have been summarized elsewhere [24]. EFB fibers were pre-carbonized at low temperature based on the method previously reported [7]. The pre-carbonized EFB was ball milled for 40 h to obtain SACG powder with particle size that can pass through 53 microns sieve. SACG was treated with nitric acid (HNO<sub>3</sub>) with 4 different concentration 1, 3, 5 and 7 Molar (*M*) at two different treatment temperatures i.e. 27°C and 100°C. For each concentration 15 g of SACG was mixed with 1125 ml of HNO<sub>3</sub> and stirred by a magnetic stirrer for 1 h at 27°C. The same process was made for the treatment at 100°C. The treated SACG was left for 15 h, before it was separated from the solution by a filtration process using filter papers (Whatman 41). The treated SACG was then dried in an oven at 105°C for a 24 hours. The green pellets, designated as samples 1 *M*, 3 *M*, 5 *M*, and 7 *M* (27°C and 100°C) were prepared by applying 21 metric tonnes of compression force on 2 g of SACG and 2 g of SACG treated with HNO<sub>3</sub> respectively in a mould of 27 mm diameter. The green pellets were carbonized up to 1000°C in a Box Furnace (*Vulcan 3-1750*) equipped with a heating rate controller facility. A multi-step heating profile was used in the carbonization process [25,26]. The heating environment in the furnace was continuously filled with a flow of nitrogen gas at 1.0 - 1.5 *l* per minute. The dimension of the pellet before and after carbonization was measured using micrometer and the density was determined by dividing the weight of the sample with its volume.

X-ray diffraction (XRD) measurements on carbon pellet were conducted using Bruker Advanced X-Ray Solution (AXS) model D8 Advance which employed Cu K $\alpha$  (0.1542 nm) radiation at a step size of 0.04° ranges from 2.3° to 60°. From the X-ray diffraction patterns it will show the disordered graphitic which assigned 2 broad peaks 002 plane and 10 plane (overlapped 100 and 101), respectively [27]. From that peak we can get the data of  $d_{002}$ ,  $L_c$  and  $L_a$ . Here,  $d_{002}$  is the interlayer spacing,  $L_c$  and  $L_a$  are the stacking height and width of the crystallite respectively. Each samples has a different full-width half maximum (FWHM) of the 002 peak, indicating the presence of a different micropore wall structural unit. From the position of the (002) peak we can calculate an estimate of the interlayer spacing  $d_{002}$ , by direct application of Bragg's Law:

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

Estimate of mean crystallite dimensions can generally be obtained from XRD data by application of the Debye-Scherrer Equation. When applied to carbon materials, the equation takes the form

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

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

where  $\beta$  equal to the peak width at half height corrected for instrumental broadening.  $L_c$  and  $L_a$  are not exactly equal to the height and width of the crystallites, but can be used as convenient relative estimates of these quantities [28].

BET surface analysis of the samples were performed using the Micromeritics ASAP 2000 – Accelerated Surface Area and Porosimetry Analyzers, by nitrogen gas adsorption at 77 K. Before measurements, the carbon pellet were degassed at 250°C. The BET surface area, porosity volume and average diameter were calculated based on the standard method of ASTM C 3663-92, ASTM D 4365-95 and ASTM 4641-94 respectively. The cross sectional area for nitrogen molecule was assumed to be 0.162 m<sup>2</sup>. The total pore volume was found from the amount of nitrogen adsorbed at a relative pressure of about 0.99. The micropore volume was calculated using a micropore analysis (*t* plot). The micropore surface area was then determined from the value obtained for the micropore volume [29].

### RESULTS AND DISCUSSION

The weight, thickness, diameter and bulk density of samples before and after carbonization are shown in Table 1.

Table 1: Weight (w), thickness (t), diameter (d) and bulk density ( $\rho$ ) of carbon pellets (+after polish)

Sample	Before Carbonization				After Carbonization			
	w (g)	t (m m)	d (mm )	$\rho$ (g/cm <sup>3</sup> )	w (g)	t (m m)	d (m m)	$\rho$ (g/cm <sup>3</sup> )
Untreated	1.99	2.80	27.0	1.24	0.6	1.7	19.	1.23 <sup>+</sup>
					3 <sup>+</sup>	6 <sup>+</sup>	25	1.13
					0.7	2.1		
1M (27°C)	2.01	2.80	27.0	1.25	0.7	1.9	19.	1.20 <sup>+</sup>
					0 <sup>+</sup>	2 <sup>+</sup>	78	1.14
					0.7	2.0		
3M (27°C)	2.01	2.66	27.0	1.31	2	6		
					0.5	1.6	19.	1.26 <sup>+</sup>
					8 <sup>+</sup>	0 <sup>+</sup>	22	1.16
5M (27°C)	2.01	2.59	27.0	1.35	0.6	1.9		
					6	5		
					0.6	1.6	18.	1.35 <sup>+</sup>
					2 <sup>+</sup>	5 <sup>+</sup>	78	1.23
					0.6	1.8		

7M (27 <sup>0</sup> C)	2.02	2.55	27.0 4	1.38	3 0.6 2 <sup>+</sup> 0.6 3	6 1.6 7 <sup>+</sup> 1.8 2	18. 75	1.38 <sup>+</sup> 1.27
1M (100 <sup>0</sup> C)	2.00	2.74	27.0 7	1.27	0.6 7 <sup>+</sup> 0.6 8	1.8 1 <sup>+</sup> 1.9 9	19. 60	1.23 <sup>+</sup> 1.14
3M (100 <sup>0</sup> C)	2.00	2.65	27.0 7	1.31	0.6 4 <sup>+</sup> 0.6 5	1.7 3 <sup>+</sup> 1.8 9	19. 01	1.31 <sup>+</sup> 1.21
5M (100 <sup>0</sup> C)	2.01	2.63	27.0 5	1.33	0.6 3 <sup>+</sup> 0.6 4	1.7 0 <sup>+</sup> 1.8 5	18. 92	1.33 <sup>+</sup> 1.23
7M (100 <sup>0</sup> C)	1.99	2.59	27.0 5	1.34	0.6 0 <sup>+</sup> 0.6 1	1.6 2 <sup>+</sup> 1.7 7	18. 86	1.34 <sup>+</sup> 1.24

For both treatment temperatures (27<sup>0</sup>C and 100<sup>0</sup>C), the data shows that carbonization causes a significant change in the weight loss and dimensional shrinkage of the samples and insignificant change in their bulk density. The bulk density of the green pellets seems to increase with increasing HNO<sub>3</sub> concentration, because the SACG possibly gains weight after chemisorbing oxygen from nitric acid [14]. The same trends occurs for the bulk density of carbon pellets after carbonization. This indicates that all the green pellets experience the same ‘net effect’ from the behaviour of the weight loss and dimensional shrinkage during carbonization. It should be noted that although the bulk density of green pellets increase but one still uses the same heating rate for carbonization of all the green pellets. According to Jenkins [30], as the green body increase in their density, one requires a slower heating rate in order to avoid the built up of internal pressure due to the fast release of volatiles from the samples during carbonization. However such a requirement does not arise for the samples 1 *M* to 7 *M* because (a) the reaction of the HNO<sub>3</sub> with SACG produces some complexes that would not vaporize during carbonization and (b) HNO<sub>3</sub> has dissolved some of the volatiles in the SACG pellets. Therefore the used of the same heating rate for all the samples did not cause significant change in the bulk density of the samples after carbonization.

Figure 1 and 2 shows the X-ray diffraction pattern for the carbon pellets prepared from the SACG treated with HNO<sub>3</sub> at 27<sup>0</sup>C and 100<sup>0</sup>C respectively. The 002 and 10 peaks for the sample 1 *M* are sharper than those of the UT samples. This shows that the treatment of 1 *M* can promote the growth of crystallites during carbonization, and the growth has taken place in the both directions, i.e parallel and perpendicular to the 002 planes. The 002 and 10 peaks for the 3 *M* and 7 *M* samples are also sharper than those of the UT samples, but they are noticeably broader than the samples 1 *M*. These behaviour can be interpreted as due to the

existence of an optimum concentration corresponding to the highest growth of crystallites during carbonization. Above 1 M the level of such a growth seems to be lower. These X-ray diffraction data also demonstrated that the concentration that can demote the crystallites growth would be higher than 7 M.

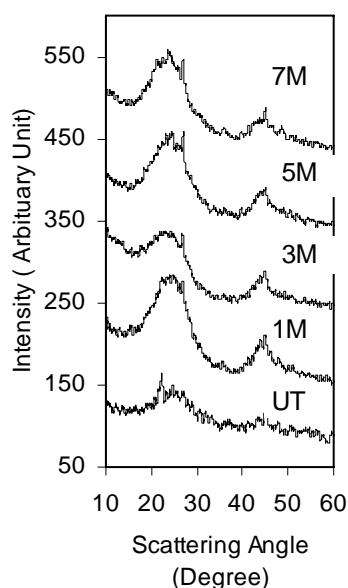


Figure 1 X-Ray diffractogram for carbon pellets from the untreated and SACG at 27<sup>0</sup>C

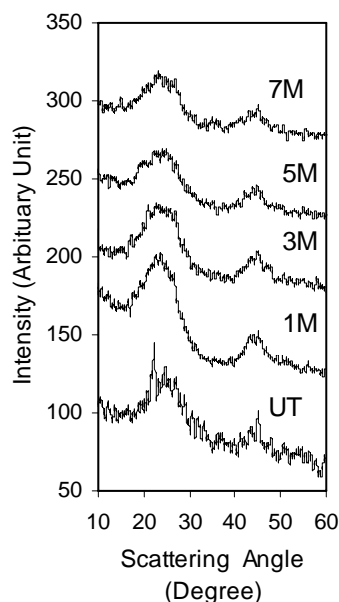


Figure 2 X-Ray diffractogram for the carbon pellets from the untreated and treated SACG at 100<sup>0</sup>C

From the 002 peaks in Figure 1 and Figure 2, the  $2\theta_{002}$  and  $\beta$  values can be measured and used in equation (1), (2) and (3) to estimate the value of  $d_{002}$ ,  $L_c$  and  $L_a$ . The values of these structural parameters are shown in Table 2.

Table 2 shows that there are slight change in the values of  $d_{002}$ , but significant change in the values of the  $L_c$  and  $L_a$ . The treated sample appear to have slightly higher values of the  $d_{002}$ , probably during the carbonization process the interaction between carbon layers resulted from the treated SACG are smaller than that from the untreated SACG. This could be due to the presence of oxygen ( $O_2$ ) from  $HNO_3$  in the interlayer spacing of the lignocellulosic structure of the treated SACG. It can be seen in Table 2 that for each treatment temperature, the treatment with 1 M significantly increase the values of  $L_c$  and  $L_a$ , that is 57% and 60% for 27<sup>0</sup>C and 57% and 24% for 100<sup>0</sup>C respectively. However further increase in the acid concentration cause the  $L_c$  and  $L_a$  to having relatively gradual and sharp decrease in their values respectively. This indicates that the mobility of atoms within the graphene layers during carbonization is greater than that in the direction perpendicular to the graphene layers. This may be due to the excessive occupancy of oxygen from  $HNO_3$  in the spacing between layers of the SACG lignocellulosic structure. It is well known that  $O_2$  from  $HNO_3$  have a tendency to be chemisorbed by the carbon samples or pre-carbonized samples and then occupied the space between layers structure of the material [18,20]. The effect of this occupancy is that it can limit the interaction between carbon layers produced during carbonization.

Table 2 The data for untreated and HNO<sub>3</sub> treated on SACG of carbon pellets

Sample	2θ <sub>002</sub>	β(°)	d <sub>002</sub> (nm)	L <sub>c</sub> (nm)	2θ <sub>100</sub>	β(°)	L <sub>a</sub> (nm)
Untreated	25.20	10.106	0.350	0.866	44.66	6.200	3.534
1 M (27°C)	23.40	7.103	0.377	1.339	44.29	4.222	8.720
3 M (27°C)	23.70	7.608	0.372	1.222	44.42	5.300	4.636
5 M (27°C)	24.60	9.393	0.359	0.942	44.52	5.503	4.318
7 M (27°C)	25.00	9.611	0.353	0.917	44.57	5.797	3.940
1 M (100°C)	23.80	6.991	0.371	1.370	44.23	4.550	6.661
3 M (100°C)	24.00	9.317	0.368	0.950	44.26	5.404	4.463
5 M (100°C)	24.30	9.636	0.363	0.913	44.35	5.769	3.971
7 M (100°C)	24.60	9.980	0.359	0.877	44.59	5.979	3.743

The BET adsorption desorption plot of the carbon pellets prepared from nitric acid oxidation are shown in Figure 4. The BET isotherm plot shows that the increase in *M* can widen the middle region of the relative pressure that has negative curves, and for *M* higher than 3 *M* the BET experiment is no longer able to produce such a plot. For the 3 *M* to 7 *M* carbon pellets, such a measurement produced incomplete adsorption curves, indicating an insensibility of these samples to the adsorption process. These behaviour may be related to the variation of the density of carbon pellets with the acid concentration (Table 1). This table clearly shows a significant difference between the density of the 0 *M* and 1 *M* carbon pellets with the density of the 3 *M* to 7 *M* carbon pellets.

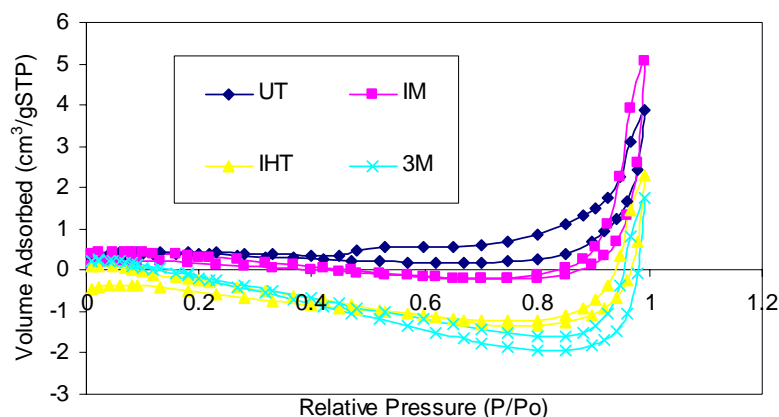


Figure 4 BET isotherm adsorption of carbon pellet from untreated and treated SACG

## CONCLUSIONS

SACG from the EFB treated with HNO<sub>3</sub> at 27<sup>0</sup>C and 100<sup>0</sup>C was pelletized and carbonized up to 1000<sup>0</sup>C to produce carbon pellets. It was found that the treatment can influence the profiles of the X-ray diffraction patterns of the carbon pellets, particularly for the treatment at higher temperature. Concentration of 1 M seems to be optimum for promoting bigger crystallites dimension. Concentration of higher than 1 M tends to decrease the optimum crystallites dimension of the carbon pellets, particularly in the direction perpendicular to the 002 graphitic planes. It is possible that this is related to the mechanism that the excessive chemisorption of oxygen from HNO<sub>3</sub> into the spacing between layers of lignocellulosic structure of the SACG can minimise the interactions between carbon layers produced during carbonization. We have also found that the treatment at the above temperatures gave a significant change on the BET adsorption-desorption plots, where the samples became more insensitive to the adsorption process as we increased the acid concentration and treatment temperature.

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