# Microcrystallite Dimension and Total Active Surface Area of Carbon Electrode from Mixtures of Pre-Carbonized Oil Palm Empty Fruit Bunches and Green Petroleum Cokes

## (Dimensi Mikrokristalit dan Luas Permukaan Aktif Total Karbon Elektrod daripada Campuran Serbuk Karbon Swa-merekat dan Kok Hijau Petroleum)

AWITDRUS, MOHAMAD DERAMAN*, IBRAHIM ABU TALIB, RAMLI OMAR, MOHD. HAFIZUDDIN HJ. JUMALI, ERMAN TAER & MANSOR MOHD. SAMAN

ABSTRACT

*Carbon pellets (CP) were prepared from the green pellets (GP) containing mixtures of pre-carbonized oil palm empty fruit bunches (SACG) and Green Petroleum Cokes (GPC), with the weight percentages (x) of SACG in the samples at 10%, 30%, 50%, 70% and 90%. Carbonization process to produce the CP was conducted up to 900ºC using a multi steps heating profile. The interlayer spacing ($d_{200}$ and $d_{100}$), stack height ($L_c$), stack width ($L_a$,) and effective dimension L of the turbostratic crystallites (microsrystallite) in the CPs were estimated from X-ray diffraction data; $d_{200}$, $d_{100}$, $L_a$, L increased and $L_c$ decreased with increasing weight percentage of SACG. The total surface area of active material of the CP ($A_{tot}$) with thickness, t, estimated from $L_c$ was found to follow the equation, $A_{tot} = [4.8086 – 0.0083x]10^{10} t$, indicating a significant influence of the SACG content in the mixture of the green body.*

*Keywords: Carbon pellet; green petroleum cokes; microcrystallite; active surface; self adhesive carbon grain*

ABSTRAK

*Pelet karbon (PK) telah disediakan daripada pelet jasad hijau (PJH) yang mengandungi campuran serbuk karbon swa-merekat (SKSM) dan kok hijau petroleum (KHP), dengan peratus berat (x) SKSM dalam sampel sebanyak 10%, 30%, 50%, 70% dan 90%. Proses karbonsasi untuk menghasilkan PK dijalankan pada suhu 900ºC dengan menggunakan profil pemanasan berperingkat. Jarak antara lapisan ($d_{200}$ dan $d_{100}$), tinggi timbunan ($L_c$), lebar timbunan ($L_a$) dan dimensi efektif (L) bagi kristalit turbostratik (mikro kristalit) dalam PK dihitung menggunakan data belauan sinar-X; peningkatan peratus berat SKSM menyebabkan $d_{200}$, $d_{100}$, $L_a$, L meningkat sedangkan $L_c$ menurun. Luas total permukaan bahan aktif ($A_{tot}$) PK dengan ketebalan t, yang dihitung menggunakan data $L_c$ didapati mematuhi persamaan $A_{tot} = [4.8086 – 0.0083x]10^{10}$ t, yang menunjukan pengaruh bahan kandungan SKSM di dalam PK adalah signifikan.*

*Kata kunci: Kok hijau petrolium; mikrokristalit; permukaan aktif; pelet karbon; serbuk karbon swa-merekat*

## INTRODUCTION

Carbon materials such as activated carbon are widely used as electrode for electrochemical double layer capacitor (EDLC). These materials are made of graphitic crystallites whose height ($L_c$) and width ($L_a$), can be determined from the XRD line broadening using Scherrer's equation (Marsh & Rodrigues-Reinoso 2006; Klug & Elexander 1970):

$$L_{c,a} = \frac{K\lambda}{\beta_{c,a} \cos\theta} \tag{1}$$

where K is the shape factor which is equal to 0.89 and 1.84 for $L_c$ and $L_a$ respectively, λ is the wave length of the X-ray radiation, $\beta_{c,a}$ is the full width at half height of symmetrical shape of the diffraction peaks and θ is the Bragg angle. The effective dimension L of the graphitic microcrystallites can be written as (Emmerich & Luengo 1993):

$$L = \left[\frac{\pi}{4} L_a^2 L_c\right]^{1/3}. \tag{2}$$

The size, mutual orientation and stacking of the microcrystallites are strongly associated with the microporosity and the high surface area. A small microcrystallite height and short range ordering between microcrystallites are necessary for the formation of super high surface area activated carbon (Kaneko et al. 1992). The relationship of the stack height of the graphitic microcrystallite and the BET surface area (S) of the material is given by the equation (Dresselhaus et al. 1992; Kumar et al. 1997):

$$S = \frac{2}{\rho_{xrd} \, L_c} \tag{3}$$

where $\rho_{xrd}$ is the X-ray density. The X-ray density is given by $\rho_{xrd} = \frac{d_{002}\left(graphite\right)}{d_{002}} x \, \rho\left(graphite\right)$, where $d_{002}$ (graphite) and ρ (graphite) are 0.33354 nm and 2.268 g/cm³, respectively.

Emmenegger et al. (2003) has developed a model to calculate the surface area of active material $A_{tot}$ in contact with solvated ions for a EDLC system consisting of two carbon electrodes using the equation:

$$A_{tot}\left(cm^2\right) = \frac{10^4\, A_E\, t}{\left(\dfrac{1}{\rho_{ap}S}\right) + 2d_D} \qquad (4)$$

where $A_E$ is geometric surface area of electrode, $t$ is the thickness of the electrode, $\rho_{ap}$ is the apparent density and $d_D$ is the pores diameter of active layer. The $A_{tot}$ is an important parameter because its value is directly related to the capacitance of a EDLC. From the equations (3) and (4), the total surface area of active material per electrode thickness becomes

$$A_{tot}^t = \frac{A_{tot}}{t}\left(cm\right) = \frac{10^4\, A_E}{\left(\dfrac{\rho_{xrd}}{\rho_{ap}}\dfrac{L_c}{2}\right) + 2_D}. \qquad (5)$$

In the present paper, the values of $A_{tot}$ were determined using this equation and the values of $L_c$, and $\rho_{xrd}$ were obtained from the X-ray diffraction data of the carbon electrode prepared from the mixture of pre-carbonized oil palm empty fruit bunches and green petroleum coke.

## MATERIALS AND METHODS

Carbon pellets (CPs) were prepared by carbonization of the green pellets (GPs) containing a mixture of pre-carbonized oil palm empty fruit bunches (SACG) and green petroleum cokes (GPC). Pre-carbonization of the EFB was carried out by low temperature carbonization process based on the method developed by our group (Deraman et al. 2002). Before mixing, the pre-carbonized EFB was ball milled for 36 hours and sieved in order to obtain self-adhesive carbon grain (SACG) powder with sizes less than 53 µm. The GPC was also ball milled for 36 hours and sieved through 53 µm mesh.

The weight percentages (x) of SACG in the GPs of the samples were 10%, 30%, 50%, 70% and 90%. The mixture was ball milled for 1 hour. The GP of the samples were prepared by applying 12 metric tones of compression force in a mould with a diameter of 20 mm. The GP were carbonized up to 900°C using a multi steps heating profile programmed with a heating rate of 1°C per min from room temperature to 340°C, remaining at this temperature for 1 hour, heating rates of 3°C per min from 340°C to 800°C, 5°C per min from 800°C to 900°C (Deraman et al. 2000). The heating environment in the furnace was continuously filled with a flow of nitrogen gas at 1.5 l/min.

X-ray diffraction (XRD) measurement over an angular range from 10° to 60° with a step size of 0.025° were conducted on the CPs using a diffractometer (Bruker AXS: model D8 Advance) which employed Cu anode with the $K_{\alpha 1}$ wave length of 1.5406 Å.

## RESULTS AND DISCUSSION

X-ray diffraction patterns for the all carbon pellets are shown in Figure 1. The positions of the peaks due to (002) and (100) reflections are shown in Table 1 for the 10%, 30%, 50%, 70%, 90% of weight percentage of SACG, respectively. The increament of the SACG weight percentage in the carbon pellets resulted in the 002 and 100 peaks to shifted to lower angular positions, respectively.
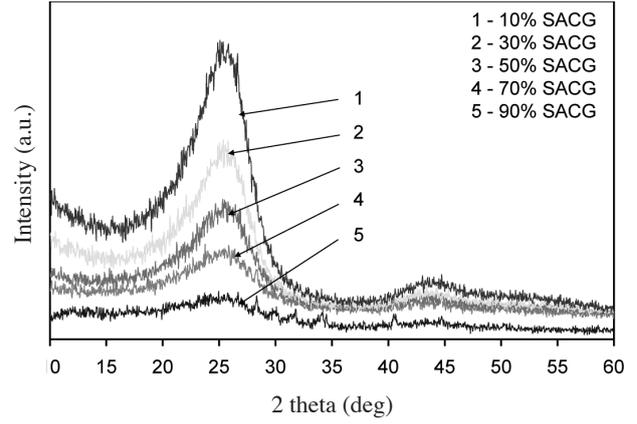


FIGURE 1. X-ray diffraction pattern of the carbon pellets

The feature of the diffraction peaks (002) and (100) in Figure 1 is an evidence that the samples have a turbostratic structure. This turbostratic model assumes that the samples is made of graphite-like microcrystallites, bounded by cross linking network, consisting of several graphite-like layers, stacked nearly parallel and equidistant, with each layer having a random orientation (Coutinho et al. 2000). The stack height ($L_c$) and width ($L_a$) of the microcrystallites determined from the intensity of the peaks (002) and (100), respectively, using expressions (1) are shown in table 1. Using the Bragg law $n\lambda = 2d \sin \theta$, the interlayer spacing ($d_{002}$ and $d_{100}$) calculated from the Bragg peaks are also shown in the Table 1. The values of $d_{002}$ and $L_c$ in this table are comparable with those reported by Kumar et al. (1997) on activated carbon cloth, i.e., $d_{002}$ is between 3.5 to 3.65 Å and $L_c$ is from 9.8 to 11.6 Å.

The variation of $d_{002}$, $d_{100}$, $L_a$, and $L_c$ with the weight percentage of SACG are graphically shown in Figures 2 and 3, respectively. These changes indicate that the number of graphitic layers in the microsrystallite of the CP are smaller for the sample with higher weight percentage of SACG. A similar behaviour has been observed in the carbon samples prepared from a Eucalyptus wood (Coutinho et al. 2000) and bituminous coal (Yang et al. 2002). The values in Table 2 also indicate that our estimated $S_{BET}$ from the XRD data are close to the range of the reported values (680 to 1256 m²/g) for the activated carbon samples (Emmenegger et al. 2003).

TABLE 1. Interlayer spacing and microcrystallite parameters of carbon pellets.

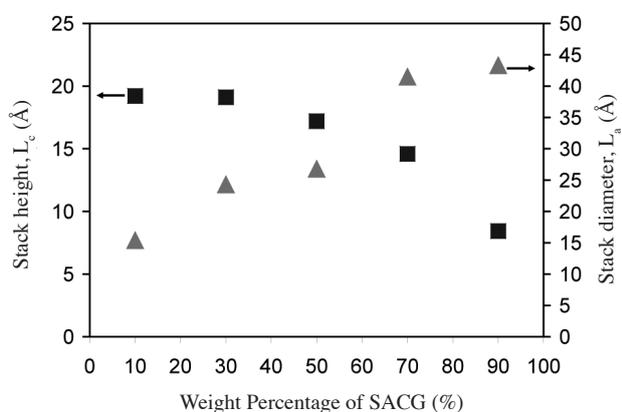| Weight percentage of SACG (%) | X-ray data | | | | Microcrystallite parameter | | Effective dimension (Å) |
|---|---|---|---|---|---|---|---|
| | $2\theta_{002}$ (deg.) | $2\theta_{100}$ (deg.) | $d_{002}$ (Å) | $d_{100}$ (Å) | $L_c$ | $L_a$ | $L$ |
| 10 | 25.12 | 45.41 | 3.5408 | 1.9945 | 19.2165 | 15.3839 | 15.2836 |
| 30 | 25.13 | 45.06 | 3.5397 | 2.0095 | 19.1225 | 24.3151 | 20.7040 |
| 50 | 25.18 | 44.56 | 3.5320 | 2.0307 | 17.2013 | 26.7933 | 21.3220 |
| 70 | 25 | 44.42 | 3.5584 | 2.0366 | 14.6025 | 41.4956 | 27.0251 |
| 90 | 24.64 | 44.30 | 3.6081 | 2.0423 | 8.4329 | 43.3212 | 23.1606 |



FIGURE 2. Microcrystallite parameters of the carbon pellets as a function of weight percentage of SACG
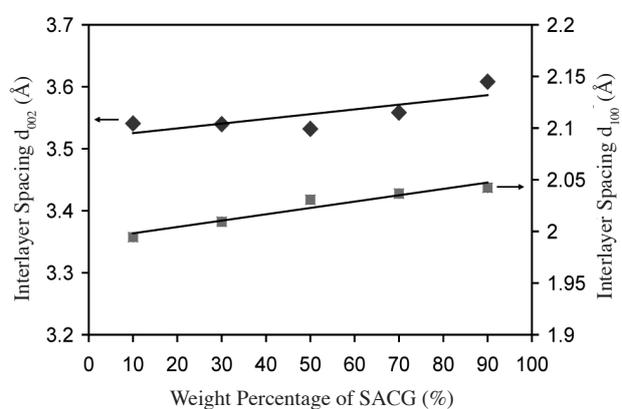


FIGURE 3. Interlayer spacing of the carbon pellets as a function of weight percentage of SACG

TABLE 2. Total active surface area of the carbon pellets as a function of thickness of electrode

| Weight percentage of SACG (%) | XRD density (g/cm$^3$) | Surface area (m$^2$/g) | Apparent density (g/cm$^3$) | $A^t_{tot} \times 10^{10}$ (cm$^2$) (function of t) |
|---|---|---|---|---|
| 10 | 2.1482 | 484.49 | 1.0549 | 4.1640 |
| 30 | 2.1489 | 486.71 | 1.0269 | 4.0025 |
| 50 | 2.1536 | 539.89 | 1.0471 | 3.9011 |
| 70 | 2.1376 | 640.73 | 0.9757 | 3.6784 |
| 90 | 2.1082 | 1125.0 | 1.0891 | 3.4856 |

The values of total active surface area estimated using equation (5) are shown in Table 2. As can be seen in Figure 4, these data show that increasing the weight percentage of SACG causes total active surface area of CP to decrease linearly according to the equation $t$ cm$^2$ with the coefficient of determination $R^2 = 0.9872$. It has been reported that the $A^t_{tot}$ for electrode from carbon nanotube is approximately $4 \times 10^5$ cm$^2$ (Emmenegger et al. 2003). Huge different between this value and our values in Table 2 could be attributed to the fact that their electrode is in the form of thin film, whereas our electrode is in the bulk form.
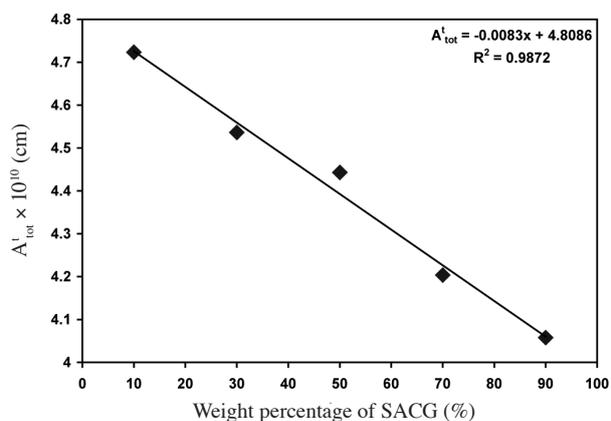


FIGURE 4. Total active surface area per electrode thickness

## Conclusion

The values of interlayer spacing $d$, stack height ($L_c$), width ($L_a$) and effective dimension ($L$) of crystallites in the CPs as a function of weight percentage of SACG in the green bodies have been estimated from the X-ray diffraction data. It was found that for higher content of SACG, the CP had higher values $d_{002}$, $d_{100}$, $L_a$ and lower values of $L_c$. Such a contrary trend of the $d_{002}$ and $L_c$ values implies the reduction of the number of graphitic layers in the microcrystallite have occurred. The total active surface area estimated using these structural parameter values was found to decrease linearly with the increasing SACG content, which is consistent with the fact that stronger adhesion property due to higher SACG content can contribute to the formation of less pore during carbonization of the samples.

## References

Coutinho, A.R., Rocha, J.D. & Luengo, C.A. 2000. Preparing and characterizing biocarbon electrodes. *Fuel Processing Technology* 67: 93-102.

Deraman, M., Zakaria, S., Omar, R. & Aziz, A.A. 2000. Electrical conductivity of carbon pellet from mixtures of pyropolymer from oil palm bunch and cotton cellulose. *Jpn. J. Appl. Phys.* 39(12A): L1236-L1238.

Deraman, M., Omar, R., Zakaria, S., Mustapa, I.R., Talib, M., Alias, N. & Jaafar, R. 2002. Electrical and mechanical properties of carbon pellets from acid ($HNO_3$) treated self-adhesive carbon grain from oil palm empty fruit bunch. *Journal of Materials Science* 37: 3329-3335.

Dresselhaus, M.S., Fung, A.W.P., Rao, A.M., diVittorio, S.L., Kuriyama, K., Dresselhaus, G. & Endo, M. 1992. New characterization techniques for activated carbon fibers. *Carbon* 30: 1065.

Emmenegger, Ch., Mauron, Ph., Sudan, P., Wenger, P., Herman ,V., Gallay, R. & Zuttel, A. 2003. Investigation of electrochemical double layer capacitors (EDLC) electrodes based on carbon nanotubes and activated carbon. *Journal of Power Sources* 124: 321-329.

Emmerich, F.G. & Luengo, C.A. 1993. Young modulus of heat treated carbon: A theory for nongraphitizing carbons. *Carbon* 31(2): 333-339.

Kaneko, K., Ishii C., Ruike M. & Kuwabara, H. 1992. Origin of superhigh surface area and microcrystalline graphitic structures of activated carbon. *Carbon* 30(7): 1075-1088.

Klug, H.P. & Elexander, L.E. 1970. *X-Ray Diffraction Procedures: For Polycrystalline and Amorphous*. New York: John Wiley and Sons.

Kumar, K., Saxena, R.K., Kothari, R.D., Suri, K., Kaushik, N.K. & Bohra, J.N. 1997. Correlation between adsorption and x-ray diffraction studies on viscose rayon based activated carbon cloth. *Carbon* 35(12): 1842-1844.

Marsh, H. & Rodrigues-Reinoso, F. 2006. *Activated Carbon*. Amsterdam: Elsevier Ltd.

Yang, S., Hu, H. & Che, G. 2002. Preparation of carbon adsorbents with high surface area and a model for calculating surface area. *Carbon* 40(3): 277-284.

Awitdrus & Erman Taer
Department of Physics
Faculty of Mathematics and Natural Sciences
University of Riau
Pekanbaru, Riau
Indonesia

Mohamad Deraman*, Ibrahim Abu Talib, Ramli Omar, Mohd. Hafizuddin Hj. Jumali & Mansor Mohd. Saman
School of Applied Physics
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor D.E.
Malaysia

*Corresponding author; email: madra@ukm.my