

POROUS CARBON PELLETS FROM KOH TREATED SELF-ADHESIVE CARBON GRAINS FROM OIL PALM EMPTY FRUIT BUNCH: EFFECT OF KOH WEIGHT PERCENTAGES AND PELLETIZING COMPRESSION FORCE

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ABSTRACT

The pre-carbonized fibers of oil palm empty fruit bunch were ball milled to produce self-adhesive carbon grains (SACG). The SACG and SACG treated with KOH (1, 3 and 5% by weight) were compressed with various compression forces in order to produce green pellets with a dimension of 27 mm in diameter and 3 mm in thickness. Carbon pellets were produced from carbonization of green pellets (GP) up to 700°C in a nitrogen atmosphere using a multi-steps heating profile. The carbon pellets were immersed in HCl (0.5 M) for 48 h and then neutralized with distilled water. It was found that the BET surface area of carbon pellets of 0% KOH unchanged with compression force whereas carbon pellets from the GP of 5% KOH compressed with 6, 8 and 10 x 10³ kg forces have the BET surface area of 733, 399 and 361 m²/g respectively. The BET surface area of the unwashed carbon pellet of 0% KOH (2.3904 m²/g) was found to be 134 times smaller than that of the washed sample (321 m²/g). It was observed that as the percentage of KOH increased from 0 to 5% the BET surface area of the carbon pellets increased remarkably from 321 to 399 m²/g. Pore size analysis showed that the KOH treated carbons are mainly microporous. A SEM study of the KOH treated carbons showed increasing porous structures as the percentages of KOH increased and the compression forces decreased.

INTRODUCTION

Porous carbons have been extensively used as adsorbents, catalysts, catalysts support, carbon molecular sieves and electrodes [1-3]. Although a wide range of carbonaceous materials can be converted into porous carbons, coal and lignocellulosic materials are the most commonly used starting materials for the production of commercial porous carbons. In addition, there are quite a large number of studies reporting the preparation of porous carbons from various agricultural by-product and polymeric materials due to the low cost and high carbon yield [4, 5, 6].

Basically, the type of porosity is mainly determined by the type of precursor employed; however, the method of preparation is another parameter which may influence the final pore size distribution [7]. In general, a particle of porous carbon is made up of a complex network of pores, which have been classified into micropores (diameter < 20 Å^o), mesopores (diameter between 20 and 500 Å^o) and macropores (diameter > 500 Å^o)[8].

One of the main solid wastes (8.5 millions tones annually) from palm-oil processing mills in Malaysia is empty fruit bunch (EFB) [9]. Numerous efforts have been made to utilise self-adhesive carbon grain (SACG) from the EFB [10, 11] and modified SACG from EFB [12, 13] as a precursor for solid carbon. This work was devoted to prepare porous carbon pellets from the powder of pre-carbonized EFB (SACG) by treatment with potassium hydroxide and to study the effects of KOH treatment, pelletising compression force on the moulded SACG and washing step after carbonization on the microstructural properties of the porous carbons.

MATERIAL AND METHOD

EFB fibers were pre-carbonized at low temperature based on the method previously reported [14]. The pre-carbonized EFB was ball-milled for 36 h and sieved in order to obtain self-adhesive carbon grain (SACG) with particles sizes less than 53 μm . SACG was mixed with KOH solution so that the mixtures have 0, 1, 3 and 5 % by weight respectively. The sample was left for 48 h before it was dried in an oven at 110°C. The mixture was ball milled again for 10 h to form a fine powder and sieved in 53 microns sieve. The green pellets (GP) with a dimension of 27 mm in diameter and 3 mm in thickness were prepared by applying 8×10^3 kg of compression force onto 2 g of SACG and KOH treated SACG. The SACG and SACG treated with KOH (5% by weight) were compressed with 6, 8 and 10×10^3 kg forces. Carbonization of the green pellets was carried out in a furnace (Vulcan Box Furnace 3-1750) using a multi step heating profile. The samples were heated in a nitrogen stream of 1.0 - 1.5 $\times 10^{-3}$ m^3/min at the rate of 1°C/min from room temperature to 375°C at which they were kept for 1 h, followed by 3°C/min from 375°C to 700°C [13, 15, 16]. Subsequently, the samples were cooled down under nitrogen flow. All the carbonized samples, except for a sample (S008 (u)) were soaked for 48 h in a 0.1 N solution of HCl and washed repeatedly with distilled water to remove residual chemical. The washed samples were dried in an oven at 70°C to obtain the final carbon products. The dimension of the pellets before and after carbonization was measured using a micrometer and the density was determined by dividing the weight of the sample with its volume. The identification of the washed samples appears in Table 1 and 2. The nomenclature of the samples includes the SACG (S), the weight percentage of KOH (i.e. 5 would be 5%), the pelletising compression force (for example 08 would correspond to 8×10^3 kg) and (u) refer to the unwashed pellet.

The adsorption isotherms of N_2 were measured on the carbon samples by using a volumetric adsorption apparatus (Micromeritics ASAP 2000) at 77 K. Prior to each analysis, the samples were outgassed at 150°C overnight to obtain a residual pressure of less than 500 $\mu\text{m Hg}$. The specific surface area of the samples was determined from nitrogen adsorption isotherms by the standard BET method [17]. The cross section-sectional area for nitrogen molecule was assumed to be 0.162 m^2 . The micropore volume was calculated using a micropore analysis (*t*-plot). The total pore volume was found from the amount of nitrogen adsorbed at a relative pressure of about 0.99. The mesopore volume was obtained by subtracting the micropore volume from the total pore volume. The BJH model was used to investigate the pore size distribution [17, 18]. A scanning electron microscope (SEM: Philips PV 99) was used to study the microstructure of the produced carbons.

RESULTS AND DISCUSSION

Table 1 summarizes the physical properties of the carbon pellets at different percentages of KOH. It is seen that by adding KOH to the SACG, weight loss is decreased as a result of the inhibition of tar production by this chemical, hence enhancing carbon yield [19]. This lower weight loss is also observed in Table 2 of the 5% KOH treated carbons. Table 1 shows that both BET surface area and total pore volume increased with increasing weight of KOH. However, it is observed that micropore and mesopore volumes doubled as the amount of KOH added to the SACG reached 3 and 5%, suggesting the formation of additional pores and widening of the existing micropores is the favored mechanism during KOH activation [4, 6, 20, 21].

Table 1: Effects of KOH amount on the surface characteristics of the carbons from SACG

Sample	Weight loss (%)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume	Mesopore (cm ³ /g)
S008	58.35	321	0.1411	0.1234	0.0176
S108	57.83	350	0.1520	0.1352	0.0168
S308	57.75	390	0.1834	0.1483	0.0351
S508	57.19	399	0.1877	0.1526	0.0351

Table 2: Effects of compression force on the surface characteristics of the carbons from SACG

Sample	Weight loss (%)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume	Mesopore (cm ³ /g)
S006	58.39	336	0.1475	0.1304	0.0171
S008	58.35	321	0.1411	0.1234	0.0176
S010	57.97	337	0.1455	0.1297	0.0158
S506	57.52	733	0.3524	0.2769	0.0756
S508	57.19	399	0.1877	0.1526	0.0351
S510	57.43	361	0.1780	0.1360	0.0420

Table 3 shows that the BET surface area, pore volume, micropore volume and mesopore volume of KOH treated carbon pellets from the GP compressed with 6x10³ kg force is approximately double than those of the carbon pellets from the GP compressed with 8 and 10x10³ kg forces. Meanwhile, the porosity of the untreated carbons seems not to be much influenced by the pelletising compression forces.

Table 3: Effects of washing step on the surface characteristics of the carbons from SACG

Sample (cm ³ /g)	BET surface area (m ² /g)	Total Pore Volume
S008 (u)	2	0.0048
S008	321	0.1411

Data in Table 3 compares the porous structure of the washed and unwashed untreated carbon pellets. The BET surface area of the unwashed carbon pellet was found to be 134 smaller

than that of the washed sample. The washing process most probably removed the tarry products that remain in the pores between the crystallites and on the carbon surface causing the carbonized material to be at least partially activated [7].

Fig.1 presents the N₂ adsorption isotherms of the carbons series obtained. All the isotherms approach the Type I isotherms according to the IUPAC classification [17], with small upward bending at higher pressure, indicating an essentially microporous solids with increasing amount of N₂ adsorbed and increasing contribution of wider pores (meso- and macropores) as the amount of KOH increased and the pelletising compression force decreased, suggesting that the pore volume increases due to KOH treatment.

Fig. 2 shows the pore size distributions (PSD) of the resulting carbons. The PSD of the porous carbons show a sharp increase in the pore size distribution curves for pore diameters less than 20 Å indicated the formation of micropores. For the mesopore size distribution, higher peaks appear in the region less than 50 Å. From here a broad and minor PSD is observed for all carbon series. As mentioned above, it is found that the

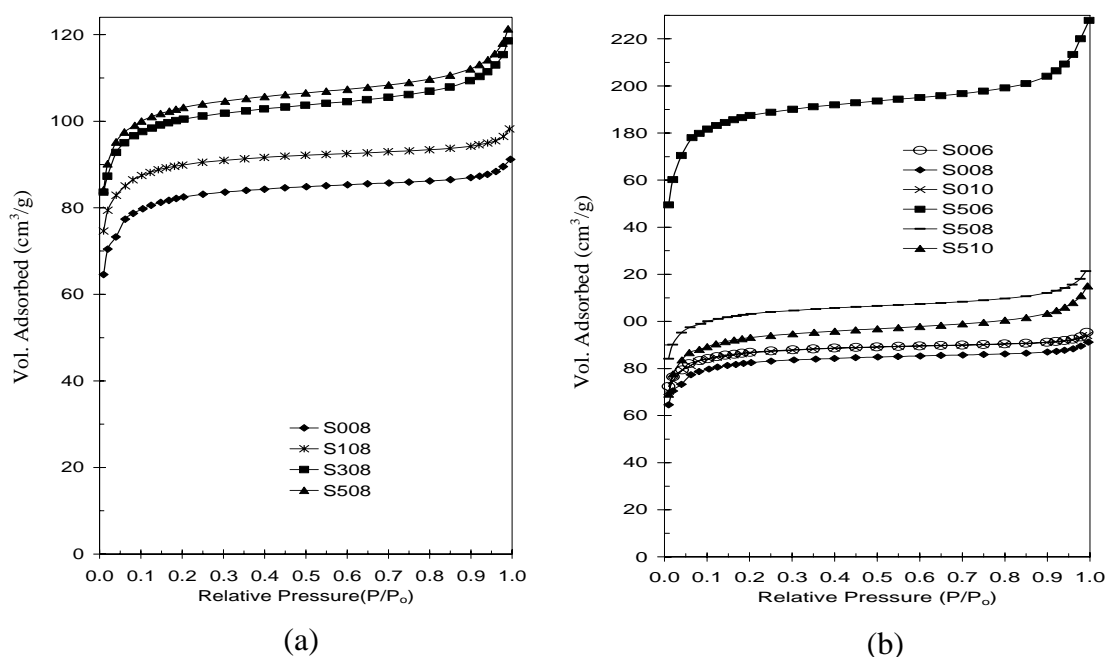
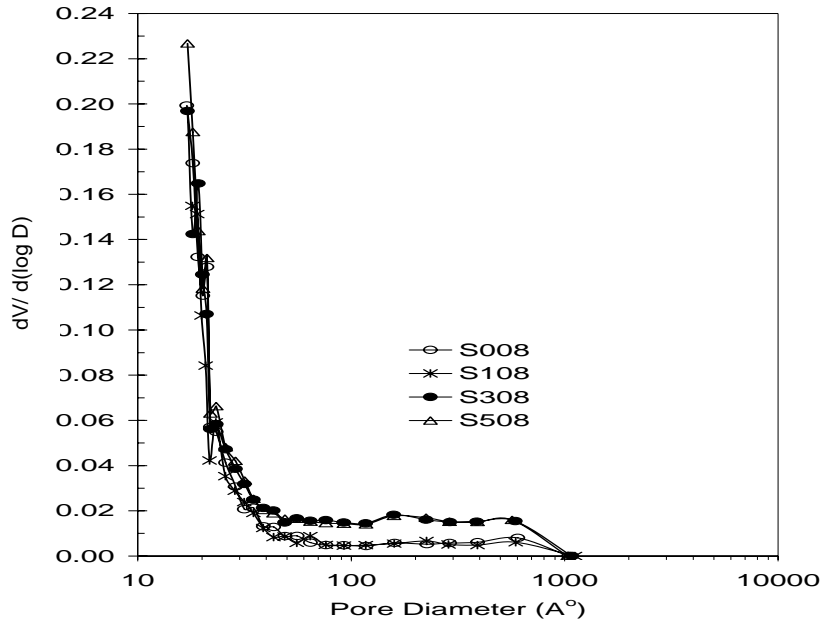
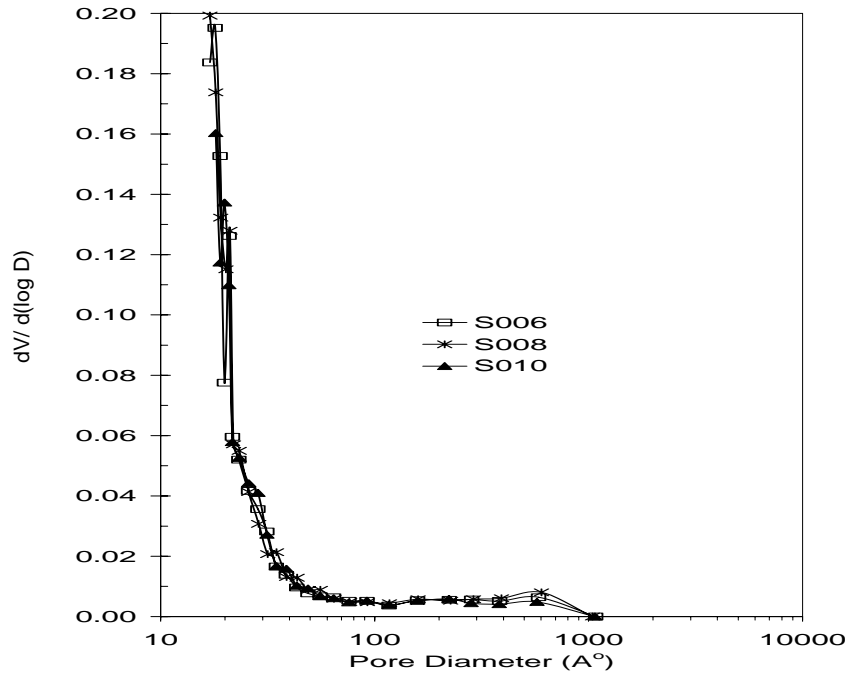


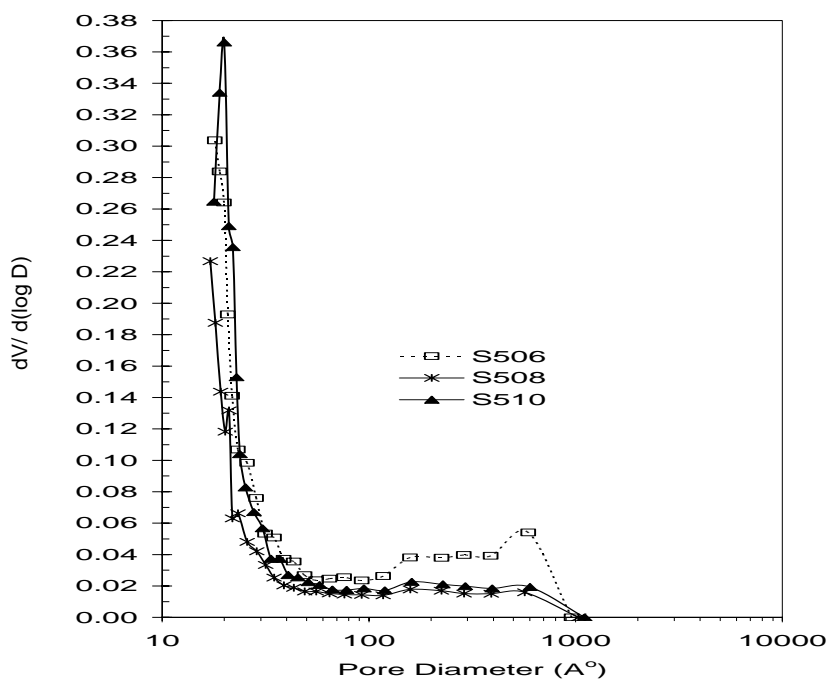
Figure 1: Nitrogen adsorption isotherms (77 K) of the porous carbons: (a) prepared using different KOH weight percentages and compressed with 8×10^3 kg force (b) prepared using 0 and 5% KOH and compressed with 6, 8 and 10×10^3 kg forces.



(a)



(b)



(c)

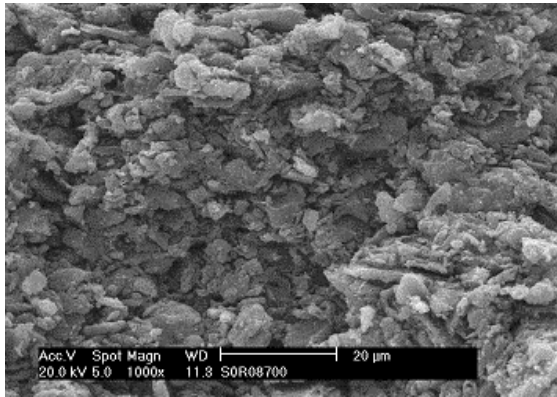
Figure 2: Pore size distributions of the porous carbons determined from the BJH model.: (a) prepared using different KOH weight percentages; (b) prepared using 0% KOH GP compressed with 6, 8 and 10×10^3 kg forces; (c) prepared using 5% KOH GP compressed with 6, 8 and 10×10^3 kg forces.

addition of KOH results in the enhancement of micropores and mesopores volumes which is shown in Figure 2a. Figure 2b shows that there is no obvious shift in the region with increasing pelletising compression force of the untreated carbons. Meanwhile, the PSD of S506 shown in Figure 2c exhibits significant increase in all its pore sizes, indicating that the pore structure developed more freely. S510 possesses a considerable amount of mesopores below 50 \AA and remarkable amounts of micropores below 20 \AA , indicating that the pore sizes were restricted by an excessive pelletising compression force.

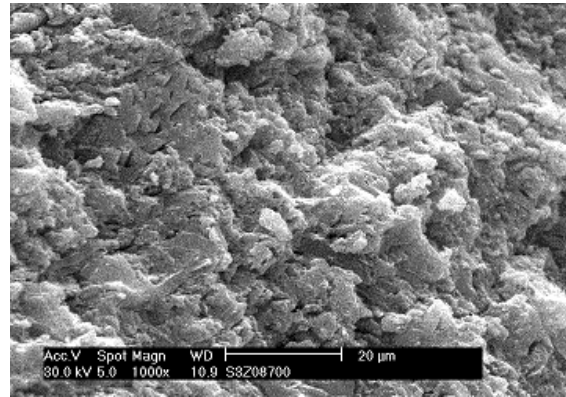
Figure 3 and 4 show the SEM photographs of the porous carbons studied. As shown in Figure 3, the porous structure of the resulting carbons increases as the amount of KOH increased. Figure 4 shows the resulting carbons of the KOH treated carbons: S506, S508 and S510 are more porous compared to the untreated S006, S008 and S010. S506 exhibits the largest pores and the least compact structure compared to S508 and S510, indicating that the most pore development occurs inside the particle of the carbon prepared using the least pelletising compression force.

CONCLUSIONS

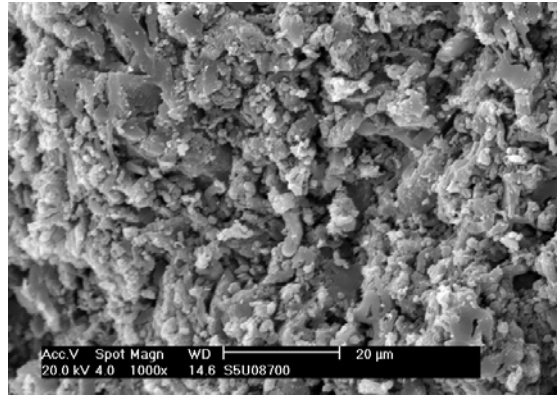
In this work, the influence of the washing process, KOH added to the SACG and the applied compression forces during pelletization on the resulting carbons has been confirmed. The washing process is a very important step in preparing porous carbons as the carbonized material is at least partially activated. The surface area and pore volume of the resulting porous carbons increased with an increase in the amount of KOH added to the SACG. The adsorption capacity of the 5% KOH treated carbons is highly depended on the compression force applied during pelletization, with higher the compression force resulted in low meso- and macropore volume and adsorption capacity.



(a)

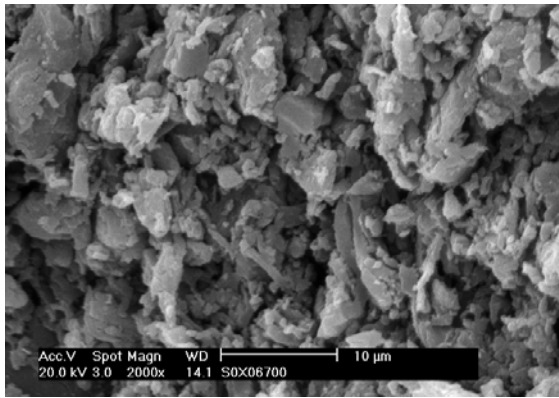


(b)

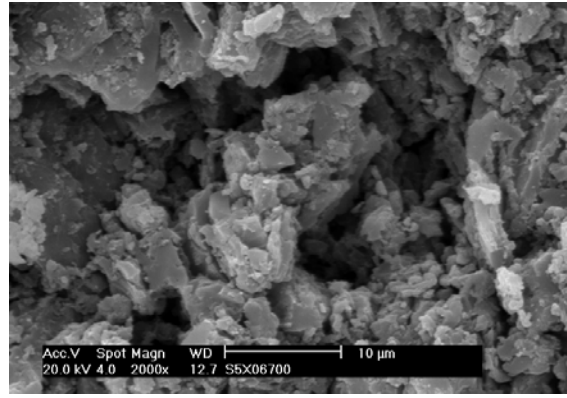


(c)

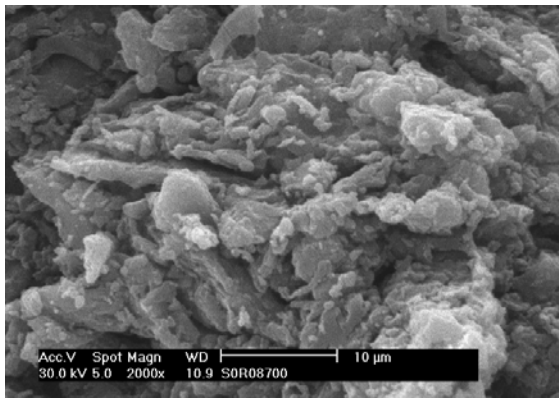
Figure 3: SEM photograph of the carbons studied prepared using different amount of KOH: (a) S008; (b) S308; (c) S508



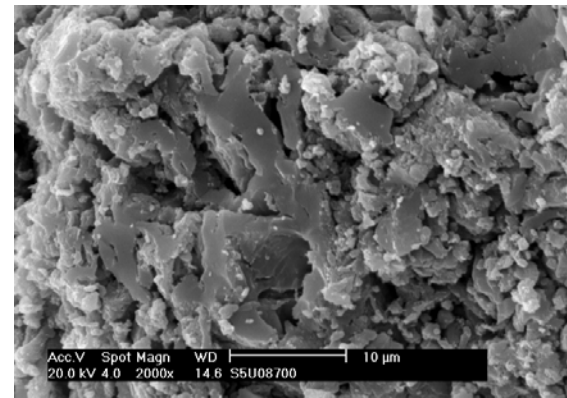
(a)



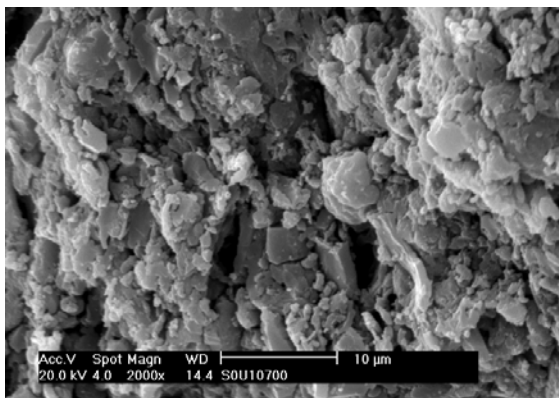
(d)



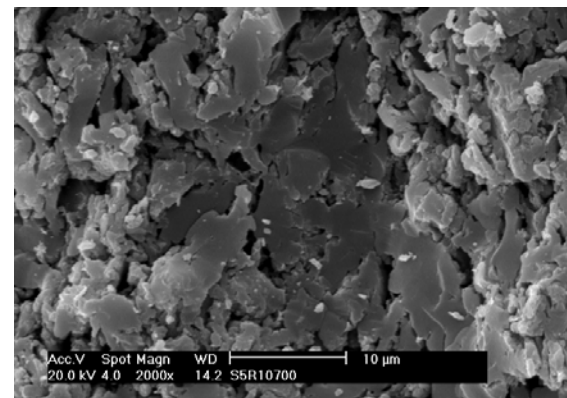
(b)



(e)



(c)



(f)

Figure 4: SEM photographs of the carbons pelletised using different compression forces: (a) S006; (b) S008; (c) S010; (d) S506; (e) S508; (f) S510.

ACKNOWLEDGEMENT

We thank the government of Malaysia for the IRPA grant (Code 09-02-02-022-EA077) for this project. We would like to acknowledge Mr. Saini Sain for his contribution to this work.

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