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PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBONS FROM OIL PALM SHELLS (*ELAEIS GUINEENSIS*) USING CO_2, H_3PO_4, K_3PO_4 AND KOH

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ABSTRACT. *Preparation, and characterization of activated carbons prepared from palm shells, a carbonaceous agricultural solid waste, treated with CO_2, H_3PO_4, K_3PO_4, and KOH were studied in this paper. The precursor was cut into 0.5-1.0cm sizes prior to activation. The palm shells were carbonized in a horizontal combustion chamber at a constant temperature of 500°C. The samples prepared from oil palm shells, pre-impregnated with phosphoric acid, AC H_3PO_4 had the highest BET and micropore surface areas. The BET surface area was 760m^2/g and the micropore surface area was 480m^2/g.*

KEYWORDS. Oil palm shells, carbonization, activation, physical and chemical properties.

INTRODUCTION

Activated carbons are carbons of highly microporous form with both high internal surface area and porosity, and commercially the most common adsorbents used for the removal of organic compounds from air and water streams. Any cheap material with a high carbon content, low inorganics can be used as a raw material for the production of activated carbon (Bansal *et al.*, 1988). Researchers have made many attempts to obtain low-cost activated carbons or adsorbents from agricultural wastes such as *coconut shells* (Laine *et. al.*, 1989), *almond shells* (Rodriguez and Molini, 1992, Gergova *et al.*, 1994), *peach stones* (Rodriguez and Molini, 1992), *grape seeds* (Gergova *et al.*, 1994), *apricot stones* (Gergova *et al.*, 1994, Philip and Girgis, 1996), *cherry stones* (Gergova *et al.*, 1994, Lussier *et al.*, 1994), *olive stones* (Rodriguez and Molini, 1992, Gonzalez *et al.*, 1994), *peanut hull, nut shells, rice husks, resak wood* (Anuar *et al.*, 2001, Anuar *et al.*, 2002), *sugarcane bagasse, Uruguayan eucalyptus* wood (Tancredi *et al.*, 1996), Melaleuca *cajuputi* (Anuar *et al.*, 2000) and oil palm shells (Anuar *et al.*, 2002, Anuar *et al.*, 2003). Agricultural by-products are renewable source of raw materials for activated carbon production. In some countries these by-products are considered as wastes and have caused significant disposal problems. Their utilization in the production of activated carbon is a viable solution to this environmental issue (Rodriguez and Molini, 1992).

In Malaysia, oil palm shell is one of the main agricultural wastes from palm oil industries. Several studies were initiated to utilize palm shells including the possibility of using it as fuel to boilers (Wigmans, 1989, Lamond and Marsh, 1963). Its use as a raw material for activated carbon production was highlighted before (Chan *et al.*, 1976) and concluded that a good quality product can be obtained. There are two principal processes for its preparation: physical and chemical activation. For physical activation, the method used in this study, involves carbonization of the carbonaceous material, followed by activation of the resulting char at 500°C in the presence of suitable oxidizing gases such as carbon dioxide. For chemical activation, the same method used in this study except that Phosphoric acid (H_3P0_4), Potassium Phosphate (K_3PO_4) and Potassium hydroxide (KOH) was used individually to impregnate the precursor, prior to the carbonisation process. However, physical and chemical properties for the activated carbon differ from one to the other due to the way they have been prepared (Laine and Calafat, 1991). This is to say that activated carbon prepared from a particular source may only be useful for a particular application.

EXPERIMENTAL

In order to prepare activated carbons treated by Phosphoric acid, AC H_3PO_4, thirty grams of the palm shells were mixed with 15ml of H_3PO_4 and 100ml of distil water in a 250ml cone flask. The concentration of the H_3PO_4 solution was 2.2M (Laine *et. al.*, 1989). To prepare activated carbons treated by Potassium Phosphate, AC K_3PO_4, thirty grams of palm shells were mixed with 9g of K_3PO_4 and 100ml of distil water in a 250ml cone flask. The concentration of the K_3PO_4 solution was 9% w/w K_3PO_4 (Laine and Calafat, 1991). To prepare activated carbons treated by Potassium Hydroxide, AC KOH, thirty grams of palm shells were mixed with 9g of KOH and 100ml of distil water in a 250ml cone flask. The concentration of the KOH solution was 9% w/w KOH (Matson and Mark, 1971). The flasks were placed in an oil bath shaker at 70°C, for 24 hours to complete the impregnation process. Then the samples were dried at 120°C overnight in an oven. The physically activated carbon, AC PHY, did not undergo any chemical treatment. Thirty grams of palm shells were placed directly in the furnace for carbonization and activation by carbon dioxide gas. A horizontal Carbolite tubular electric furnace was used for the carbonization process. The impregnated precursors were carbonized in the reaction chamber filled with N_2 gas at 500°C for 3 hours, followed by the activation process using CO_2 gas for an hour at the same temperature. The activated carbons obtained were allowed to cool to room temperature before removal. This was to prevent the activated carbons from turning into ash. After that, the activated carbons were refluxed in an acid solution (1M HNO_3), 1 time for 3 hours to remove metal elements and ash followed by distilled water (10 times, 3 hours each time) to remove the acid. The activated carbons were then dried in an oven at 120°C for a week, after which, analysis of the activated carbons were done.

RESULTS AND DISCUSSIONS

Temperature, heating period, starting materials and the method of preparation are some of the important factors, which contribute to the properties of the resulting activated carbon. Previous work in our laboratories suggested that the temperature played an important role to produce optimum surface area for the activated carbon (Hussein *et al.*, 1995). Heating the material for about 3 hours at a temperature of 500-700°C yielded an activated carbon with approximately 90% of the adsorptive efficiency of that obtained under optimal condition (Badri *et al.*, 1989).

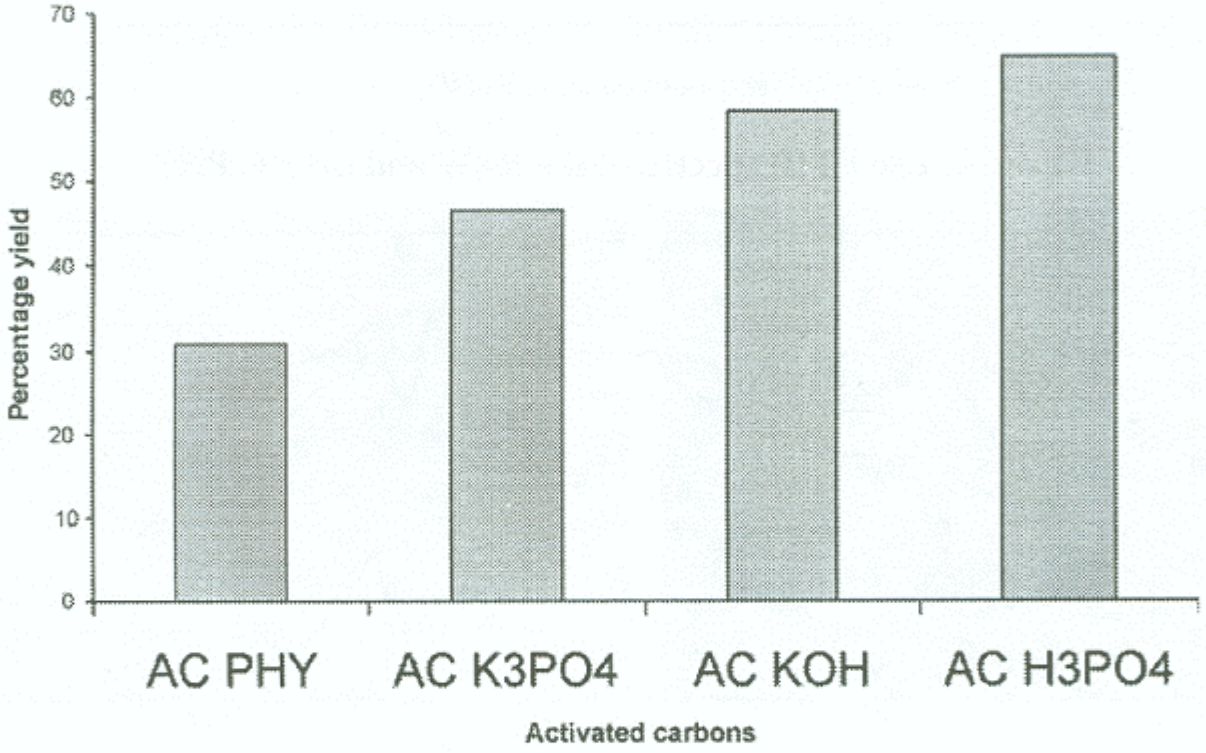


Figure 1. The percentage of yield of the various activated carbons produced.

Percentage of yield, moisture and ash content

The percentage of yield of the activated carbons obtained was between 30-64% (Figure 1). The AC H_3PO_4 had the highest percentage of yield, which was 64.71%, whereas the AC PHY had the lowest percentage of yield, which was 30.7%. The ash content was between 0.8 to 1.7%. This was within acceptable limits as high ash content in the activated carbon is undesirable because the mechanical strength and adsorptive capacity will be reduced. The proximate analysis data of fixed carbon and ash content in palm shell shows that it is a suitable raw material for the production of activated carbon (Bansal *et al.*, 1988). In general, the moisture content of the activated carbon was less than 6%. Our observation recorded that the pH of the oil palm shells was about 5.0

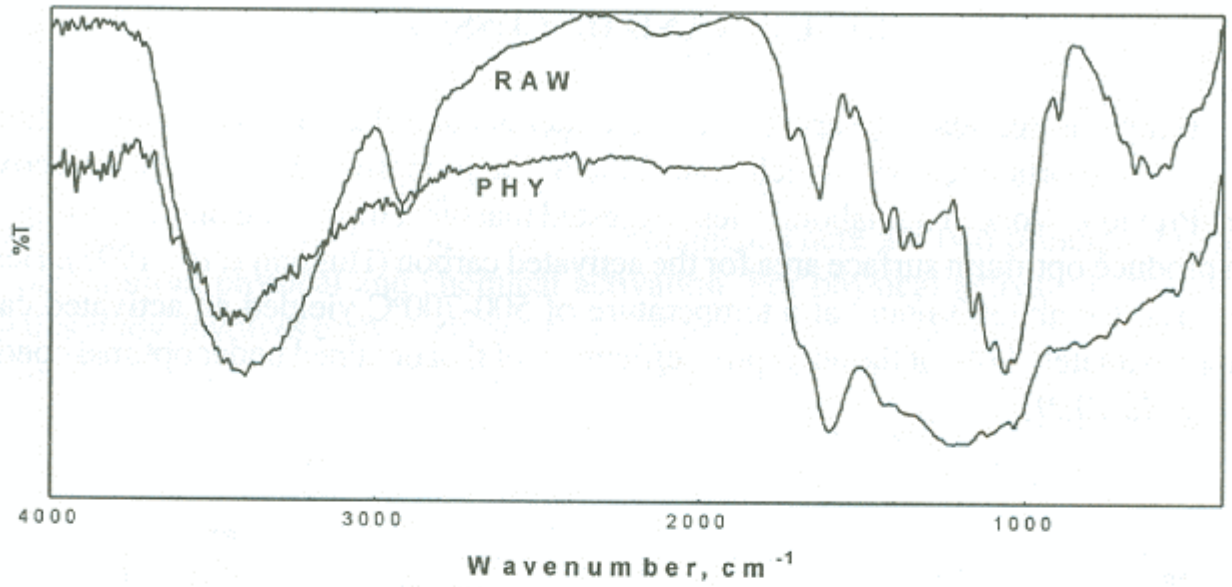


Figure 2. The FTIR spectra of the RAW and the AC PHY.

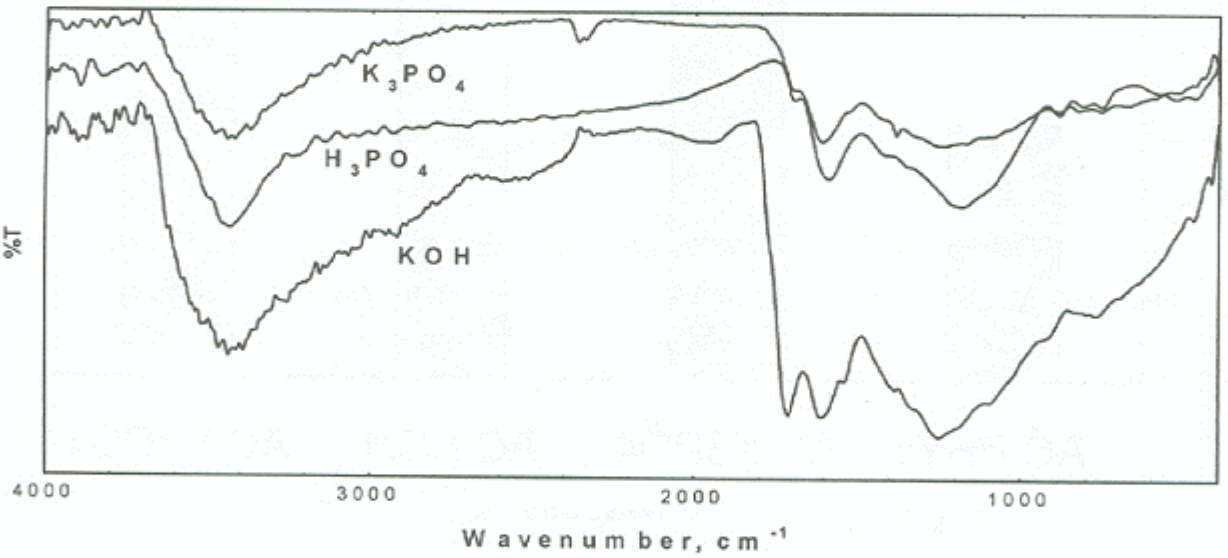


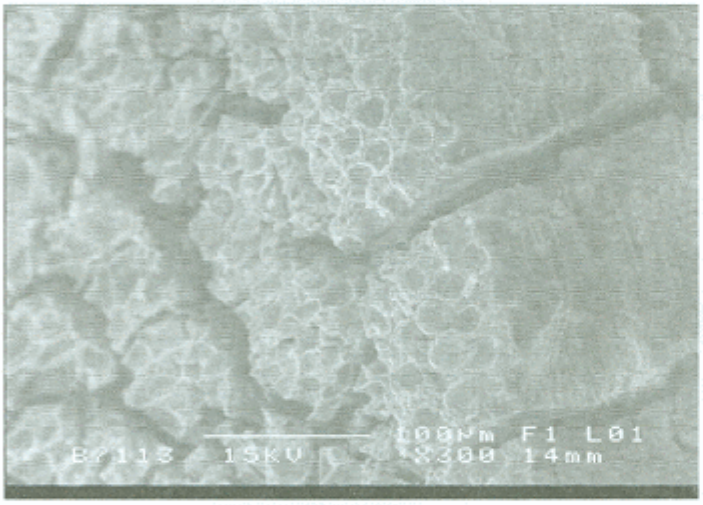
Figure 3. The FTIR spectra of the AC K_3PO_4, AC H_3PO_4 and AC KOH activated carbons.

Fourier Transform Infrared Spectrometer (FTIR)

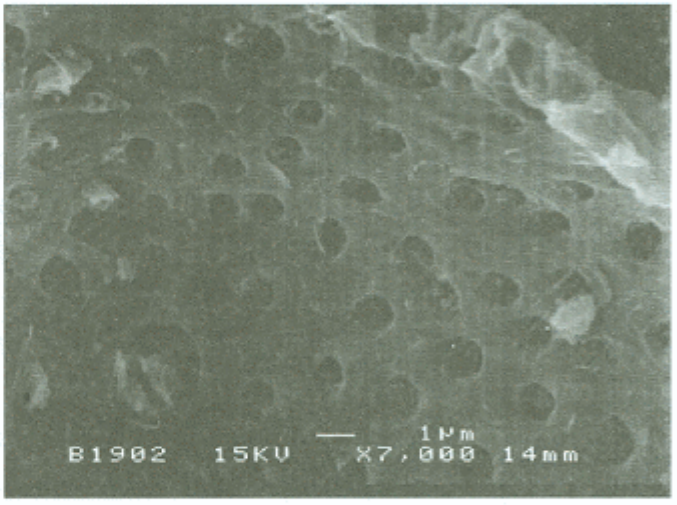
All of the FTIR spectra (Figure 2 and Figure 3) show a similar pattern (based on the spectra produced) except for the raw oil palm shell. Since of the raw oil palm shell (Figure 2) contains various functional groups; among them were O-H, olefinic or aromatic C-H, aliphatic C-H and carbonyl groups (Whiffen, 1971; Ferraro and Bsile, 1985). The AC PHY had a less pronounce C-O stretch, C-C stretch and O-H bend compare to the raw oil palm shell. In the figure 3, the AC KOH had the largest O-H and C=O groups compared to the AC K_3PO_4 and AC H_3PO_4. Carbonization, activation and acid washing did have an effect on the functional groups in the activated carbons.

Scanning Electronic Microscopy (SEM)

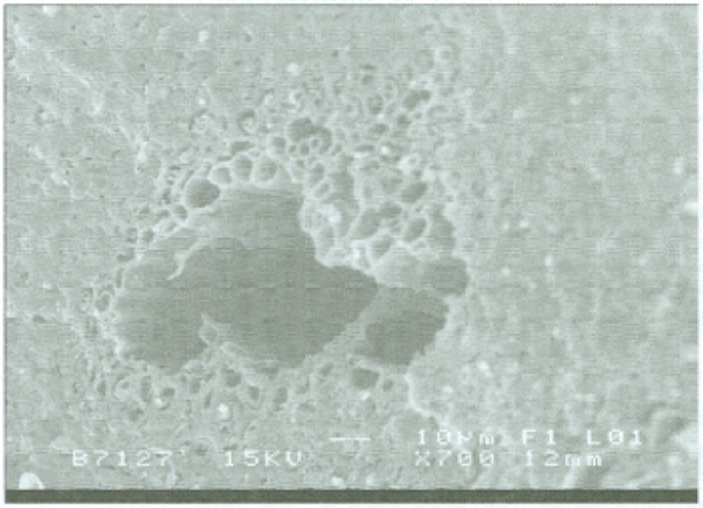
SEM was used to study the morphological structure on the activated carbons (Figure 4). Figure 4(a) shows the surface structure of the oil palm shell. It shows dirt-covered and unclear pores. Figure 4(b) shows the surface structure of the AC PHY. It shows a surface of clean and burnout pores with no tunnel or honeycomb-like structures. The figure 4(d), AC K_3PO_4 shows similar traits but the pores are deeper and clearer. Figure 4(c), AC H_3PO_4 shows tunnel and honeycomb-like structures. It also shows clear, deep and long tunnels. In contras, figure 4(e), AC KOH shows a remarkable morphological change. The pores has a burn-out and altered look with no tunnels. It also had a sponge-like appearance. This was due to extensive gasification (Anuar *et al.*, 2003). Our results suggest that the chemical activators played an important part in clearing and producing better pores. These findings are consistent with the findings of other researchers.



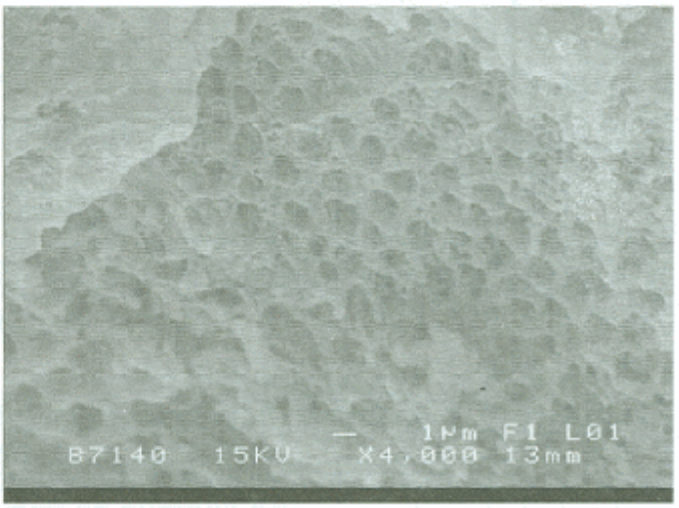
(a)



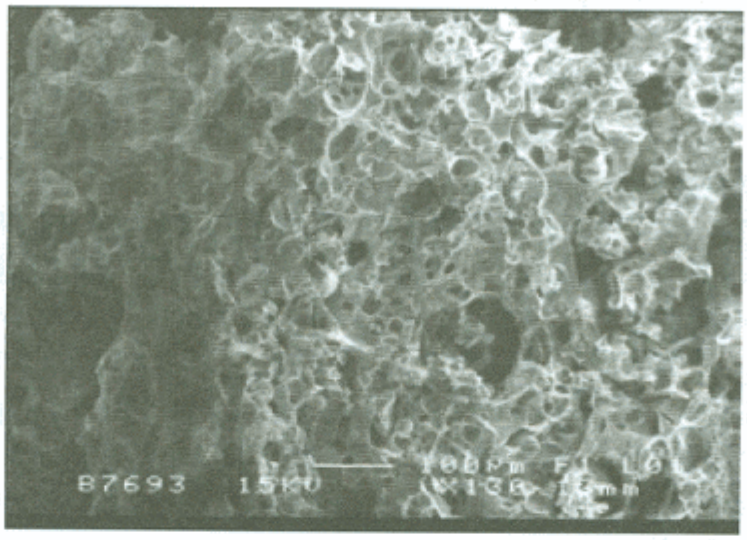
(b)



(c)



(d)



(e)

Figure 4. The electron micrographs of the (a) raw oil palm shell, (b) AC PHY, (c) AC H_3PO_4, (d) AC K_3PO_4 and (e) AC KOH.

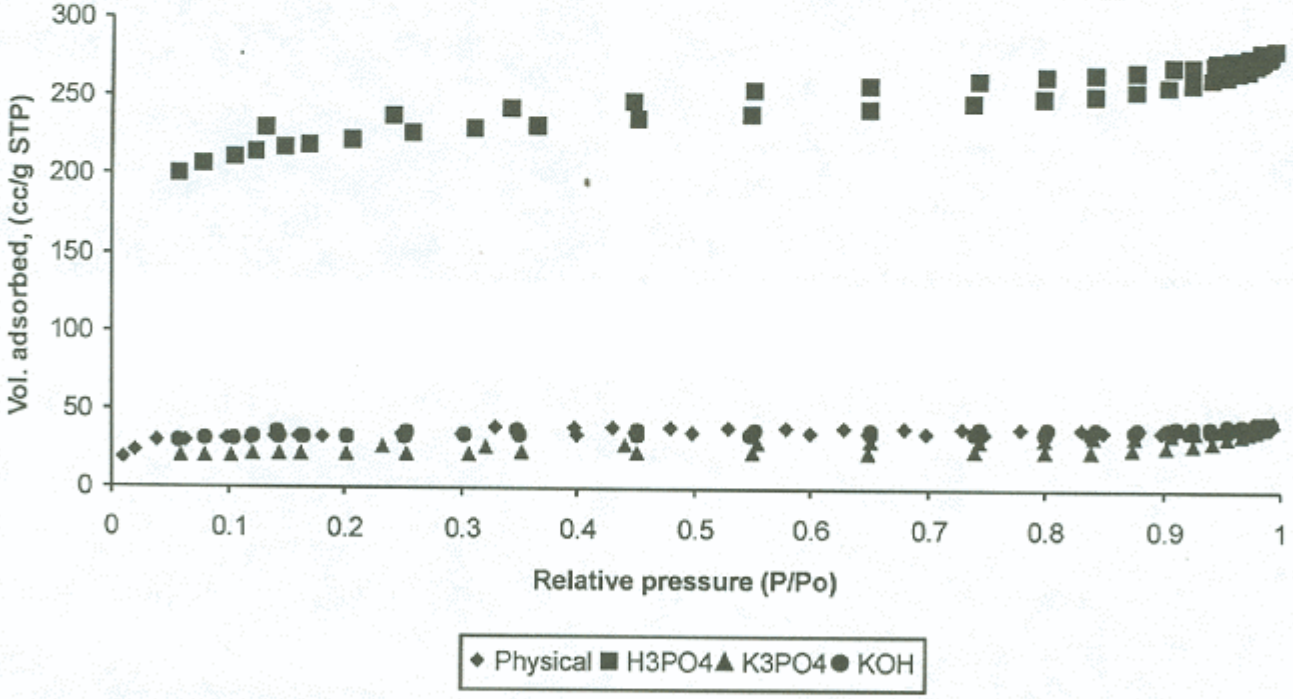


Figure 5. BET isotherms of the physically (AC PHY) and chemically (AC K_3PO_4, AC KOH, AC H_3PO_4) activated carbons.

Table 1. Surface area, volume and diameter data of the physically and chemically activated carbons.

	AC PHY	AC K_3PO_4	AC KOH	AC H_3PO_4
BET surface area (m^2/g)	130	75	112	760
Micropore surface area (m^2/g)	124	48	80	480
Micropore volume (cc/g)	0.05	0.02	0.03	0.02
Average pore diameter (Å)	9	25	17	17
% of micropores	94.76	64.24	71.18	63.22

Surface Area Analysis

Surface area, micropore volume, average pore diameter and BET isotherms were determined according to the Brunauer, Emmett and Teller (BET) method (Jankowska *et al.*, 1991) using a Micromeritic ASAP 2000 instrument. Figure 5 shows the BET isotherms of the activated carbons. All of the isotherms are of Type 1 isotherms with open hysterisis. Type 1 corresponds to the Langmuir isotherm: it tends monotonically to the limiting adsorption associated with a complete monolayer. BET isotherms were determined from the adsorption and desorption capacity of the activated carbons placed in inert atmosphere (N_2 gas). It is assumed that the nitrogen molecules will form a single layer filling the pores on the surface of the activated carbon, which is known as the adsorption process. When the pressure in the chamber is gradually reduce, the single layer of molecules will leave the surface of the activated carbon, which is known as the desorption process. This technique was used to determine BET and micropore surface areas, micropore volume, average pore diameter and percentage of micropore, which are given in Table 1. The BET surface area of the AC H_3PO_4 was $760m^2/g$, which was the highest. The activated carbon with the lowest BET surface area was AC K_3PO_4; at $75m^2/g$. AC H_3PO_4 also had the highest micropore surface area, which was $480m^2/g$ and AC K_3PO_4 had the lowest micropore surface area; at $48m^2/g$. The micropore volume was between 0.02cc/g to 0.05cc/g. The chemically activated carbons had lower micropore volume compared to the physically activated carbon because some of the pores in the chemically activated carbons were still covered with the chemical salts in spite of the washing process. The AC K_3PO_4 had the highest average pore diameter, which was 25Å. AC KOH and AC H_3PO_4 both had an average pore diameter of 17Å while the AC PHY had the lowest, which was 9Å. The percentage of micropore showed that the AC PHY had the highest percentage at 94.76%. This indicates that almost all the pores in it were micropores. The AC KOH, AC K_3PO_4 and AC H_3PO_4 individually had 71.18%, 64.24%

and 63.22% of micropores. This shows that while the majority of the pores were micropores, a large amount of pores have been enlarged to either mesopores or macropores. Therefore it is possible to suggest that the chemical activators had an effect in increasing pore sizes. The chemical activators limit catalytic gasification, protecting the palm shells from excessive burn-off leading to pore enlargement. The proportion of mesopores apparently increases as phosphate salt concentration increases (Laine and Calafat, 1991). This observation correlates to the average pore diameter figures as well.

CONCLUSION

In conclusion, this study shows that the usage of physical and chemical activators such as CO_2, H_3PO_4, K_3PO_4 and KOH, greatly improved the pore structures of the activated carbons. The chemical activators, H_3PO_4 and KOH produced larger pores while K_3PO_4 produced the largest pore diameter. Potassium Phosphate limits the catalytic gasification protecting the product from excessive burn-off that leads to surface area decrease while at the same time promotes mesoporosity (Laine and Calafat, 1991). Surface area studies indicated that the physically activated carbon was microporous with small pores, while the chemically pre-impregnated activated carbons had larger pores. AC H_3PO_4 had the highest BET and micropore surface areas due to the acidity of the phosphoric acid, which reacted with the surface oxide on the activated carbon while simultaneously protecting the palm shells from excessive oxidation, causing the pores to widen and deepen. Morphological structure of the activated carbons also changed due to the activation by the chemical activators especially KOH, which caused excessive gasification, producing activated carbon with sponge-like appearance. Our results suggest that the amount of hydroxyl group (3400cm^{-1}) and carbonyl group (1600 cm^{-1}) on the product were reduced by the impregnations of the chemical activators.

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