

## Effects of $H_3PO_4$ and KOH on Pyrolysis of Bituminous Coal in Preparation of Activated Carbon

<sup>1</sup>Baba Jibril, <sup>1</sup>Rashid S. Al-Maamari, <sup>2</sup>Omar Houache, <sup>1</sup>Mousa Al-Aamri and <sup>1</sup>AlMutasim Al-Qalhati

<sup>1</sup>Petroleum and Chemical Engineering Department, Sultan Qaboos University,  
PO Box 33, Al Khod, PC 123, Muscat, Oman.

<sup>2</sup>Oman Polypropylene LLC, Sohar Industrial Port Complex, P.O. Box 277,  
Postal Code 322, Flag Al-Qabail, Sohar, Sultanate of Oman.

**Abstract:** Effects of  $H_3PO_4$  and KOH on the degree of pyrolysis of bituminous coal to obtain activated carbon were studied. Different chemicals to coal impregnation ratios -  $H_3PO_4$ /coal (0.0 – 4.25) and KOH/coal (0.0 - 3.0) - were carbonized at different temperatures (450, 450 or 600 °C). The respective acid or base addition to the precursor exhibited marked differences in the true densities, SEM micrographs, BET surface areas and pore volumes of the activated carbon. Microporous samples were obtained with average pore diameters in the range of 17.4 to 21.4 Å. Increase in  $H_3PO_4$  concentration showed increase in porosity and surface area at all temperatures. Addition of KOH led to higher surface area, more porous structure with wider pore size distributions than that of acid. At high temperatures (550 or 650 °C), the average pore diameters were observed to be less dependent on the nature of the chemical used.

**Keyword:** activated carbon, chemical activation, SEM, surface area, porosity

### INTRODUCTION

Coals are favored precursors for preparation of activated carbon. This is due to their abundant supply and low cost. The differences in compositions and organic matter contents of coals make them suitable as raw materials for preparation of activated carbon of different porosities, textural and surface properties. These properties are receiving new research interests due to potentials of tailoring them to many applications. They are being improved to meet new requirements in high-performance double-layer capacitors<sup>[1,2]</sup>, natural gas storage<sup>[3]</sup>, activated carbon-expanded graphite composites<sup>[4]</sup> and other applications in separation and purification processes<sup>[5,6]</sup>. Bituminous coal, due to its microstructure and surface composition has been proposed as a precursor for preparation of microporous activated carbon by many researchers<sup>[7,9]</sup>.

The precursor may be mixed with chemicals and be subjected to different degrees of pyrolysis to obtain activated carbon of desired properties. In general, addition of chemical agents to the precursor leads to dehydration, dehydrogenation, formation of cross-links and hence polymerized, rigid matrix<sup>[10,14]</sup>. Furthermore, some of the added species may act as oxidation retardants. Therefore, lead to less release of volatiles and lower carbon burnt-off<sup>[12]</sup>. Recent studies have shown that KOH post-treatment of activated carbon

could lead to a more microporous structure suitable for gas storage<sup>[15]</sup>. However, similar post-treatment attempt using air gasification exhibited no significant changes on the product<sup>[16]</sup>. The effects of the chemicals in the carbonization and post treatment of the carbon need to be further studied.

Pretreatment of the coal by washing to decrease ash level<sup>[16,17]</sup>, by ion exchange<sup>[18]</sup> and oxidation<sup>[19]</sup> have been reported to improve the performance of the final products. Recently, we have demonstrated the significance of feedstock pre-drying on the porosity and surface area development of the KOH-activated carbon<sup>[20]</sup>. Therefore, in addition to activation, different pre- and post activation operations could be employed to obtain activated carbon of desired properties. The aim of this work was to study the effects of  $H_3PO_4$  and KOH on pyrolysis of a bituminous coal at different temperatures. Post-treatment of the products may then be considered. Here, we report preliminary results on the effects of chemical additions to the pyrolysis reactions and the properties of the activated carbon obtained.

### Experimental:

**Sample Preparation:** The precursor used for the preparation of the activated carbon is a bituminous high volatile A coal (ASTM-American Society for Testing and Materials). Its proximate and ultimate analyses

results indicate that it has low moisture and high sulfur contents. The preparation was done using a procedure similar to one reported earlier<sup>[21]</sup>. About 20.0 g of dry coal sample (particle diameter of 1.0 – 1.18 mm) was impregnated with 20 wt% H<sub>3</sub>PO<sub>4</sub>. The mixture was continuously stirred at 85 °C for 24 hr. This was repeated for 40, 60 and 80 wt% H<sub>3</sub>PO<sub>4</sub> concentrations. Thereafter, the samples were vacuum dried until no observable change in weight. The dried samples were carbonized in a Carbolite fixed-bed furnace at a given carbonization temperature (450, 550 or 650 °C), using a heating rate of 30 °C/min, under a flow of nitrogen (250 ml/min). In each case, the sample was mounted in the furnace at room temperature and the heating started. When the temperature attained a specified carbonization temperature, the sample was allowed to stay for an activation time of 1hr. The samples were washed to remove excess acid using distilled water at 70 °C. This was done by continuously stirring the sample in distilled water until pH > 6 was obtained. The procedure was repeated by replacing the acid with KOH of 20, 40 and 60 wt% concentrations.

**Samples Characterization:** Samples of the activated carbon were characterized by physical gas adsorptions of N<sub>2</sub> at 77.4 K, using a Quantachrome Autosorb 1C analyzer. The samples were heated at 300 °C for 3 hrs, under flow of helium prior to analysis. The properties obtained are: (i) BET surface area (S<sub>BET</sub>, m<sup>2</sup>/g), (ii) total pore volume from nitrogen held as liquid at P/P<sup>o</sup> = 0.95 (V<sub>p</sub>, cm<sup>3</sup>/g) and (iii) average pore diameter. True densities of the samples were measured by displacement of helium using a Quantachrome UltraPycnometer 1000. The textures of samples of the products were observed using scanning electron microscope (JEOL JSM 840A). It was equipped with an energy dispersive X-ray analyzer that allowed semi-quantitative analysis of solids.

## RESULTS AND DISCUSSIONS

The coal used as a precursor for the activated carbon was characterized as bituminous high volatile A coal (ASTM)<sup>[20]</sup>. Its proximate and ultimate analyses results are given in Table 1. Figure 1 shows true densities of the coal and activated carbon obtained using different concentrations of either H<sub>3</sub>PO<sub>4</sub> or KOH at different temperatures. Generally, the products exhibited true densities higher than the untreated coal. This indicates development of porosity from the volatilization of lighter coal components and cross-linking reactions. After the release of lighter components and thorough washing of the sample, the remaining solid matrix occupies a relatively reduced volume, thereby exhibiting increase in densities.

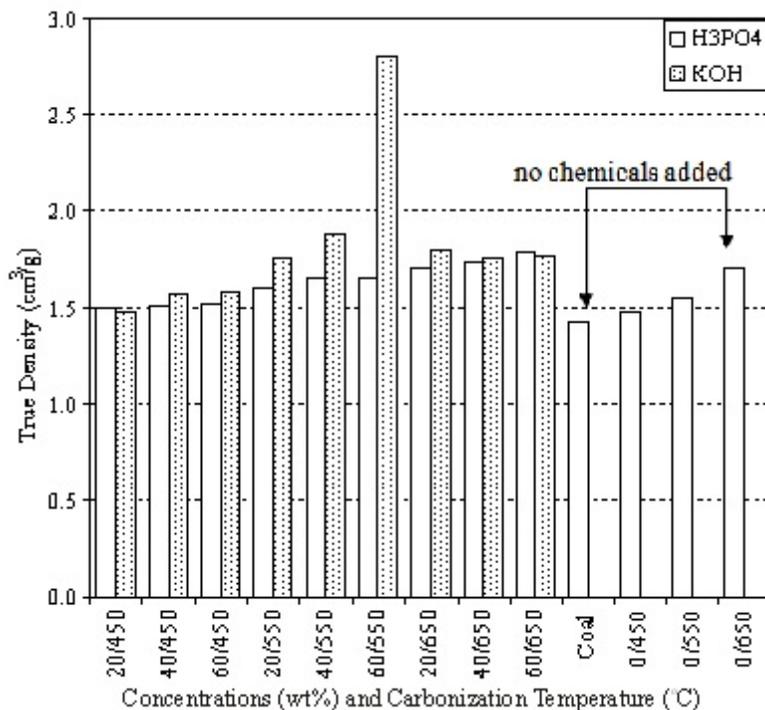
**Table 1:** Analysis of AlKamil Bituminous Coal

Ultimate (wt% dry-ash-free basis)		Proximate (wt%, dry-basis)	
Carbon	77.70	Ash	14.84
Hydrogen	5.51	Volatile Matter	37.46
Nitrogen	1.43	Fixed Carbon	47.70
Sulfur	5.30		
Oxygen	10.39	Heat Value	7,119 kcal/kg
Ash Composition (wt%)			
Al <sub>2</sub> O <sub>3</sub>	19.99	P <sub>2</sub> O <sub>5</sub>	0.12
CaO	9.84	SiO <sub>2</sub>	30.70
Fe <sub>2</sub> O <sub>3</sub>	15.96	TiO <sub>2</sub>	1.02
K <sub>2</sub> O	1.03	SO <sub>3</sub>	13.80
MgO	3.33	LOI	5.20
Na <sub>2</sub> O	2.67		

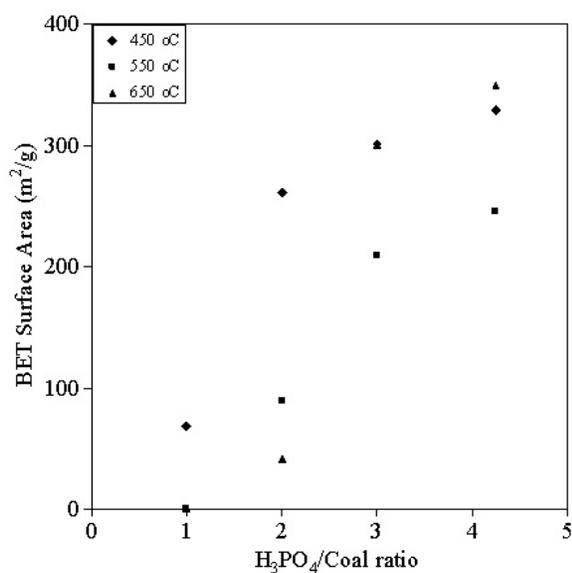
This was achieved by addition of chemicals and/or carbonization without chemicals. The devolatilization of the coal increases with increase in either chemicals concentrations or temperature. At 450 °C, some of the species and their linkages in the impregnated coal attained their limit of thermal stability<sup>[22]</sup>. This led to structural contraction and hence increases in the true density. At same temperature, the densities increase with increase in H<sub>3</sub>PO<sub>4</sub> or KOH concentrations (20 – 60 wt%). When the temperature was increased to 550 °C or higher, the density increases for both acid and base impregnated samples.

This observation could be discussed in the light of literature information. An earlier study has shown that volatiles and tar yields are function of carbonization or peak devolatilization temperature. They evolve from the coal matrix following certain mechanisms. One mechanism was described as follows<sup>[23]</sup>: (i) initiation of volatiles formation by the evaporation of mobile phase released from either disruption of guest-host bondage or by bond cleavage of the coal structure. (ii) This is accompanied by release of free radicals that may take part in chemical reactions. It leads to nucleation and growth of molecules as they move to the exterior of the coal particle. (iii) So, part of the volatiles is evaporated and released to outside the coal matrix. (iv) Part may be involved in radical initiation and reaction that forms cross-linkages within the coal structure. The reactions in step (iv) increase with increase in peak temperature especially for slow heating rate we employed<sup>[23,24]</sup>. Therefore, as shown in fig. 1, the overall mass of resultant material per unit volume will increase with temperature within the narrow range we employed.

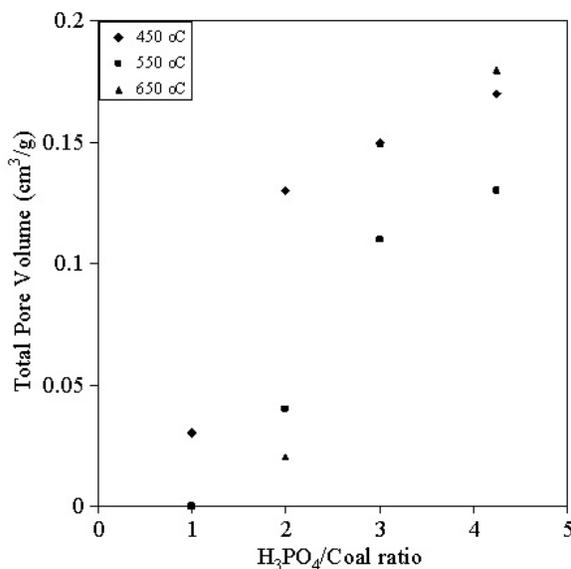
Furthermore, steps (i) and (ii) will be enhanced by the presence of chemical agents, due to weakening of bonds and provision of alternative reaction paths. Therefore, at a fixed temperature the nature and concentration of the chemicals may affect cross-linking reactions that lead to growth of molecules and hence increase in density<sup>[25,26]</sup> and lower carbon burnt-off<sup>[12]</sup>. However, the reactions depend on the nature of



**Fig. 1:** True densities for samples obtained using H<sub>3</sub>PO<sub>4</sub> and KOH activation at different carbonization temperatures



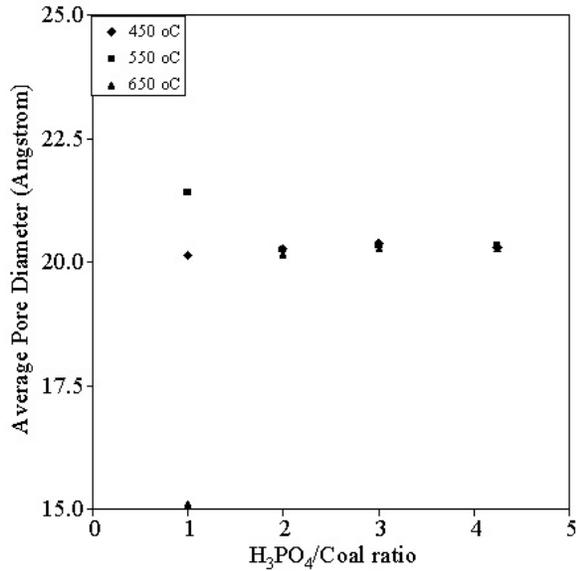
**Fig. 2a:** Variation of surface area with H<sub>3</sub>PO<sub>4</sub>/Coal ratio at different carbonization temperatures



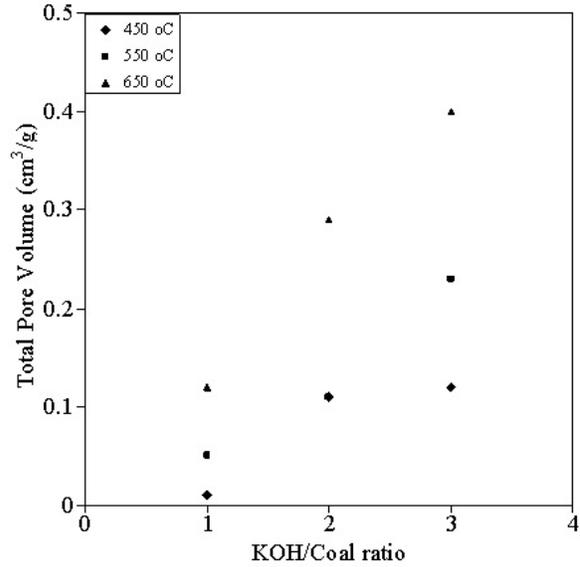
**Fig. 2b:** Variation of total pore volume with H<sub>3</sub>PO<sub>4</sub>/Coal ratio at different carbonization temperatures

volatiles released, chemical moieties accompanying them, the chemical activating agent employed and the temperature. This could be the reason of exponential increase in density with increase in KOH concentration at 550 °C. At this temperature, in the presence of KOH certain reactions might be favored. Furthermore,

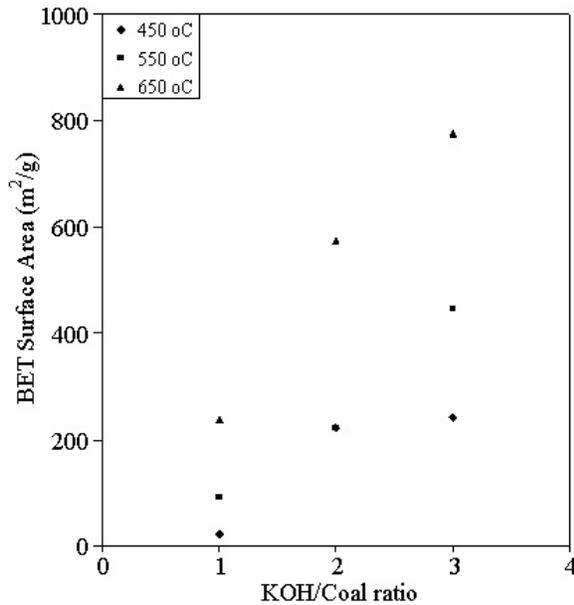
oxygen-containing structure in the coal may interact with the chemical agent to enhance cross-linking reactions. This starts with aliphatic ether linkages because in both thermal and catalytic reactions they are shown to be among the weakest<sup>[27]</sup>. Since the reactions may involve decarboxylation and dehydrogenation,



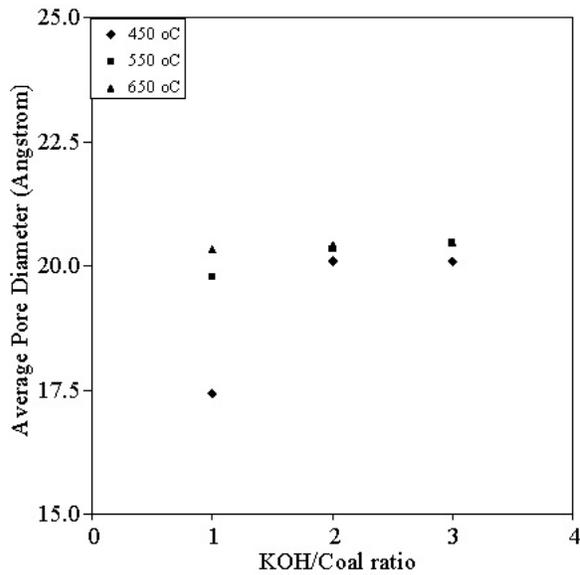
**Fig. 2c:** Variation of average pore diameter with H<sub>3</sub>PO<sub>4</sub>/Coal ratio at different carbonization temperatures



**Fig. 3b:** Variation of total pore volume with KOH/Coal ratio at different carbonization temperatures



**Fig. 3a:** Variation of surface area with KOH/Coal ratio at different carbonization temperatures

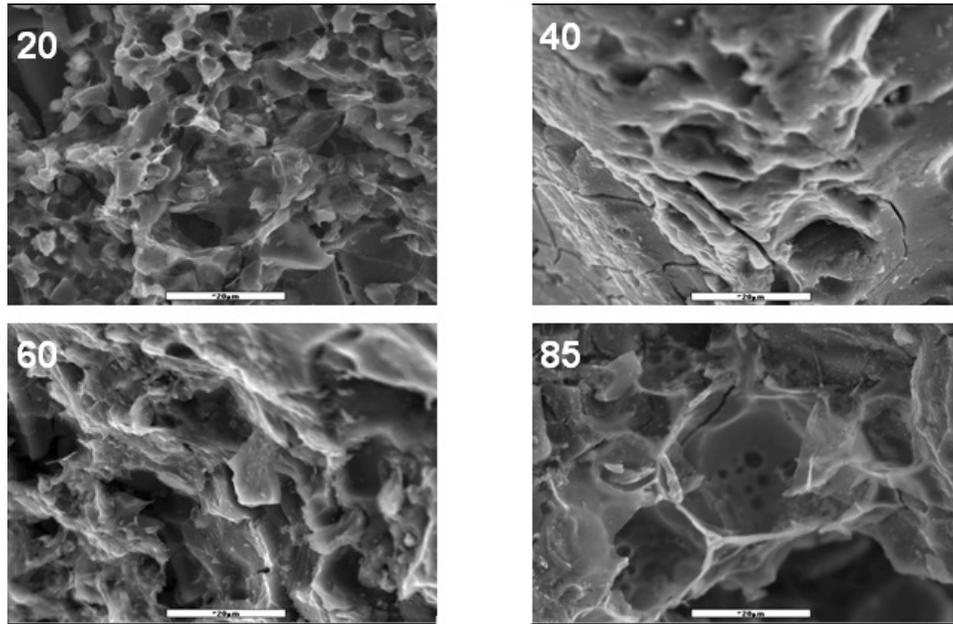


**Fig. 3c:** Variation of average pore diameter with KOH/Coal ratio at different carbonization temperatures

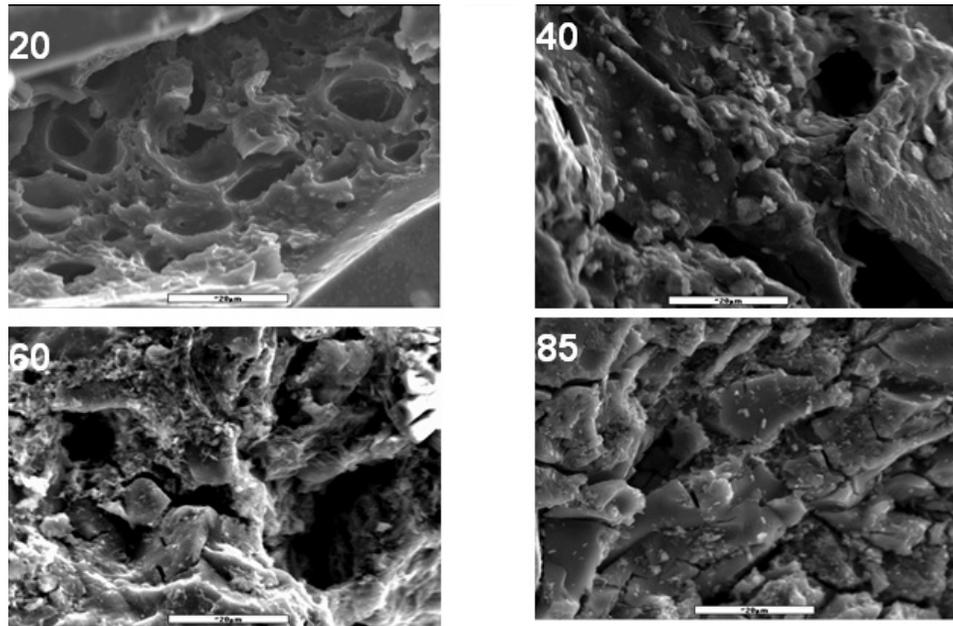
chemicals such as H<sub>3</sub>PO<sub>4</sub> and KOH enhance the reactions and cross-linking; hence increase in true densities.

The bond cleavages and cross-linkings also lead to different degrees of porosity developments. Figure 2 shows; (a) surface area, (b) total pore volume and (c) average pore diameter for the samples obtained by H<sub>3</sub>PO<sub>4</sub> activation. The pore volume and surface area

increase with increase in H<sub>3</sub>PO<sub>4</sub> concentration for all temperatures. For the two lower temperatures, monotonic increases could be observed. At a fixed temperature (450 °C), as the concentration increases, more volatiles are removed - partly transported to outside as vapors and partly cross-linked structure<sup>[28]</sup>. This brings about increase in porosity and surface area. The cross-linking may increased due to increase in the



**Fig. 4a:** SEM micrograph of activated carbon obtained with different H<sub>3</sub>PO<sub>4</sub> concentrations at carbonization temperature of 450 °C

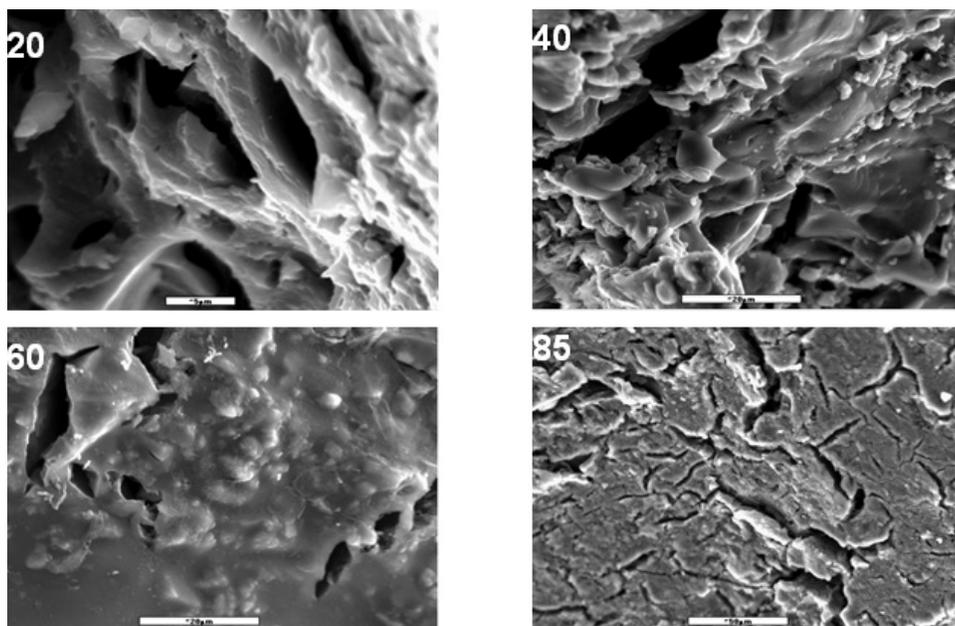


**Fig. 4b:** SEM micrograph of activated carbon obtained with different H<sub>3</sub>PO<sub>4</sub> concentrations at carbonization temperature of 550 °C

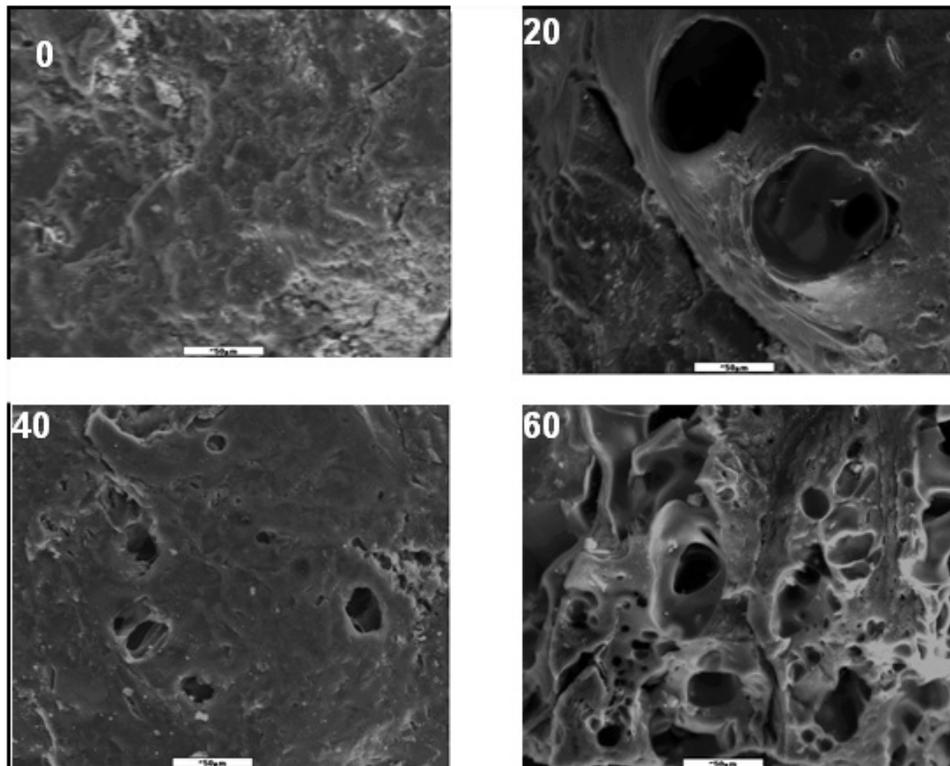
concentration of species produced by the cleavage of bonds. This is in accordance with the increase in true density with the concentration as shown in fig. 1. However, further increase in temperature to 550 °C and higher lead to more bond cleavages and more pronounced repolymerization that may lead to collapse

of pore, pore blockage and impediment to porosity development<sup>[16,22]</sup> which may be partly responsible for the observed lower pore volume in fig 2b.

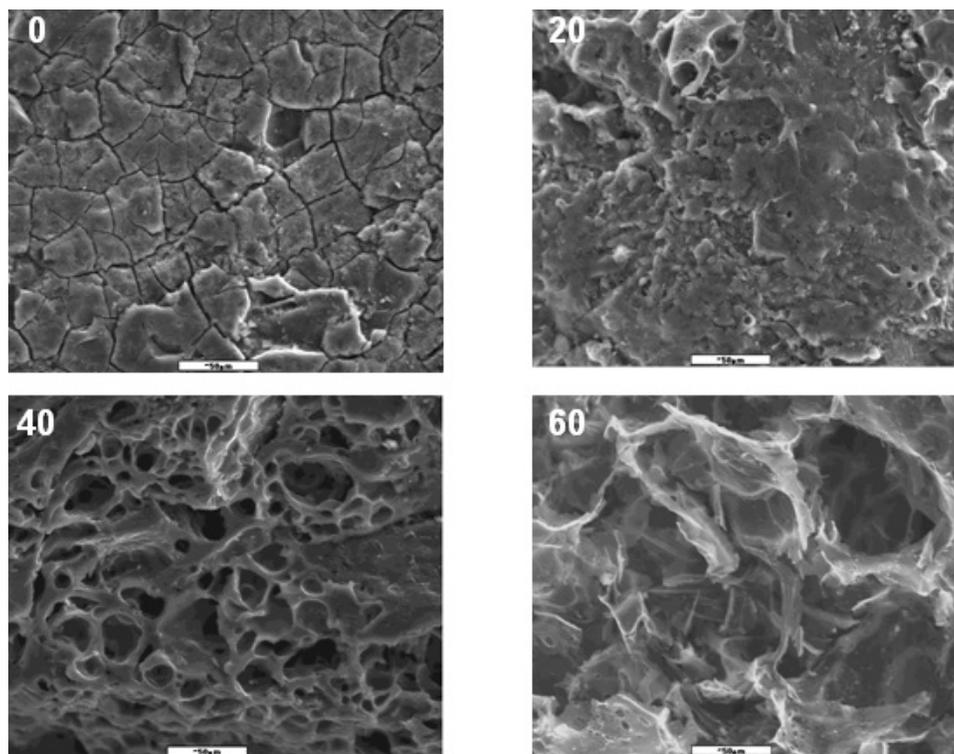
Higher temperature increases impediments to porosity development. However, depending on temperature, higher acid concentration could retard post



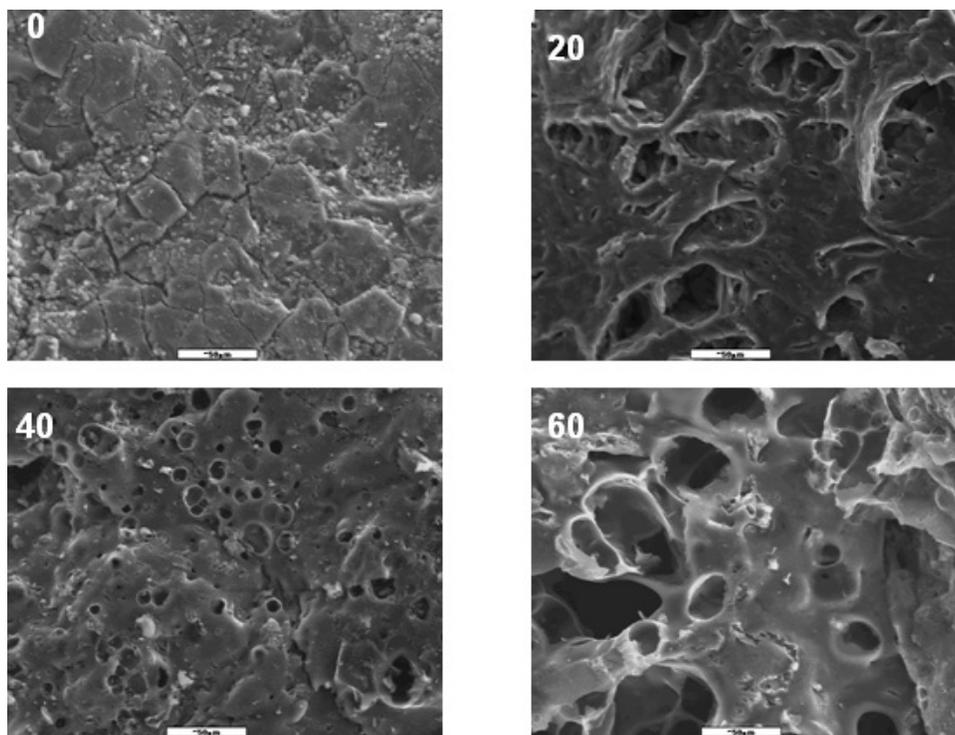
**Fig. 4c:** SEM micrograph of activated carbon obtained with different H<sub>3</sub>PO<sub>4</sub> concentrations at carbonization temperature of 650 °C



**Fig. 5a:** SEM micrograph of activated carbon obtained with different KOH concentrations at carbonization temperature of 450 °C



**Fig. 5b:** SEM micrograph of activated carbon obtained with different KOH concentrations at carbonization temperature of 550 °C



**Fig. 5c:** SEM micrograph of activated carbon obtained with different KOH concentrations at carbonization temperature of 650 °C

cleavage reactions<sup>[29]</sup>. The higher acid concentration also occupies more space in the matrix thereby leaving more vacancies and hence exhibiting higher porosity after washing the samples. The highest surface area was obtained at the highest acid concentration and highest carbonization temperature. There was more significant decrease in surface area when the temperature was decreased to 450 °C at a constant concentration. This shows that the acid concentration is more significant in porosity development than the temperature. Although the total volume of pores increase with increases in both acid concentration and carbonization temperature, the average pore diameters appear to show insignificant changes at ratio higher than 2 (fig. 2c). This suggests that the increase in acid concentration has more effects on the increase in the rate of cross-linking reactions rather than developing new reaction routes.

The total pore volume and surface area increase with increase in KOH concentration as shown in fig. 3 (a and b). Contrary to the case of H<sub>3</sub>PO<sub>4</sub> activation (fig. 2); for the KOH activation, the lowest temperature exhibited the lowest surface area and pore volume. When the temperature was increased, the properties increased correspondingly. The highest carbonization temperature and KOH concentration led to highest surface area (775 m<sup>2</sup>/g). This indicates different modes of interactions between KOH and the coal constituents; compared with that of H<sub>3</sub>PO<sub>4</sub>. As discussed earlier, the acid and base may react with the volatiles in reactions such as dehydrogenation, cyclization and condensation. The species from these reactions are cross-linked with the main carbon skeleton at temperatures higher than thermal stability limit of the carbon structure. Furthermore, the acid reacts with -OH groups on cellulosic part of the coal to form esters. This leads to further cross-linking of the polymer chains by dimerization or oligomerization of cellulosic species. The mode of interaction of the acid with the coal was<sup>[14,18]</sup> reported to be mainly through oxygen functional groups. This leads to dehydration, dehydrogenation and repolymerization reactions with the carbon structure. On the other hand, KOH is involved in both dehydrogenation and oxidation reactions<sup>[30,31]</sup>. The overall stoichiometric reaction of KOH in coal activation was also shown to involve direct attack on carbon center<sup>[31]</sup>. This leads to more aliphatic chains, hence higher porosity and surface area. In addition, the smaller size of KOH than that of H<sub>3</sub>PO<sub>4</sub> enhances the rate of the reaction and porosity development (fig. 3)<sup>[7,21]</sup>. The enhancement of porosity by KOH was recently demonstrated when an activated carbon was subjected to post-treatment with KOH<sup>[15]</sup>. Increase in microporosity was observed.

The effects of the chemical agents were further explored by analyzing the microtextural structure of the samples surfaces. Figures 4 (a,b and c) show the surface micrograph of the H<sub>3</sub>PO<sub>4</sub> activated carbons. As the concentration increases (20 – 85 wt%), the pores increase. The surface texture of the sample activated with the highest concentration indicates high population of small pits on the surface that may be as a result of washing out or evaporation of the acid. Similar increase in the number of pores could be observed at higher temperatures (550 and 650 °C). There are narrow slits indicative of crack at the highest concentration. Figures 5(a,b and c) display the surface texture of the KOH activated samples. The porosities increase with increase in KOH concentration (0 – 60 wt%) and carbonization temperature (450 – 650 °C). The coal carbonized in the absence of KOH showed flat impervious surface. Addition of KOH leads to development of wider pore sizes distribution (fig. 5a). Probably, this developed from leaching or vaporization of KOH, K<sub>2</sub>CO<sub>3</sub>, K or hydrogen moving out of the carbon matrix<sup>[31]</sup>. Similar pattern persisted at 550 and 650 °C. However, there are more pores of different sizes, compared with acid activation. Samples activated with the highest concentrations of KOH exhibited irregular pore with flaky mouth. This indicates large total pore volume and surface area as observed in fig. 2a. The results show that KOH activation developed larger pore volume and wider surface area than H<sub>3</sub>PO<sub>4</sub> treatment.

**Conclusions:** The effects of H<sub>3</sub>PO<sub>4</sub> or KOH on the pyrolysis of bituminous coal have been demonstrated at different temperatures. Activated carbon was obtained. Its properties – surface area, porosity, microtexture and density – depended on the nature of the activating agent (H<sub>3</sub>PO<sub>4</sub> or KOH) and their concentrations. The highest surface area was obtained using KOH activation. In addition, SEM micrograph of the samples indicated higher population of pores with wider size distributions using KOH activation. However, at high temperature, the average pore diameters are similar for all samples irrespective of the carbonization temperature.

## REFERENCES

1. Miller, J.M., B. Dunn, T.D. Tran and R.W. Pekala, *J. Electrochem. Soc.*, 144, L309.
2. Saliger, R., U. Fisher, C. Herta and J. Fricke, 1998. *J. Non-Cryst. Solids*, 225: 81.
3. Zhou, Y., Y. Wang, H. Chen and L. Zhou, 2005. *Carbon*, 43 2007.
4. Py, X., E. Daguerre and D. Menard, 2002. *Carbon*, 40: 1255.

5. Sircar, S., T.C. Golden and M.B. Rao, 1996. *Carbon*, 34: 1.
6. El-Sayed, Y., T.J. Bandoz and J. Colloid, 2004. *Interface Sci.*, 273: 64.
7. Hsu, L.Y. and H. Teng, 2000. *Fuel Process. Tech.*, 64: 155.
8. Teng, H. and H.C. Lin, 1998. *AIChEJ*, 44: 1170.
9. Linares-Solano, A., I. Martin-Gullon, C. Salinas-Martinez de Lecea and B. Serrano-Talavera, 2000. *Fuel*, 79: 635.
10. Jagtoyen, M. and M. Thwaites, 1992. *J. Stencil*, B. McEnaney, F. Derbyshire, *Carbon*, 30: 1089.
11. Illan-Gomez, M.J., C. Garcia-Garcia, C. Salinas-Martinez de Lecea and A. Linares-Solano, 1996. *Energy Fuels* 10: 1108.
12. Jagtoyen, M. and F. Derbyshire, 1993. *Carbon* 31: 1185.
13. Díaz-Díez, M.A., V. Gómez-Serrano, C. Fernández González, E.M. Cuerda-Correa and A. Macías-García, 2004. *Appl. Surf. Sci.*, 238: 309.
14. Cazorla-Amorós, D., D. Ribes-Pérez, M.C. Román-Martínez and A. Linares-Solano 1996. *Carbon*, 34: 869.
15. Baker, F.S., R.K. Beckler, J.R. Miller and Z.Q. Yan, 1965. US patent number, 5: 483.
16. Ganan, J., C.M. Gonzalez-Garcia, J.F. Gonzalez, E. Sabio, A. Macias-Garcia and M.A. Diaz-Diez, 2004. *Appl. Surf. Sci.*, 238: 347.
17. Rivera-Utrilla, J., M.V. López-Ramón, F. Carrasco-Marín, F.J. Maldonado-Hódar and C. Moreno-Castilla, *Carbon*, 34: 917.
18. Seggiani, M., S. Vitolo and P. De Fillipis, 2005. *Fuel*, 84: 1854.
19. Lorenc-Grabowska, E., G. Gryglewicz, S. Gryglewicz, 2004. *Micro. Meso. Mater.* 76: 193.
20. Jibril, B.Y., R.S. Al-Maamari, G. Hegde, N. Al-Mandhary and O. Houache, *J. Annal. Appl. Pyro.*
21. Teng, H., T.S. Yeh, Li Y. Hsu, 1998. *Carbon*, 36: 1387.
22. Price, L.C., 1993. *Geochimica et Cosmochimica Acta*, 57: 3261.
23. Khan, M.R., 1989. *Fuel*, 68: 1522.
24. Gibbind, J.R. and R. Kandiyoti, 1989. *Fuel*, 68: 895.
25. Pugmire, R.J., M.S. Solum, D.M. Grant, S. Critchfield and T.H. Fletcher, 1991. *Fuel* 70: 414.
26. Fletcher, T.H., M.S. Solum, D.M. Grant, S. Critchfield and R.J. Pugmire, 1990. 23<sup>rd</sup> Int. Symp. Combustion, The Combustion Institute, Pittsburgh, PA, pp: 1231-1237.
27. Brendenberg, J.B., M. Huuska and A. Vuori, 1987. Latest advance in thermal and catalytic reactions of the ether bond in coal and related model compounds, in *Coal Science and Chemistry* (A. Volborth, ed), pp: 1-30, Elsevier, Amsterdam.
28. Smith, K.L., L.D. Smoot, T.H. Fletcher and R.J. Pugmire, 1994. *The Structure and reaction processes of coal*. The Plenum Chemical Engineering Series, Plenum Press, New York.
29. Bourbrigot, S., M. Le Bras, R. Delobel, P. Breant, J.M. and Tremillon, 1995. *Carbon*, 33: 283.
30. Mochida, I., E. Nakamura, K. Maeda and K. Takeshita, 1976. *Carbon*, 14: 123.
31. Lillo-Rodenas, M.A., D. Cazorla-Amoros and A. Linares-Solano, 2003. *Carbon*, 41: 267.