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Biochar As a Precursor of Activated Carbon

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Abstract

Biochar was evaluated as a precursor of activated carbon. This product was produced by chemical activation using potassium hydroxide. The effects of operating conditions of activation process, such as temperature, activating agent to biochar mass ratio, and nitrogen flow rate, on the textural and chemical properties of the product were investigated. Activated carbon produced by this method has internal surface area at least 50 times than that of the precursor and is highly microporous, which is also confirmed by scanning electron microscopy analysis. Fourier-transform infrared spectroscopy analysis showed development of aromatization in the structure of activated carbon. X-ray diffraction data indicated the formation of small, two-dimensional graphite-like structure at high temperatures. Thermogravimetric study showed that when potassium hydroxide to biochar mass ratio was more than one, the weight loss decreased.

Index Entries: Biochar; activated carbon; chemical activation; potassium hydroxide.

Introduction

Activated carbon is a highly porous material which has high surface area and exhibits good adsorptive capacities. It can be used as a catalyst *(1)* or as a catalyst support *(2,3)*. The high porosity and considerable catalytic and adsorptive properties are the results of activation process. There are two kinds of activation process, physical or chemical *(4)*. In chemical activation, carbon precursor reacts with a chemical reagent (dehydrating agent). After preparation of the mixture, it is heated, according to a specific heat treatment schedule, in an inert atmosphere and then the reaction product is washed to remove the activating agent. In a recovery unit, the chemical agent is recovered from solution. Carbon, after separation from the slurry, is dried and classified *(5)*. Commercial processes for making activated carbon use degraded and coalified plant matter (e.g., peat, lignite, and all types of coal) or of botanical origin (e.g., wood, coconut shells, and nut shells) as precursors *(6)*. Biochar is a product of fast pyrolysis process of biomass (including forest residues such as bark, sawdust, and shavings;

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and agricultural wastes such as wheat straw and bagasse). The other products of this process are gases and a liquid mixture of organic compounds. The liquid phase can be converted to a high-value-added product, known as bio-oil. This oil can be used in diesel engines and furnaces. Biochar is a high-heating-value solid fuel that is commonly used in kilns and boilers. Owing to high demand for activated carbons, the pyrolytic solid product may be converted to activated carbon, a high-value end product. The intent of this work is to produce high-quality activated carbon from biochar and then to study the effects of chemical activation process by evaluating the internal surface area and surface chemistry of the product.

Experiment

Raw Material

Biochar, received from the Dynamotive Corporation (Vancouver, BC, Canada), was used as the starting material. The as-received char was sieved, and particles between –30 and +100 mesh (150–600 μm) were collected for activation.

Process

The schematic diagram of the experimental setup is shown in Fig. 1. A fixed bed, inconel tubular reactor (25.4-mm outer diameter, 22-mm internal diameter, and 870-mm length), was used to produce activated carbons from biochar. A furnace mounted vertically on a steel frame was installed to supply heat to the reactor. For chemical activation, 20 g of the char was placed on glass wool supported by a steel web welded to the wall of the reactor. Bed temperatures were recorded by placing a K-type thermocouple in the middle of the char bed. Nitrogen flow (as the carrier gas) into the reactor was controlled by a mass flow controller (Brooks Instrument, 5850S/B). Temperature of the furnace was controlled by a temperature controller (Eurotherm 2416). The system can be operated to a maximum temperature of 1200°C. An ice bath was used to condensate any trace of steam in outlet flow.

KOH, in the form of pellet, was mixed with the biochar at the desired ratios, and then 100 mL of water was added until all the activating agent was dissolved. This mixture was kept at room temperature for 2 h to ensure the access of KOH to the interior of the biochar and then the mixture was dried overnight at 120°C in an oven. The samples were placed in reactor and were heated from room temperature to 300°C at 3°C/min and then held at this temperature for 1 h. This step was introduced to prevent carbon loss through the direct attack of steam *(7)*. The temperature was further increased to a final activation temperature at the same heating rate and held for 2 h before cooling down under nitrogen flow. Biochar was impregnated with 0.25–3 g KOH/g char and the heat treatment was performed to reach the final temperature in the range 550–800°C. After heat treatment, products were thoroughly washed with water, followed by

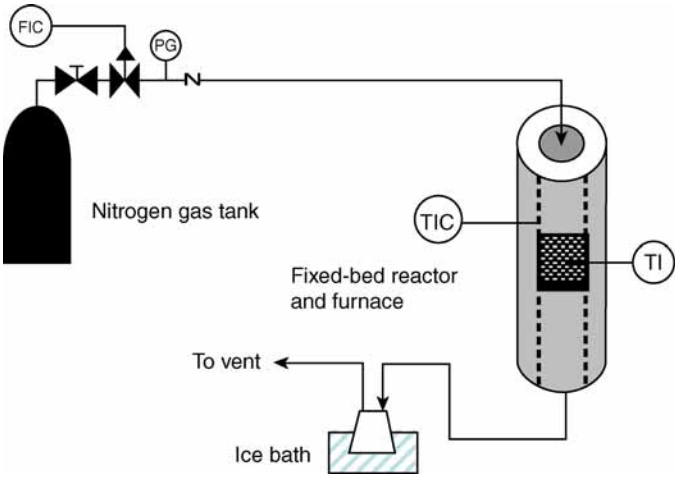

Fig. 1. Activation reactor setup.

washing with 0.1 *M* HCl, and finally with distilled water until the pH of the solution was between 6.0 and 7.0. Then the sample was dried at 110°C for 12 h and then characterized for its physical and chemical properties. Acid-washing step removes the soluble salts *(5)* and the potassium compounds, which results in the development of an accessible microporosity *(8)*. Chlorine ions are also removed from the carbon by distilled water *(9)*.

Design of Experiments

The activation process was studied with a standard response surface method (RSM) design called central composite design (CCD). It is suited for fitting a quadratic surface. This method helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction effect between those parameters. Generally, the CCD consists of a 2^k factorial runs with $2k$ axial or star runs and n_c center runs (six replicates) *(10)*. Activation temperatures (T), mass ratio of potassium hydroxide (KOH) to biochar (R), and flow rate of nitrogen (F) were three parameters investigated and their related ranges were 550–800°C, 0.25–3 g/g, and 80–250 cm^3/min, respectively. Six replications were performed at the center point in order to estimate the residual error. Therefore, the total number of experiments (N) required, for this investigation on activated carbon, is as follows:

$$N = 2^k + 2k + n_c = 2^3 + 2(3) + 6 = 20 \tag{1}$$

Characterization

Activated carbons were characterized by nitrogen gas adsorption, scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared spectrometry (FTIR), and thermogravimetry/differential thermal analysis (TG/DTA). To determine the surface area and pore structure of raw material and activated carbons, the nitrogen adsorption–desorption isotherms at 77 K were measured by an automated gas adsorption analyzer ASAP2000 (Micromeritics, Norcross, GA) with ±5% accuracy. SEM analysis of samples was performed by using a Phillips SEM-505 scanning electron microscope. The SEM instrument was operated at 300 kV/SE and 50°C inclination. Before analysis, all samples were gold-coated in a sputter-coating unit (Edwards Vacuum Components Ltd., Sussex, England) for electrical conduction. The micrographs were recorded using photographic techniques. XRD analysis was performed using Rigaku diffractometer (Rigaku, Tokyo, Japan) using Cu-K_α ($\lambda = 1.5406$ Å) radiation filtered by a graphic monochromator at a setting of 40 kV and 130 mA. The powdered catalyst samples were smeared on glass slide with methanol and dried at room temperature. The XRD analysis was carried out in the scanning angle (2θ) range of 3–85° at a scanning speed of 5°/min. FTIR spectra were obtained using a spectroscope (Spectrum GX; Perkin-Elmer, Norwalk, CT) at a resolution 4/cm. Undiluted activated carbons, in the powdered form, were scanned and recorded between 4000 and 450/cm. TG studies were carried out to study the effects of an activating agent on the product yield and thermal stability, by a pyres-diamond TG/DTA (Perkin-Elmer instruments) under the flow of argon gas. The pH of biochar and products were measured according to ASTM D 3838-80. Iodine number and ash content of activated carbons were measured according to ASTM D4607-94 and D2866-94, respectively.

Results and Discussion

Analysis of the Char

The biochar was analyzed for ultimate and bulk ash analysis by the Loring laboratory in Calgary (Canada). The ultimate analysis of biochar (moisture free) is 83.07 wt% carbon, 3.76 wt% hydrogen, 0.11 wt% nitrogen, 0.01 wt% sulphur, 9.6 wt% oxygen, and 3.44 wt% ash. The bulk ash analysis of biochar is 53.48 wt% SiO_2, 7.73 wt% Al_2O_3, 0.1 wt% TiO_2, 2.52 wt% Fe_2O_3, 17.98 wt% CaO, 4.2 wt% MgO, 2.07 wt% Na_2O, 6.93 wt% K_2O, 0.94 wt% P_2O_5, 1.06 wt% SO_3, and 2.99 wt% undetermined. The pH of biochar is 7.64 and its BET (Brunauer, Emmett, and Teller) surface area is 10 m^2/g.

Product Quality and Thermal Stability

Chemical activation by KOH is an effective method for developing highly microporous activated carbon *(11)*. A typical isotherm of activated carbon prepared from chemical activation of biochar using KOH, at 537.5°C, KOH–biochar mass ratio of 1.63, and a nitrogen flow rate of 165 cm^3/min, is shown in Fig. 2, indicating the development of microporous structure in the product. This product has BET surface area of 585 m^2/g, micropore area of 470 m^2/g, total pore volume of 0.286 cm^3/g, micropore volume of 0.222 cm^3/g, and average pore diameter of 14.5°A. Therefore, micropores

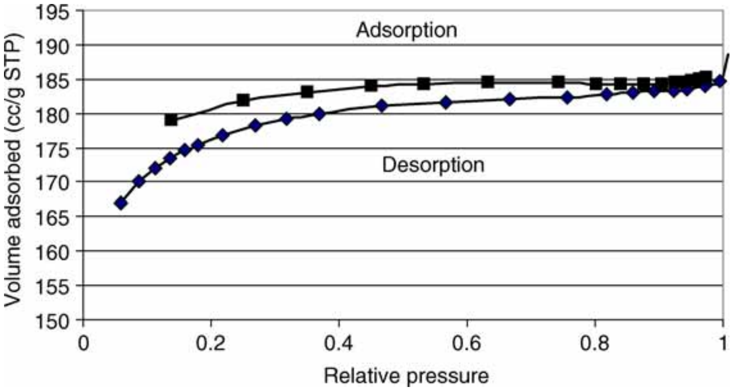

Fig. 2. Isotherm plot of activated carbon prepared at 537.5°C, KOH–biochar mass ratio of 1.63, and nitrogen flow rate of 165 cm^3/min.

Table 1
Effect of Temperature on the Porosity of Activated Carbon Prepared With KOH to Biochar Mass Ratio of 1.63 and Nitrogen Gas Flow Rate of 165 cm^3/min

Temperature (°C)	BET surface area (m^2/g)
537.5	585
675	927
812.5	1578

Table 2
Effect of Mass Ratio of KOH to Biochar on the Porosity of Activated Carbon Produced at 675°C and Nitrogen Flow Rate of 165 cm^3/min

KOH–biochar mass ratio	BET surface area (m^2/g)
0.11	248
1.63	927
3.14	659

account for 80.3% of the surface area and 77.6% of the pore volume of this activated carbon. Table 1 shows the effect of temperature on the porosity of activated carbon. It shows that by increasing the temperature from 537.5 to 812.5°C, BET surface area increased from 585 to 1578 m^2/g. Increasing the temperature increases the rate of reaction between char and KOH, thus creating new pores. Table 2 shows the effect of mass ratio of activating agent (KOH) to biochar on the porosity. It shows that the BET surface area increased from 248 to 927 m^2/g by increasing the ratio from 0.11 to 1.63 and then it decreased to 659 m^2/g. This trend has been observed for chemical activation of other precursors using KOH (*8,12*). This is owing to the

Table 3
Effect of Nitrogen Flow Rate on the Porosity
of Activated Carbon Prepared at 675°C
and KOH–Biochar Mass Ratio of 1.63

Nitrogen flow rate (cm^3/min)	BET surface area (m^2/g)
71.5	582
165	927
258	1210

Table 4
Comparison of Properties of Chemically Activated Carbon Produced
From Biochar With Those of Three Commercial Activated Carbons

	Activated carbon from Envirotrol Inc., coconut shell EI-48S	Activated carbon from Fisher Scientific Co., coconut shell S-690-A	Norit FGD activated carbon	Chemically activated carbon from biochar
BET surface area (m^2/g)	960	640	556	1578
Micropore area (m^2/g)	830	450	246	1355
Total pore volume (cm^3/g)	0.46	0.31	0.54	0.75
Micropore volume (cm^3/g)	0.39	0.21	0.11	0.63
Average pore diameter (Å)	14	14	28	14
Iodine number (mg/g)	902	446	608	1576
Ash content (wt%)	0.6	27.70	26.67	0.5

widening of micropores in product by increasing the mass ratio. Table 3 shows the effect of nitrogen flow rate on the porosity of activated carbon. BET surface area increased from 582 to 1210 m^2/g by increasing the flow rate of gas from 71.5 to 258 cm^3/min. It can be related to the faster removal of gases evolved during the activation process at increased nitrogen flow and therefore shifting the equilibrium of the reaction to the further production of these gases and micropore materials *(8)*.These results indicate that in order to develop a highly porous activated carbon with surface area more than 1000 m^2/g, temperature more than 675°C, KOH–biochar mass ratio equal to 1.63, and gas flow rate more than 165 cm^3/min are required. A sample prepared at 812.5°C, mass ratio of 1.63, and nitrogen flow rate of 165 cm^3/min has a BET surface area equal to 1578 m^2/g. In Table 4, the

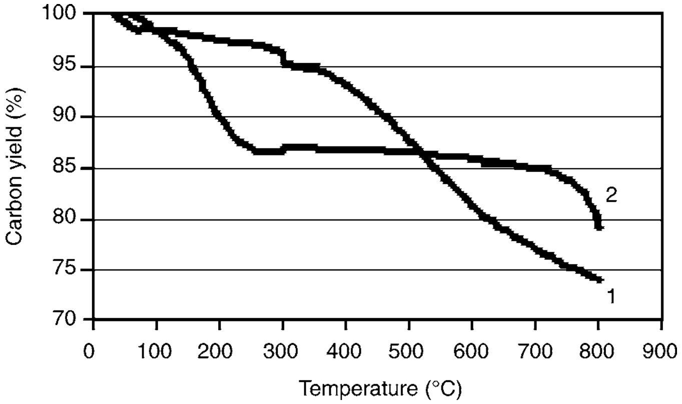

Fig. 3. TGA of biochar (1) and activated carbon (2) prepared at 675°C, KOH–biochar mass ratio of 1.63, and nitrogen flow rate of 165 cm^3/min.

characteristics of this chemically activated carbon have been compared with three commercial activated carbons (activated carbon from Envirotrol Inc., Sewickley, PA [coconut shell EI-48S], activated carbon from Fisher scientific Co., Ottawa, ON, Canada [coconut shell S-690-A], and Norit FGD activated carbon, Marshall, TX). The average pore diameter of EI-48S and S-690-A are equal to that of chemically activated carbon. But the BET surface area, total pore volume, micropore surface area, and micropore volume of the product from biochar are more than those of these two commercial activated carbons. Norit FGD has a bigger average pore diameter and lower porous characteristics than chemically activated carbon. The iodine number, as a relative indicator of porosity in activated carbon, shows that the product from biochar has high porous structure. The ash content of this product, as a result of low ash content of its precursor, is obviously less than the ash contents of these commercial activated carbons. It shows that by using biomass as the main precursor, activated carbon can be produced with highly porous characteristics and low ash content. Therefore, biochar produced in fast pyrolysis of biomass, instead of using as solid fuel, can be converted to an attractive byproduct that can be used as a sorbent for liquids and gases or as catalyst or catalyst support.

Figure 3 shows the results in the TG analyses carried out examining the thermal stability of materials during activation process, under an inert (Ar) atmosphere for biochar and activated carbon, prepared at 675°C, KOH-biochar mass ratio of 1.63, and nitrogen flow rate of 165 cm^3/min. It can be obviously seen that addition of an activating agent increases the carbon yield. Table 5 shows the amount of weight loss of sample for different mass ratios of KOH to biochar. According to this table, KOH acts as dehydrating agent, influences the pyrolytic decomposition, inhibits tar formation, and increases carbon yield *(14)*. In order to minimize the weight loss of activated carbon, the ratio of the activating agent to biochar should be maintained more than one.

Table 5
Effect of Mass Ratio on the Weight Loss of Precursor During Activation Process for Activated Carbon Prepared at 675°C and Nitrogen Flow Rate of 165 cm^3/min

KOH/biochar (g/g)	Total weight loss %
0	26.4
0.25	36.4
1	28.4
1.63	21.5
3	19.7

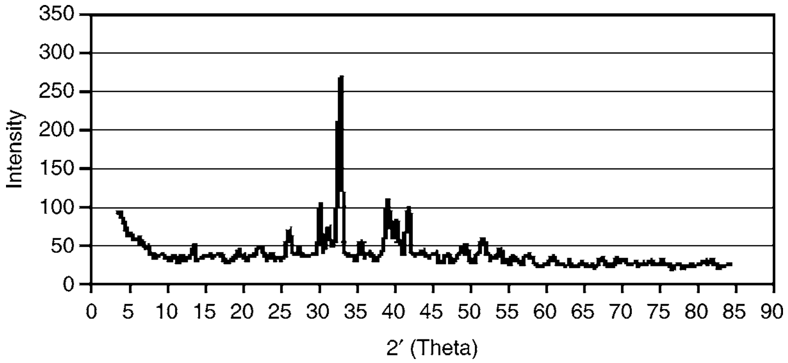

Fig. 4. X-ray diffraction (XRD) of activated carbon prepared at 675°C, KOH–biochar mass ratio of 1.63, and nitrogen flow rate of 165 cm^3/min, before acid-washing.

Crystallinity and Surface Chemistry of Activated Carbon

Figure 4 shows the XRD plot of activated carbon prepared at 675°C, KOH–biochar mass ratio of 1.63, and nitrogen flow rate of 165 cm^3/min, before acid-washing. According to the observed peaks, KO_3 and $K_2CO_3 \cdot (1.5)H_2O$ were identified in the product of chemical activation before acid-washing (peaks at $2\theta = 32.5°$, $39.8°$, and $41.9°$ for KO_3 and peaks at $2\theta = 12.8°$, $29.8°$, $32.2°$, $32.5°$, $32.7°$, and $41.5°$ for $K_2CO_3 \cdot [1.5H_2O]$). More study is required to specify the other possible potassium compounds in the product before acid-washing. The products were then acid-washed and subjected to XRD analysis.

Figure 5 shows the XRD spectra for biochar and two activated carbons prepared at the same mass ratio and nitrogen flow rate but at different temperatures. It shows that by increasing activation temperature from 537.5°C to 675°C a small graphite-like structure forms on activated carbon (peaks at $2\theta = 26.6°$ and $44.5°$). This structure, known as turbostratic *(11)*, can be of two-dimensional order created by parallel orientation of carbon layer planes. This also indicates that potassium species are completely removed from the activated carbon.

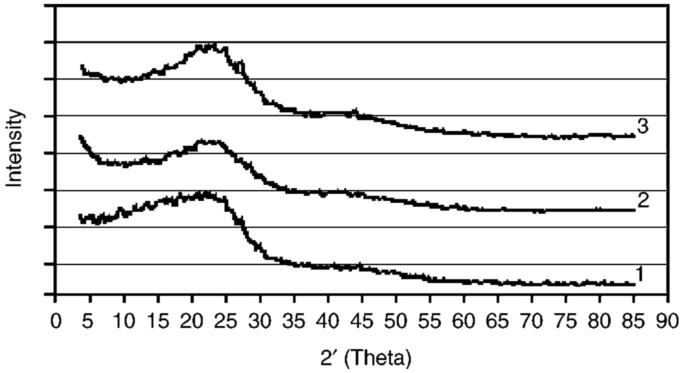

Fig. 5. X-ray diffraction (XRD) of biochar (1) and activated carbon prepared at 537.5°C (2) and 675°C (3) (at constant KOH–biochar mass ratio of 1.63 and nitrogen flow rate of 165 cm^3/min for both activated carbons).

The scanning electron micrographs were taken for biochar, activated carbon prepared at 675°C, KOH–biochar mass ratio of 1.63, and nitrogen flow rate of 165 cm^3/min before and after acid-washing to examine their microporsity (*see* Fig. 6A–C). According to these micrographs, biochar does not have a porous structure, as confirmed by very low BET surface area of it, and for activated carbons, before acid-washing pores are blocked by potassium and basic compounds, but washing with HCl/water removes them and exposes the porosity of the product.

Diffuse-reflectance FTIR is a powerful technique for IR analysis of fine particles and powders in the concentration range from undiluted to parts per thousand. In the IR technique, the interpretation of the spectra is complicated because each group indicates several bands at different wave numbers, therefore each band may include contributions from various groups *(13)*. The IR bands which can be associated with aromatic hydrocarbons are as follows.

Peak between 900 and 675/cm (out-of-plane bending of the ring C–H bonds), peak between 1300 and 1000/cm (in-plane bending bands), peaks between 1600 and 1585/cm as well as 1500 and 1400/cm (skeletal vibrations involving carbon–carbon stretching within the ring), peak between 3100 and 3000/cm (aromatic C-H stretching bands), and peak between 2000 and 1650/cm (weak combination and overtone bands). Figure 7 shows the FTIR results for biochar, the product of heat treatment of biochar to the final temperature of 675°C without using an activating agent and activated carbon prepared at 675°C, KOH–biochar mass ratio of 1.63, and nitrogen flow rate of 165 cm^3/min. The spectrum of activated carbon prepared by activating agent shows the effect of this agent in aromatization of the product.

Figure 7 shows that there are low levels of aromatic compounds in biochar, which have disappeared after heat treatment without any activating agent. However, use of activating agent with the same heat treatment

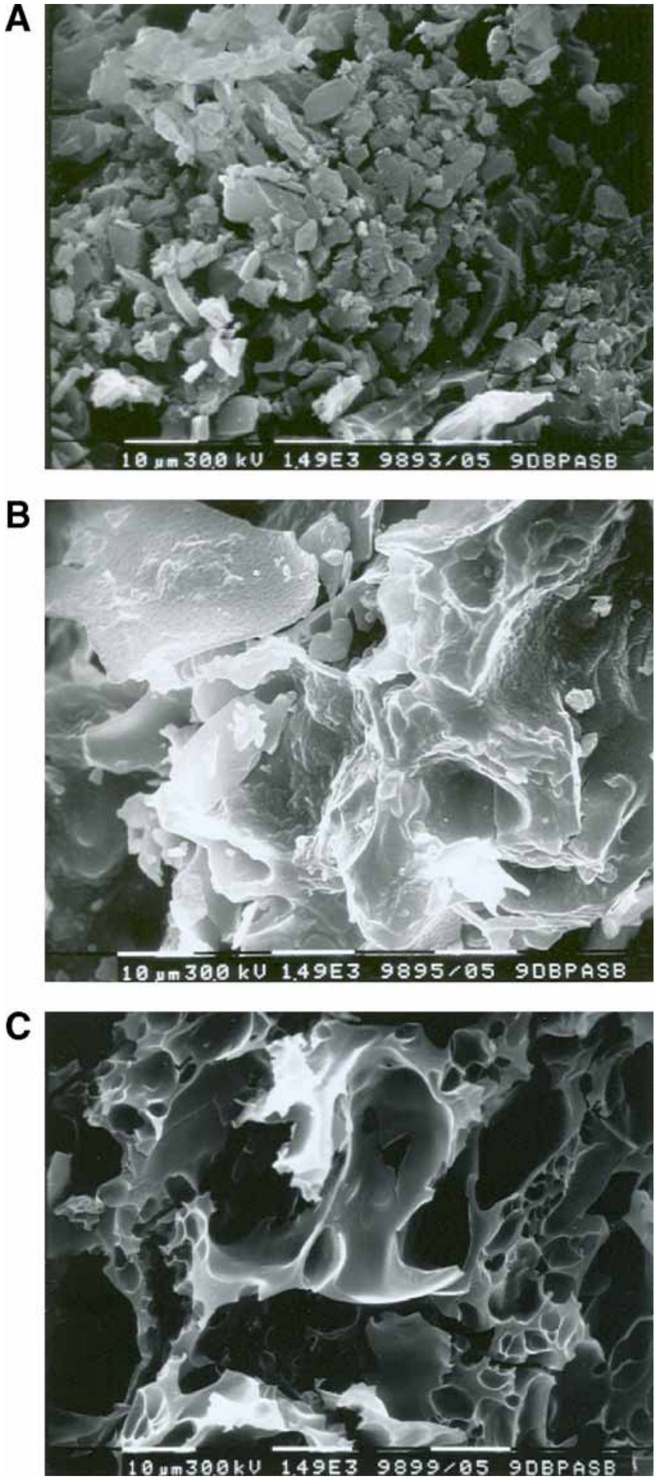

Fig. 6. Scanning electron micrographs of biochar **(A)** and activated carbon before acid-washing **(B)** and after acid-washing **(C)** (prepared at 675°C, KOH–biochar mass ratio of 1.63, and nitrogen flow rate of 165 cm^3/min).

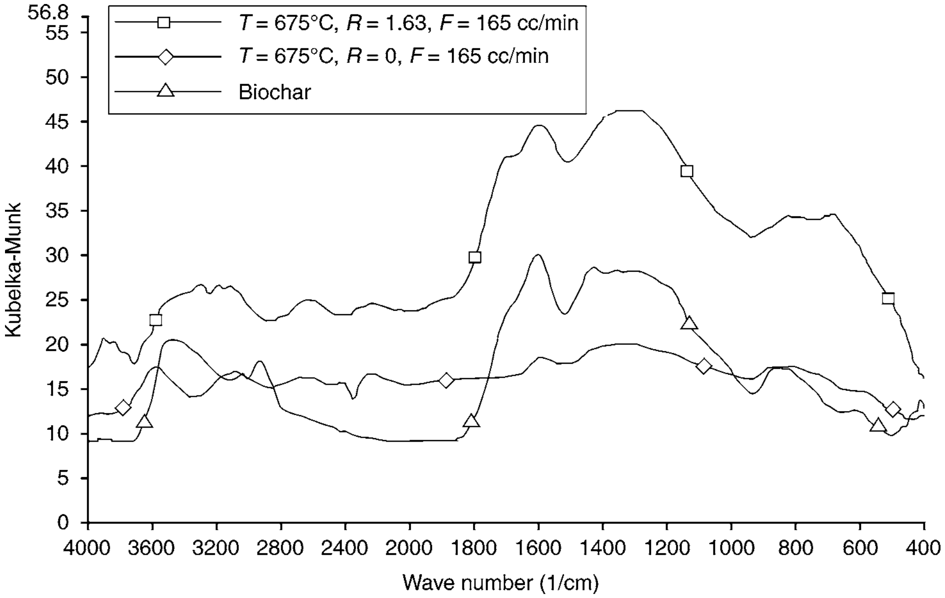

Fig. 7. Effect of KOH–biochar mass ratio on the surface chemistry.

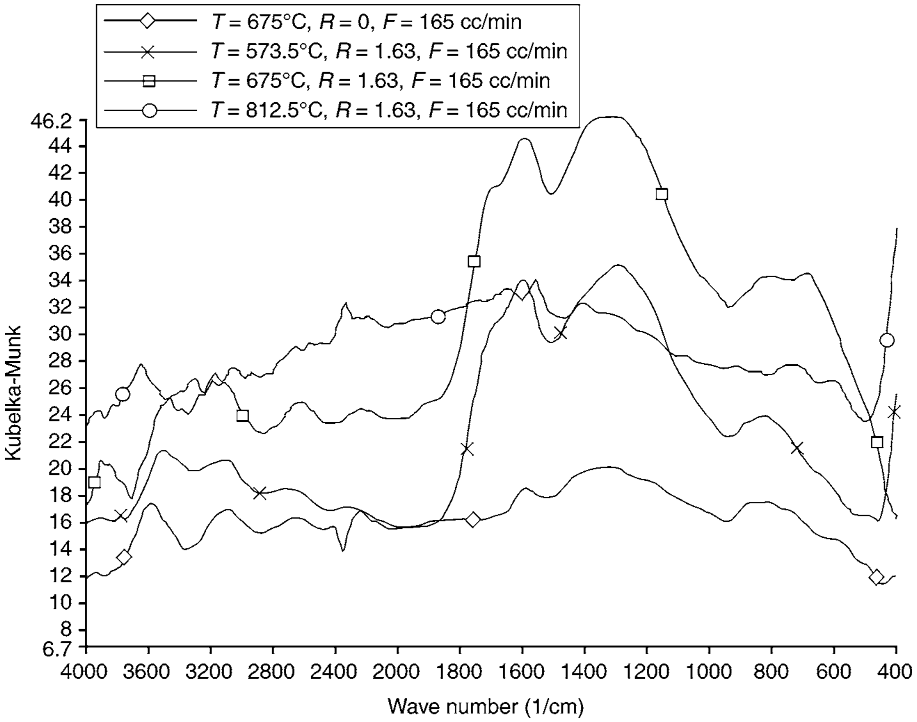

Fig. 8. Effect of temperature on the surface chemistry.

and gas flow rate has developed the aromatic structure. Figure 8 shows that the activation temperature up to 675°C increases apparent aromatization of structure of activated carbon, after which the aromaticity decreases.

Conclusions

Biochar, the solid product of fast pyrolysis of biomass, instead of using as fuel for energy generation, can be converted to activated carbon, which is a value-added product. Chemical activation of biochar, using KOH, produces activated carbon with high porous structure and low ash content, which is comparable with commercial, activated carbons. Some potassium compounds, such as KO_3 and $K_2CO_3 \cdot (1.5H_2O)$, were identified in the activated carbon before acid-washing, which were completely removed by acid-washing. BET surface area of activated carbon produced by this material can be as large as 1500 m^2/g. There was presence of small graphite-like structure in the activated carbon produced at higher temperatures. For KOH–biochar ratios of more than one, chemical activation increases the carbon yield. The activating agent increases apparent aromatization in the product.

References

1 Dalai, A. K., Majumdar, A., Chowdhury, A., and Tollefson, E. L. (1993), *Can. J. Chem. Eng.* **71,** 75.

2 Rodriguez-Reinoso, F. (1995), In: *Porosity in Carbons: Characterization and Applications*, Patrick, W., Jr., ed., Edward Arnold, London, Chapter 10.

3 Radovic, L. R. and Rodriguez-Reinoso, F. (1997), In: *Chemistry and Physics of Carbon*, Vol. 25, Thrower, P. A., ed., Marcel Dekker, New York, p. 243.

4 Kyotani, T. (2000), *Carbon* **38,** 269–286.

5 Rodriguez-Reinoso, F. In: *Handbook of Porous Solids*, Schuth, F., Sing, K. S. W., and Weitkamp, J., eds., Wiley-VCH Verlag Gmbh, Weinheim, Germany, 2002, p. 4.8.1.

6 El-Hendawy, A. A., Samra, S. E., and Girgis, B. S. (2000), *Colloids Surf. A: Physicochem. Eng. Aspects* **180,** 209–221.

7 Otowa, T., Nojima, Y., and Miyazaki, T. (1997), *Carbon* **35,** 1315.

8 Lozano-Castello, D., Lillo-Rodenas, M. A., Cazorla-Amoros, D., and Linares-Solano, A. (2001), *Carbon* **39,** 741–749.

9 Lillo-Rodenas, M. A., Lozano-Castello, D., Cazorla-Amoros, D., and Linares-Solano, A. (2001), *Carbon* **39,** 751–759.

10 Montgomery, D. C. (1997), *Design and Analysis of Experiments*, 4th ed., John Wiley & Sons, USA, Chapter 13.

11 McEnaney, B. (2002), In: *Handbook of Porous Solids*, Schuth, F., Sing, K. S. W., and Weitkamp, J., eds., Wiley-VCH Verlag Gmbh, Weinheim, Germany, p. 4.8.2.

12 Ghen, X. S. and McEnaney, B. (2001), In: Extended abstracts, 25th American carbon conference, Lexington, KY.

13 Byrne, J. F. and Marsh, H. (1995), In: *Porosity in Carbons: Characterization and Applications*, 1st ed., Patrick, W., Jr., ed., Halsted Press, London, Chapter 1.

14 Figueiredo, J. L., Pereira, M. F. R., Freitas, M. M. A., and Orfao, J. J. M. (1999), *Carbon* **37,** 1379–1389.