



Preparation of porous carbons from phenol–formaldehyde resins with chemical and physical activation

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Abstract

Porous carbons with high porosities were prepared from phenol–formaldehyde resins using chemical and physical activation methods. The resin precursor employed was synthesized with an initial formaldehyde-to-phenol ratio of 1.33 by mole. The chemical activation process consisted of KOH impregnation followed by carbonization in nitrogen at 500–900°C for 0–3 h, whereas the physical activation was performed by carbonizing the resins at 900°C followed by gasifying the char in CO₂ to different degrees of burn-off. Both activation methods can produce carbons with surface areas and pore volumes greater than 2000 m²/g and 1.0 cm³/g, respectively. The influence of different parameters during chemical activation, such as carbonization temperature and time, KOH/resin ratio and heating rate, on the carbon yield and the surface characteristics was explored, and the optimum preparation conditions were determined. With physical activation the resulting carbons are mainly microporous and their porosity is an increasing function of the degree of burn-off. At similar porosity levels the carbon yield during physical activation was found to be lower than that with chemical activation. An SEM study showed that carbons produced from CO₂ activation have a more compact surface than those produced from KOH activation. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Porous carbons, which have the collective name of activated carbon, have become more and more attractive materials for use in many adsorption and catalytic processes due to their high adsorptive capacity [1]. These carbons are prepared by physical activation, gasification of a char in oxidizing gases, or by chemical activation, carbonization of carbonaceous materials impregnated with chemical reagents [2]. In addition to serving as an adsorbent, high porosity carbons have recently been used in the manufacture of high-performance double layer capacitors [3–6].

Almost any carbonaceous material can be converted into activated carbon. Among the various types of naturally occurring carbonaceous materials, coal is the most commonly used precursor for activated carbon production [7–9]. However, the considerably large amount of mineral

species contained in coal generally restricts the porosity development of the derived carbon, since the resulting ash has a negligible porosity compared to microporous carbon. Phenol–formaldehyde resins have structural features similar to those in coals, but contain much fewer mineral impurities. These can be controlled to very low levels in the synthesis process [10,11]. Because of the low ash content, activated carbons prepared from these resins are expected to have a high specific porosity compared with those derived from coal. In general, activated carbons with both a high surface area and porosity, allowing significant adsorption, are desirable. Thus, the porosity development of carbons prepared from phenol–formaldehyde resins merits a thorough investigation and study.

Basically, the type of porosity is mainly determined by the type of precursor employed; however, the method of activation is another parameter which may influence the final pore size distribution [12]. In physical activation, steam and carbon dioxide are generally preferred in the gasification step, since the slow gasification kinetics allow gas molecules to diffuse into the carbon micropores and develop a large surface area. The temperature for the

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carbonization of the precursor has been reported to have an influence on the surface properties [13–15]. Following carbonization, changes in pore structures during further gasification are often monitored and controlled to produce various porous carbons for different applications. In chemical activation, the chemical reagents may promote the formation of cross-links, leading to the formation of a rigid matrix that will be less susceptible to volatile loss and volume contraction upon heating to high temperatures [16]. Among the numerous chemical reagents, due to the difference in the chemical activation mechanism, alkali metal hydroxides were found to be effective in creating the porosities of chars derived from phenol–formaldehyde resins [17].

Within the preceding scope, this study was devoted to the effects of the preparation parameters on the pore structures of porous carbons derived from phenol–formaldehyde resins with KOH and CO₂ activation. The surface characteristics of the carbons prepared using the physical and chemical methods will be compared. The optimum conditions for producing high porosity carbons will also be recommended.

2. Experimental

2.1. Materials

Phenol–formaldehyde resins were used as the starting material for the preparation of porous carbons. The resins were synthesized under an environment of nitrogen at 95°C, using an initial formaldehyde-to-phenol ratio of 1.33 by mole. A base-catalyzed method was used in the synthesis, with ammonium hydroxide as the base. After synthesis, the resins were cured by heating in vacuum for 2 h at 60°C, followed by 12 h at 120°C. The proximate and ultimate analyses of the resulting resins are shown in Table 1.

2.2. Chemical activation

Chemical activation of the resins was performed using KOH as the chemical reagent. In a 250 ml glass-stoppered flask, the activation process was initiated by mixing 1 g of the resins with a KOH solution containing 50 g of water. The flask was immersed in a constant-temperature shaker

bath, with a shaker speed of 100 rpm. The mixing was performed at 85°C and lasted for 3 h. The concentration of the KOH solution was adjusted to give a ratio of chemical reagent to resin (i.e. the chemical ratio) varying in the range 0–4 by weight.

After mixing, the resin–KOH slurry was subjected to vacuum drying at 110°C for 24 h. The chemical-loaded samples were then carbonized in a horizontal cylindrical furnace (60 mm i.d.) in a N₂ atmosphere, with a flow of 100 ml/min. Carbonization was carried out by heating the samples at 30°C/min from room temperature to a temperature in the range 500–900°C, followed by holding the samples at that temperature for different lengths of time (0–3 h) before cooling under N₂.

After cooling, the carbonized products were washed by stirring with 250 ml of 0.5 N HCl solution at 85°C for 30 min, followed by filtration. The acid-washed sample was then leached by mixing with 250 ml of distilled water at 85°C, followed by filtration of the mixtures. Leaching was carried out several times until the pH of the water–carbon mixture was >6. The leached products were then dried in vacuum at 110°C for 24 h, to give the final carbon products.

2.3. Physical activation

Physical activation of the resins consisted of carbonization of the resins in N₂ followed by gasification of the resulting carbon in CO₂. Carbonization was performed in the same manner as for KOH-treated samples to 900°C under a stream of N₂. Following this process the samples were gasified, also in the furnace, in a stream of CO₂ at the carbonization temperature. Carbons with various degrees of burn-off were prepared.

2.4. Carbon characterization

Specific surface areas and pore volumes of the activated samples were determined by gas adsorption. An automated adsorption apparatus (Micromeritics, ASAP 2010) was employed for these measurements. Adsorption of N₂, as probe species, was performed at –196°C. Nitrogen surface areas and micropore volumes of the samples were determined from the BET and Dubinin–Radushkevich (D–R) equations, respectively. The amount of N₂ adsorbed at pressures near unity corresponds to the total amount adsorbed at both micropores and mesopores and, consequently, subtraction of the micropore volume (from the D–R equation) from the total amount (determined at $p/p_0 = 0.98$ in this case) will provide the volume of the mesopore [18]. The average pore diameter can be determined according to the surface area and total pore volume (the sum of the micropore and mesopore volumes) if the pores are assumed to be parallel and cylindrical.

A scanning electron microscope (Jeol, JXA-840) was used to study the structural features of the carbon surface.

Table 1
Analysis of phenol–formaldehyde resins

Ultimate (wt%, dry-ash-free basis)		Proximate (wt%, as-received)	
Carbon	72.9	Moisture	1.0
Nitrogen	0.5	Volatile matter	58.6
Hydrogen	6.0	Fixed carbon	40.4
Oxygen	20.5	Ash	0.0

3. Results and discussion

3.1. Chemical activation

One of the advantages of the chemical activation of coals compared with physical activation is the lower temperature of the process. Previous studies [9,19–21] have shown that chemical activation of bituminous coals with ZnCl_2 or H_3PO_4 gives the highest porosity of the resulting activated carbon at a carbonization temperature around 500–600°C, which is much lower than the gasification temperature in physical activation [13,14]. In our preliminary study, chemical activation of phenol–formaldehyde resins with ZnCl_2 and H_3PO_4 was examined, and the results showed that we were unable to produce high porosity carbon with these activation processes.

In comparison with ZnCl_2 and H_3PO_4 , KOH was found to be more effective in creating the porosity of carbons derived from the resins. The porosity development of the carbons prepared from KOH activation was investigated by N_2 adsorption. Fig. 1 shows typical isotherms of N_2 adsorption on the carbons prepared from the resins at different carbonization temperatures (500–900°C) with a carbonization time of 2 h. The chemical ratio of KOH to resins was fixed at 2. It can be seen from Fig. 1 that the

isotherms are typical of microporous carbons, since the knees of the isotherms are sharp and the plateaus are fairly horizontal [7]. The data show that the adsorption capacity increases with the carbonization temperature in the low-temperature regime, and reaches a maximum at 800°C. Above 800°C, N_2 adsorption decreases with increasing carbonization temperature. It can also be seen from Fig. 1 that there is a widening of porosity with increase in activation temperature, as inferred from the opening of the knee of the isotherm and the higher slope of the plateau [7].

In order to discuss the influence of the variation in activation parameters explicitly, the isotherms of N_2 adsorption on different carbons were obtained and employed to deduce the surface characteristics of these carbons. The effects of the carbonization temperature, the chemical ratio of KOH to resin, and the carbonization time and heating rate were explored, and the data are presented in Tables 2, 3 and 4, respectively.

The yield of the final carbon products was found to vary with the activation parameters. Table 2 shows that the carbon yield is a decreasing function of the carbonization temperature. The decrease in carbon yield at low temperatures (<700°C) can mainly be attributed to the increased volatile evolution with temperature [22], whereas the

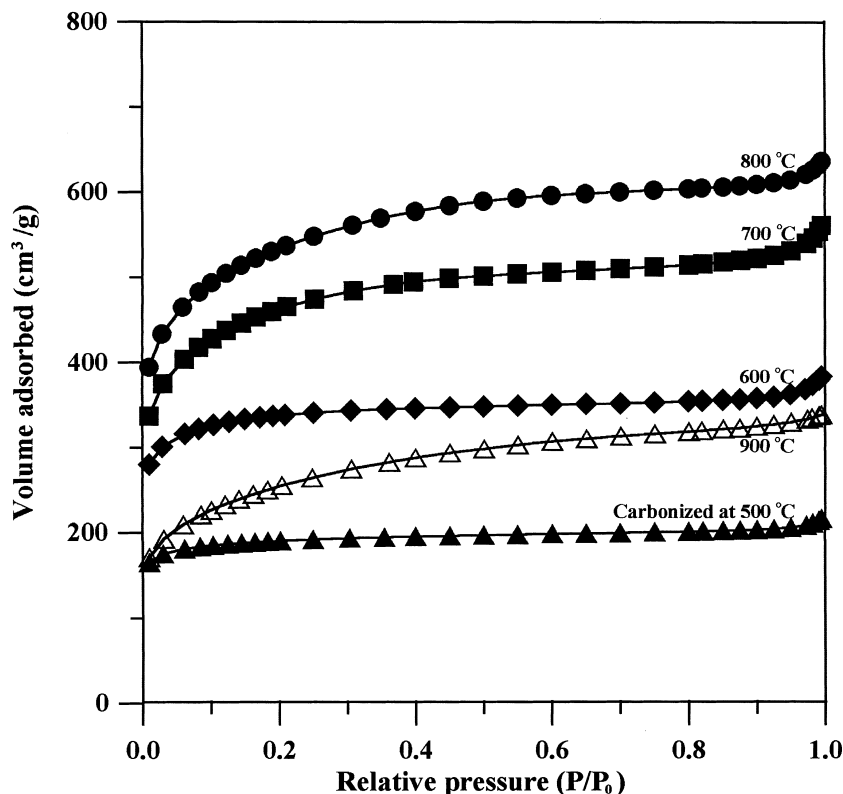


Fig. 1. Adsorption isotherms of N_2 on carbons prepared from carbonization of KOH-treated resins at different temperatures (prior to carbonization, which lasted for 2 h at the carbonization temperature, the resins were impregnated with KOH to obtain a chemical ratio of 2).

Table 2

Effects of carbonization temperature on the surface characteristics of the carbons from phenol–formaldehyde resins with KOH activation^a

Carbonization temp. (°C)	Carbon yield (%)	BET SA (m ² /g)	Pore vol. (cm ³ /g)	Pore size distribution (%)		Average pore diameter (nm)
				Micro	Meso	
500	63	640	0.32	92	8	2.0
600	46	1140	0.57	94	6	2.0
700	29	1590	0.84	88	12	2.1
800	19	1840	0.96	88	12	2.1
900	13	900	0.52	77	23	2.3

^a The activation was performed by impregnating the resins with a KOH/resin ratio of 2, followed by heating the sample to the carbonization temperature at a heating rate of 30°C/min and maintaining the temperature for 2 h before cooling.

Table 3

Effects of the chemical ratio (KOH/resin) on the surface characteristics of the carbons from phenol–formaldehyde resins with KOH activation^a

Chemical ratio	Carbon yield (%)	BET SA (m ² /g)	Pore vol. (cm ³ /g)	Pore size distribution (%)		Average pore diameter (nm)
				Micro	Meso	
0	55	200	0.09	100	0	1.8
1	54	1170	0.58	95	5	2.0
2	29	1590	0.84	88	12	2.1
4	21	2220	1.16	82	18	2.1

^a The carbonization was performed by heating the impregnated sample to a carbonization temperature of 700°C at a heating rate of 30°C/min and maintaining the temperature for 2 h before cooling.

decrease at higher temperatures is attributable to carbon gasification by CO₂ or oxygen in the alkali [9,16]. It has been reported that, at high temperatures, the release of CO₂ from K₂CO₃ formed during carbonization becomes significant [16]. The evolved CO₂ can react with carbon atoms to open up closed pores and enlarge existing micropores, resulting in an increase in porosity. Apart from the gasification by CO₂, at temperatures higher than 700°C,

potassium-containing compounds (such as K₂O and K₂CO₃) can be reduced by carbon to form K metal [17,23,24], thus causing carbon gasification, as well as oxidation.

Because of the gasification mechanisms, the carbon yield was found to decrease with an increase in chemical ratio and in carbonization time, as shown in Tables 3 and 4, respectively. In Table 3 the final carbons were obtained

Table 4

Effects of carbonization time and heating rate on the surface characteristics of the carbons from phenol–formaldehyde resins with KOH activation^a

Carbonization time (h)	Carbon yield (%)	BET SA (m ² /g)	Pore vol. (cm ³ /g)	Pore size distribution (%)		Average pore diameter (nm)
				Micro	Meso	
<i>Heating rate 17.5°C/min</i>						
2	20	2120	1.03	93	7	1.9
<i>Heating rate 30°C/min</i>						
0	28	1630	0.79	96	4	1.9
1	25	2070	1.05	88	12	2.0
2	21	2220	1.16	82	18	2.1
3	18	2120	1.14	76	24	2.2
<i>Heating rate 60°C/min</i>						
2	22	2270	1.21	80	20	2.1

^a The activation was performed by impregnating the resins with a chemical ratio of 4, followed by heating the sample to a carbonization temperature of 700°C.

by carrying out the carbonization at a fixed temperature of 700°C for 2 h. Carbonization experiments with chemical ratios >4 were also conducted at 700°C, but the results are not presented here. It was found that, at a chemical ratio of 6, the carbon yield was only 7% for a carbonization time of 1 h and the carbon was completely gasified after 2 h of carbonization. These data suggest that carbon loss resulting from gasification should be considered as an important issue in KOH activation.

As for the variation of surface characteristics with activation parameters, it can be seen from Table 2 that both surface area and pore volume increase with increasing carbonization temperature to a maximum at 800°C, and then decrease with further increase in temperature. The increase in porosity on raising the temperature from 500 to 800°C can be attributed to enhanced carbon gasification, as well as the release of volatiles, leaving a space that was previously occupied by the decomposed materials [20,22]. In addition, the metallic potassiums formed at high temperatures may also intercalate to the carbon matrix, resulting in an increase in pore volume [24].

At temperatures higher than 800°C, the surface area and pore volume were found to decrease with carbonization temperature. The decrease can be attributed to the severe thermal treatment which causes the breakdown of cross-links in the carbon matrix, with a consequent rearrangement of carbonaceous aggregates and the collapse of pores. It is also possible that the extensive gasification at high temperatures results in the destruction of pore structures [13].

In addition to the temperature, increasing the chemical ratio and the carbonization time also results in enhanced carbon gasification, and thus higher porosity development, as reflected in Tables 3 and 4, respectively. In Table 4, at a heating rate of 30°C/min, the slight decrease in porosity with increased carbonization time from 2 to 3 h implies that the extensive gasification of carbon particles to diminish the porosity becomes appreciable [13].

It is shown in Fig. 1 that the pore structures developed by KOH activation are mainly microporous. However, Table 2 shows that the proportion of mesopore volume generally increases with an increase in carbonization temperature, especially at high temperatures. This increase at high temperatures can be attributed to pore enlargement caused by gasification, since pore widening, rather than pore deepening, is the favored mechanism at high temperatures [14]. Because of the increase in mesopore fraction, a corresponding increase in average pore diameter with carbonization temperature can be observed.

How the pore size distribution varies with the chemical ratio and the carbonization time is also shown in Tables 3 and 4. It can be seen that the increase in the values of these two parameters results in a decrease in the proportion of micropore volume, and a corresponding increase in the mesopore fraction and average pore diameter. Again, these observed trends can be explained by the fact that carbon

gasification is enhanced by the increased KOH impregnation and the extended carbonization time, thus causing the removal of carbon atoms on pore walls to widen the micropores.

The effects of heating rate on the surface characteristics of the resulting carbons are also revealed in Table 4 for a carbonization time of 2 h. The data show that the carbon yield, surface area and pore volume increase with increasing heating rate. It is generally agreed that mass transfer limitations play an important role in determining the rate of escape of tar during coal carbonization [25], and the situation is most likely to be similar for the carbonization of phenol–formaldehyde resins. Under these circumstances, the increase in heating rate implies a higher concentration of tar precursors in the particle, thus allowing a larger fraction to be repolymerized into the solid structure. The enhanced repolymerization would result in an increase in carbon yield with heating rate, as shown in Table 4. Once reincorporated into the solid matrix, the tar precursors can promote the formation of cross-links that would retard structure contraction upon heating to high temperatures. Thus, similar to the carbon yield, the surface area, pore volume, mesopore fraction and average pore diameter were found to be increasing functions of the heating rate, as shown in Table 4. However, based on the data in Table 4, the heating rate should be considered as a parameter of minor importance that affects the properties of the carbon products during activation.

3.2. Effects of carbon burn-off in physical activation

In physical activation the carbons obtained from carbonization of the resins were subjected to gasification in CO₂ at 900°C, in order to increase the surface area and pore volume of the carbons. Variations in surface area and pore volume with carbon burn-off during physical activation are normally taken as the essential characteristics of a particular activation process.

Adsorption isotherms of N₂ on the physically activated carbons, with different degrees of burn-off, are shown in Fig. 2. The horizontal plateaus of the isotherms reflect that these carbons are mainly microporous. However, as the gasification proceeds there is a widening of the porosity, as inferred from the opening of the knee of the isotherm and the higher slope of the plateau [7]. The adsorption capacity of the carbons generally increases with the extent of burn-off, indicating that most of the gasification and pore development occur inside the carbon particles.

The isotherms in Fig. 2 were employed to deduce the surface characteristics of the carbons, and the results are shown in Table 5. It can be seen from the table that the surface area, pore volume, mesopore fraction and average pore diameter show a monotonical increase with the extent of burn-off, even at high extents of burn-off, indicating that gasification mainly results in the opening of closed pores as well as deepening and widening of the micro-

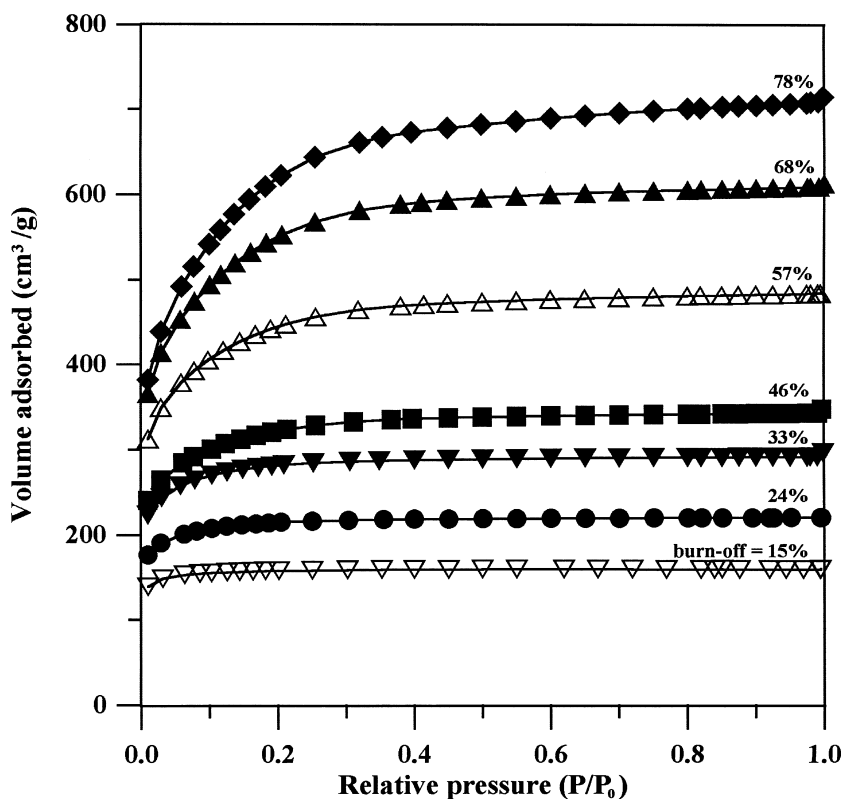


Fig. 2. Adsorption isotherms of N_2 on the carbons prepared from phenol-formaldehyde resins with CO_2 activation at $900^\circ C$ to various degrees of burn-off.

pores, and the breaking through of pore walls is not an important mechanism [26]. The pore size distribution shows that physically activated carbons have a lower mesopore fraction than chemically activated carbons. The presence of alkali to retard structure contraction during carbonization may be the reason for the higher proportion of mesopore volume in chemical activation.

The data in Table 5 indicate that carbons with high surface area and pore volume can be produced from resins with CO_2 activation. However, in comparison with the chemical activation process, at similar porosity levels the carbon yield during physical activation was found to be lower than that with chemical activation. This can be attributed to the fact that the dehydrogenation properties of

Table 5

Surface characteristics of the carbons from phenol-formaldehyde resins with CO_2 activation^a to various degrees

Char burn-off (%)	Carbon yield (%)	BET SA (m^2/g)	Pore vol. (cm^3/g)	Pore size distribution (%)		Average pore diameter (nm)
				Micro	Meso	
0	54	66	0.028	100	0	1.7
8	50	370	0.17	100	0	1.9
15	46	530	0.25	100	0	1.9
24	41	720	0.34	100	0	1.9
33	36	960	0.45	100	0	1.9
46	29	1100	0.53	96	4	1.9
57	23	1540	0.75	95	5	1.9
68	17	1940	0.94	93	7	1.9
78	12	2220	1.10	90	10	2.0

^a The activation was performed by carbonizing the resins at $900^\circ C$, followed by gasifying the resulting char at the same temperature.

the alkali decrease pyrolytic decomposition during chemical activation.

3.3. Comparison of the external surfaces of porous carbons

Scanning electron micrographs (SEMs) of the external structures of the porous carbons prepared using physical and chemical methods are compared in Fig. 3. Figs. 3a,b show typical SEMs of carbons prepared from KOH activation at different temperatures, whereas an example of an SEM of carbons activated by CO_2 is shown in Fig. 3c.

It can be seen from these micrographs that the external surface of the carbon activated by KOH at 700°C is full of cavities. It seems that the cavities result from the removal of impregnated KOH and KOH-derived compounds, leaving the space previously occupied by the compounds. Highly rugged surfaces are normally observed for carbons prepared from chemical activation of bituminous coals, using reagents such as ZnCl_2 and H_3PO_4 [20,21]. On the other hand, Fig. 3b shows that the carbon activated by KOH at 900°C does not exhibit obvious cavities on its external surface, reflecting that, at high temperatures, caking and agglomeration occur on the carbon structure,

thus smoothing the surface. Because of the void structure, mechanical properties such as hardness and abrasion resistance should be carefully evaluated for producing porous carbons from KOH activation.

As for the physically activated carbon, Fig. 3c shows that, unlike the chemically activated carbons, it has a compact external structure with a number of pits distributed over the surface, indicating that most pore development occurs inside the particle.

4. Conclusions

This study has demonstrated that microporous carbons with high porosities can be prepared from phenol–formaldehyde resins, using both chemical and physical activation processes. Chemical activation with KOH produces porous carbons having surface areas and pore volumes as high as $2300 \text{ m}^2/\text{g}$ and $1.2 \text{ cm}^3/\text{g}$, respectively, while an area of $2200 \text{ m}^2/\text{g}$ and a volume of $1.1 \text{ cm}^3/\text{g}$ can be achieved by physical activation with CO_2 .

The effects of different parameters during chemical activation were investigated. The carbon yield was found to decrease with carbonization temperature and time and

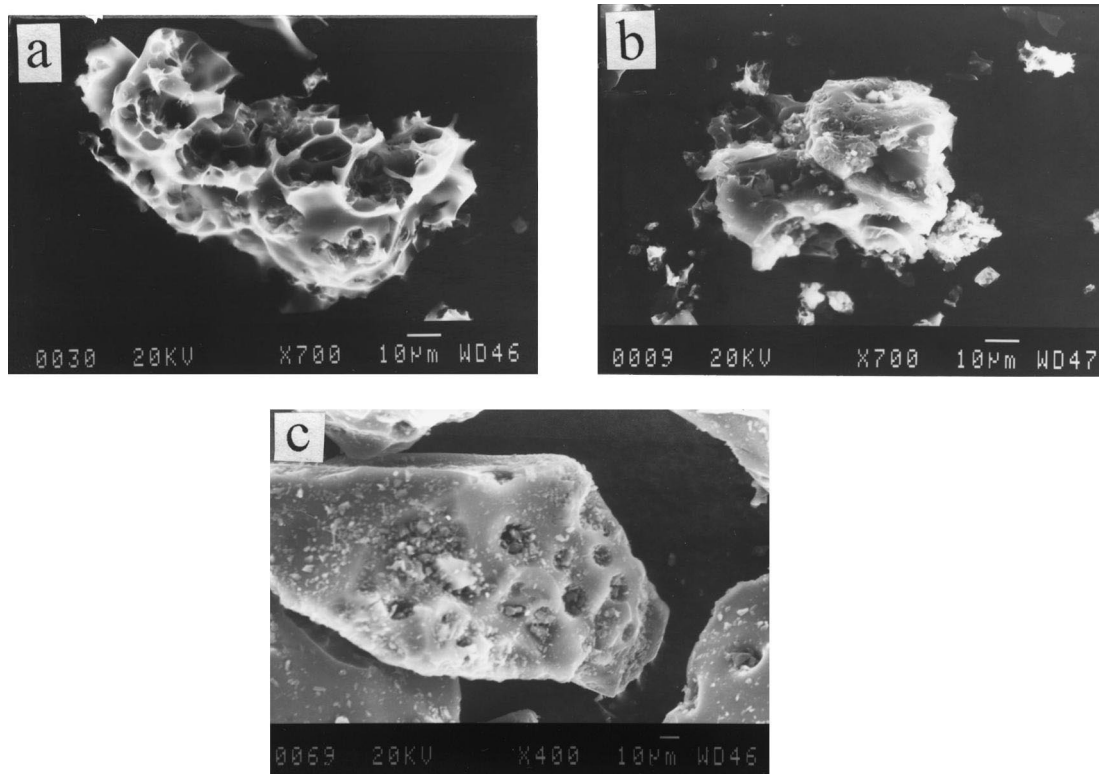


Fig. 3. SEMs of carbons prepared by: (a) chemical activation with a KOH/resin ratio of 2 and a carbonization process at 700°C for 2 h; (b) chemical activation with a KOH/resin ratio of 2 and a carbonization process at 900°C for 2 h; (c) physical activation at 900°C in CO_2 with a burn-off level of 33%.

the KOH/resin ratio, and to increase with heating rate. At a KOH/resin ratio of 2 and a carbonization time of 2 h, both the surface area and pore volume of the resulting carbons increase with carbonization temperature to a maximum at a temperature of 800°C and then begin to decrease with temperature, whereas the proportion of mesopore volume generally increases with temperature. Under the experimental conditions investigated, the surface area, pore volume and mesopore fraction were found to be increasing functions of the KOH/resin ratio, the carbonization time and the heating rate. It is recommended, based on the results of the present work, that a KOH/ratio of 4, a carbonization temperature of 700°C and a carbonization time of 2 h are the optimum parameter values for producing high surface area carbons by KOH activation.

Physical activation of resin chars with CO₂ at 900°C shows that the surface area and pore volume are increasing functions of the extent of carbon burn-off. The carbons produced are mainly microporous, and a slight increase of the average pore size with the extent of burn-off was found. At similar porosity levels the carbon yield during physical activation was found to be lower than that with chemical activation. Comparison of the external surfaces of the resulting carbons shows that the carbons prepared from CO₂ activation have a more compact surface than those produced from KOH activation.

Acknowledgements

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