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Effects of Burn-off and Activation Temperature on Preparation of Activated Carbon from Corn Cob Agrowaste by CO_2 and Steam

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Previous studies have successfully demonstrated that corn cob is a suitable precursor for production of good activated carbon by chemical activation. However, respond to the need for cleaner production, this study focuses on the physical activation by gasifying agents such as CO_2 and steam. The activation temperatures under investigation are 1073 and 1173 K. Within the limit of 50 wt% burn-off, experimental results reveal that the BET surface area, pore volume, and average pore diameter of the resulting activated carbon generally increase with the extent of burn-off in both gasifying agents and at both temperatures. The higher activation temperature can overcome the drawbacks of a longer period of activation required to attain larger surface area and can offer higher potential to produce activated carbon of greater adsorption capacity from agriculture wastes such as corn cobs. Additionally, the BET surface areas of properly prepared activated carbons can satisfy commercial requirements, when compared with commercial activated carbon. The BET surface areas of the activated carbons after about 71 and 59 wt% burn-off of CO_2 and steam activations at 1173 K are 1705 and 1315 m^2/g, respectively, indicating high adsorption capacities. Thus, it is feasible to produce high-quality microporous activated carbon from corn cob agrowaste using N_2 carbonization followed by physical activation with CO_2 or steam. © 2000 Academic Press

Key Words: burn-off; activation; activated carbon; corn cob; carbon dioxide activation; steam activation.

INTRODUCTION

Activated carbons are widely used as highly porous industrial adsorbents for separation, purification, and recovery processes. Over the past few years, numerous studies have been made on the precursor materials and preparation methods of activated carbon from biomass. Any inexpensive material with high carbon content, but low inorganics, can be used as raw material for the production of activated carbon (1). As is generally recognized, there are two different processes for the preparation of activated carbon, namely, physical activation and chemical activation. Chemical activation is performed in only one step for carbonization and activation at low temperatures (e.g., 673–1073 K) (1). Physical activation involves the carbonization of

a carbonaceous precursor followed by the gasification of the resulting char in the presence of suitable oxidizing gasifying agents such as CO_2 and steam at high temperatures (e.g., 1073–1373 K) (1). In chemical activation, the precursor materials are impregnated with chemical agents such as $ZnCl_2$ and H_3PO_4 to inhibit the formation of chars, reduce the evolution of volatile matter, and enhance the yield of the resulting activated carbon. In our previous works (2, 3), the agricultural byproduct corn cob was used as the precursor material through chemical preparation with $ZnCl_2$. The BET surface areas of the resulting activated carbons were greater than 1400 m^2/g. It is obvious that the agricultural byproduct corn cob was a suitable carbonaceous precursor for the production of activated carbon. However, chemically activated carbon has considerable inorganic content, which may cause environmental contamination. In order to heed the appeal for cleaner production, physical activation is more favorable than chemical activation.

The purpose of this study is to investigate the feasibility of using physical activation to manufacture activated carbon from the agricultural byproduct corn cob. Process parameters, such as gasifying agents, activation temperatures, and burn-off, on system performance and the characteristics of resulting activated carbon are examined in this paper.

EXPERIMENTS AND METHODS

Precursor Material

Corn cob was ground and sieved to the size of 12–16 mesh (i.e., 1.19–1.68 mm) and dried at 378 K overnight before carbonization. A typical analysis of corn cob was as follows: moisture, 4.3 wt%; volatiles, 78.7 wt%; fixed carbon, 16.1 wt%; ash, 0.9 wt%. A typical elemental analysis of corn cob was as follows: C, 45.21 wt%; H, 6.12 wt%; N, 0.94 wt%; O, 47.73 wt%. The results reveal that corn cob has high carbon, but low ash, content, which makes it a good precursor material for adsorbents.

Experimental Apparatus and Methods

The apparatus and experimental methods used for physical activation were similar to those for chemical activation, as reported previously (2, 3).

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Carbonization. About 10 g of corn cob was put into a stainless steel crucible (i.d. 45 mm) and heated at 10 K/min from 303 K to a specific temperature (1073 or 1173 K) under a constant N_2 stream of 200 cm^3/min (measured at room temperature).

Activation. The char obtained from carbonization was followed by activation at the final carbonization temperature for the specified time. For the activation agent, CO_2 (purity of 99.99%), the flow rate was maintained at 200 cm^3/min (measured at room temperature). In the steam runs, water flow rates of 0.6 and 0.05 g/min at activation temperatures of 1073 and 1173 K, respectively, were maintained by a syringe pump (Model 355, Sage Instruments). The water was injected into a quartz reactor wrapped with a heating belt (catalog no. HT353, Electrothermal Engineering Ltd.) to produce water vapor by evaporation, using N_2 at a flow rate of 100 cm^3/min (measured at room temperature) as a carrier gas. The subsequent experiments were conducted to different burn-off levels, which are defined as the difference between the masses before and after activation and are a function of activation time (i.e., soaking time). All flow rates were metered precisely to the experimental reactor system using mass flow rate controllers (Model HFC202, Hastings Instruments).

For characterization measurements, the resulting char and activated carbon were mixed with 100 cm^3 of 3 N HCl and stirred at 250 rpm for 1 h. After filtration, the sample was washed with deionized water and then dried in a vacuum oven at 378 K.

Characterization measurements. Specific surface areas and pore volumes of the resulting chars and activated carbons were determined by N_2 gas adsorption at 77 K with an automated adsorption instrument (ASAP 2000, Micromeritics). Prior to the determination of isotherm analysis, the sample (about 0.2 g) was degassed for 24 h at 573 K in a vacuum of about 10^{-5} mmHg to remove moisture and other volatiles from the sample.

The specific surface areas (A_B) of the resulting chars and activated carbons were obtained by the standard BET method applied in a relative pressure range from 0.06 to 0.2. The total pore volume (V_t) was obtained by converting the amount of N_2 gas adsorbed (expressed in cm^3/g STP) at a relative pressure of 0.99 to the volume of liquid adsorbate. The average pore diameter ($\approx 4V_t/A_L$) can be estimated according to the Langmuir surface area (A_L) and the total pore volume, by assuming that the pores are straight, cylindrical, and not interconnected and that they have the same diameter and depth (4). The micropore surface area (A_i) and volume (V_i) were determined by the t-plot method (5).

RESULTS AND DISCUSSION

Carbonization and Activation

From our previous study (6), the pyrolysis of corn cob at a heating rate of 10 K/min under a N_2 stream can be divided into three regions: 373–523, 523–673, and 673–1273 K. The peaks of evolution rates of volatiles were sharp before 673 K. The curve of mass losing rate was gradually smooth after 673 K. The results showed that when the temperature of carbonization was higher than 673 K, the resulting chars became richer in carbon and had built the fundamental porous structure. The porosity of resulting char was not obtainable because disorganized materials resulting from the deposition and decomposition of tar filled or blocked the pores of the resulting char (7). As is widely known, activation with steam and CO_2 as gasifying agents involves the C–H_2O and C–CO_2 reactions, respectively, resulting in the removal of carbon atoms and causing the main weight loss of the resulting char (7). This is the chief mechanism of development of micropore volume and diameter in the resulting char. The extent of activation of the resulting char depends on the extent of burn-off, as shown in Table 1. The correlation coefficients (r^2) of plots of burn-off vs soaking time in all cases are greater than 0.98, when applying least-squares regression analysis. This indicates that the slopes representing the gasification burn-off rates for the four cases studied are almost constant throughout the entire experimental range. For the CO_2 activation, the rate of activation at 1173 K is about four times faster than that at 1073 K. In addition, it also indicates a similar tendency (about 2.5 times) for the steam activation, although the amount of water at 1173 K is 1/12th that at 1073 K. As a result, activation temperature is more important in controlling activation extent than the concentration of gasifying agents in this study. Regarding the comparison of activation rates between the two gasifying agents, activation rate in steam is faster than that in CO_2 (7), which is consistent with the findings of Walker (8) when dealing with other precursor materials.

Surface and Pore

The characteristics of the resulting activated carbons determined by N_2 gas adsorption at 77 K are illustrated in Table 1. The percentage of microporous volume in total pore volume of the activated carbons is presented in Fig. 1. The surface areas of the chars (i.e., 0% burn-off) at 1073 and 1173 K are 91 and 549 m^2/g, respectively, indicating that the higher temperature char has a more developed pore structure. Also, high temperature can obviously reduce the activation time of the same burn-off. Thus, higher temperature can overcome the drawbacks of a longer period of activation time required to attain a larger surface area and offer higher potential to produce activated carbon of greater adsorption capacity from agriculture waste corn cob. Additionally, the BET surface areas of resulting activated carbons which are properly prepared are close to or larger than the 1000 m^2/g of the commercial activated carbon Calgon F-400. This implies that gasification by CO_2 and steam not only removes the disorganized materials but also efficiently develops microporosity and widens the micropore with increasing burn-off.

The BET surface area (A_B), total pore volume (V_t), and percentage of micropores are all raised with burn-off in the case of CO_2 activation at 1073 K, due to the opening of blocked pores and the development and widening of microporosity. Nevertheless, different results are observed in three other cases. As is

TABLE 1
Characteristics of Resulting Activated Carbons by Nitrogen Gas Adsorption at 77 K

Soaking Time (min)	Burn-off (wt%)	Surface area (m²/g)		Micropore area (A_i) (m²/g)	Pore volume (cm³/g)				Average pore diameter (Å)[b]
		Langmuir (A_L)	BET (A_B)		Total (V_t)	Micro (V_i)	Meso[a] (V_e)	Macro[a] (V_a)	
				CO₂ activation at 1073 K (□)					
0	0	NA[c]	91	21	0.022	NA[c]	0.012	0.010	9.6[d]
20	1.34	543	405	302	0.194	0.140	0.033	0.021	14.3
40	6.94	634	473	392	0.245	0.184	0.043	0.018	14.4
60	9.41	814	608	497	0.297	0.234	0.051	0.012	14.6
90	16.64	883	658	572	0.324	0.269	0.053	0.002	14.7
120	29.39	924	670	578	0.342	0.284	0.056	0.002	14.8
				Steam activation at 1073 K (■)					
20	2.90	762	568	495	0.275	0.234	0.031	0.010	14.4
40	22.10	1106	823	701	0.411	0.331	0.066	0.014	14.6
60	31.34	1213	897	725	0.452	0.339	0.099	0.014	14.9
90	38.20	1279	930	763	0.483	0.362	0.108	0.013	15.1
120	60.20	1341	998	819	0.511	0.382	0.117	0.012	15.2
				CO₂ activation at 1173 K (○)					
0	0	698	549	466	0.251	0.216	0.030	0.005	14.4
20	19.35	758	569	471	0.277	0.220	0.033	0.002	14.6
40	35.38	1297	863	555	0.441	0.285	0.185	0.004	14.6
60	46.96	1441	1014	697	0.545	0.343	0.197	0.005	15.1
80	71.26	2295	1705	1000	0.884	0.452	0.404	0.028	15.4
				Steam activation at 1173 K (●)					
20	22.76	918	685	600	0.337	0.283	0.038	0.016	14.7
30	32.77	1356	1006	861	0.501	0.406	0.082	0.013	14.8
40	45.97	1617	1201	965	0.600	0.452	0.129	0.019	14.8
50	59.28	1774	1315	1035	0.657	0.485	0.148	0.024	14.8
60	67.88	1443	1063	847	0.536	0.399	0.0119	0.018	14.9
				Calgon F-400					
—	—	1391	1026	627	0.614	0.289	0.288	0.037	17.65

[a] Calculated by using $V_t - V_i = V_e + V_a$, with the Barrett–Joyner–Hanlenda (BJH) adsorption pore distribution, which gives the proportions of mesopore to macropore volumes.
[b] Calculated by using $4V_t/A_L$.
[c] NA, not available.
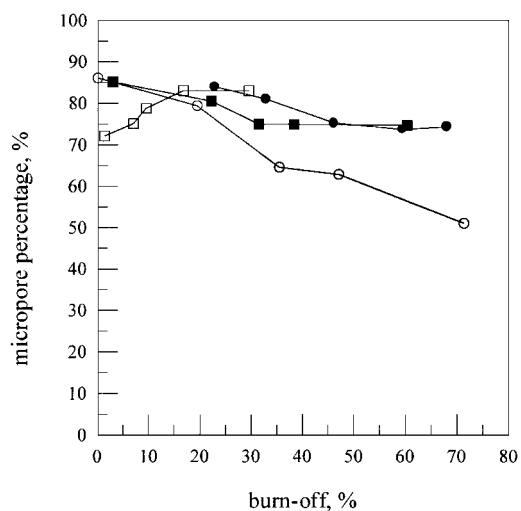[d] Calculated by using $4V_t/A_B$.

FIG. 1. Relation between percentage of microporous volume in total pore volume and burn-off (see Table 1 for symbols).

widely known, the microporosity of the resulting chars can be effectively developed during the activation, and the specific surface area (A) and pore volume (V) commonly increase with soaking time and burn-off. However, in the case of steam activation at 1173 K, the surface area and total pore volume at 60 min of soaking time are smaller than those at 50 min. This may be attributed to the fact that, for the burn-off at 60 min, destruction of high porosity by external ablation of carbon particles is more pronounced than development and widening of microporosity (7). As a result, the BET surface area and total pore volume are reduced at 60 min. In the case of steam activation at 1073 K and CO₂ activation at 1173 K, the BET surface areas increase while the percentage of micropore volume decreases with increase of burn-off, indicating not only the development of microporosity but also the great widening of microporosity due to reactions of crystallites on the opened walls with gasifying agents. The increases of pore size of the activated carbons in these two cases (Table 1) agree with the deduction of the percentage of micropore volume. In summary, the characteristics of the activated
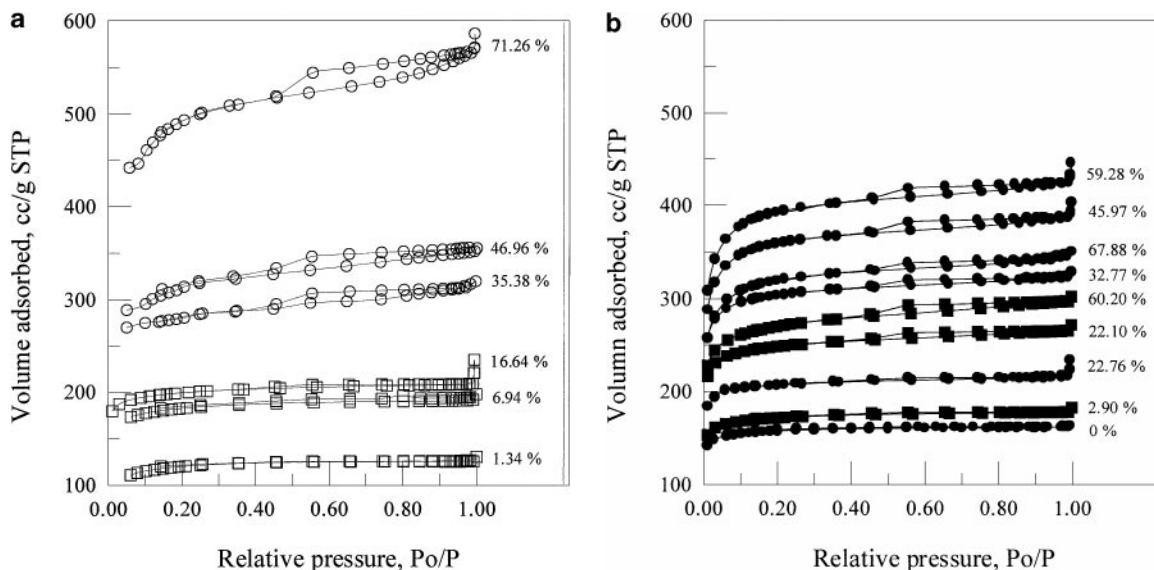
FIG. 2. Adsorption and desorption isotherms of N_2 at 77 K of activated carbons at various extents of burn-off (see Table 1 for symbols): (a) from CO_2 activation; (b) from steam activation.

carbons, such as the BET surface area, pore volume, and average pore diameter, increase with extent of burn-off, within the limit of 50 wt% burn-off.

Comparison of the results with different gasifying agents at 1173 K indicates that the activated carbons obtained with steam activation have greater microporosity (micropore volume) and smaller pore diameter at the same BET surface areas. In this study, using steam in N_2 with a concentration of 40 vol% as the gasifying agent was more favorable in producing an activated carbon of greater microporosity than pure CO_2. Similar experimental results were reported by Rodriguez-

Reinoso and Molina-Sabio (7) for olive stone with pure CO_2 and steam–N_2 mixture (10 vol%) activations. They attributed the great development of microporosity when using steam activation to the low partial pressure of steam, which would produce a more selective attack on the carbon structure, while in the case of pure CO_2, the much higher concentration was less selective.

Figures 2a and 2b present the adsorption and desorption isotherms of N_2 on activated carbons obtained with CO_2 and steam activation, respectively. It is seen that the adsorption isotherms of N_2 for adsorbed volume below or near 200 cm^3/g
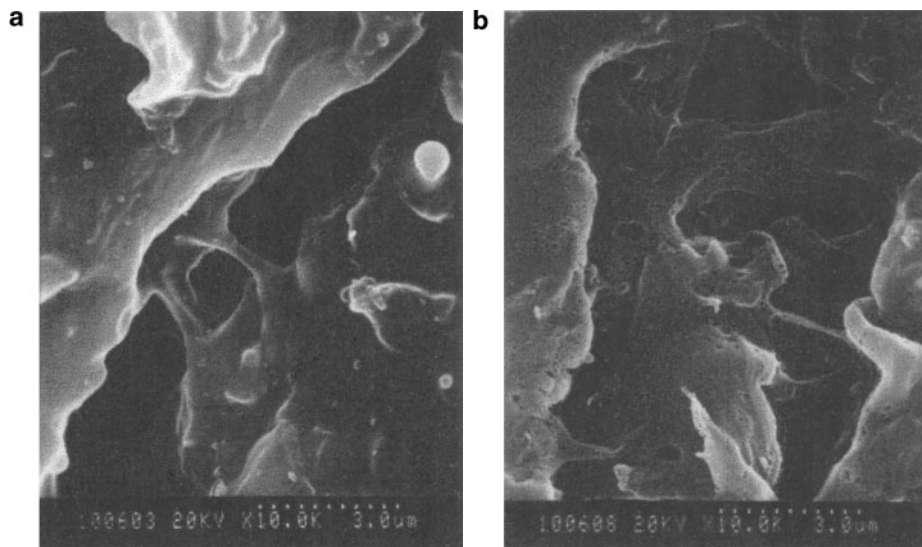

FIG. 3. SEM of activated carbons obtained with CO_2 activation: (a) 29 wt% burn-off at 1073 K; (b) 47 wt% burn-off at 1173 K.

STP belong to Type I of the BDDT (Brunnauer–Deming–Deming–Teller) classification with well-defined plateaus, supporting that the pores are microporous. With increasing N_2 adsorbed volume, the adsorption isotherms change to Type II, representing that the original micropores are transformed into mesopores with increasing burn-off. In addition, the adsorption–desorption curves show hysteresis loops at high extents of burn-off. The lower curves in both figures are Type H4 in the IUPAC classification, with nearly parallel branches, being an indication of microporosity (5), while the upper curves resemble a combination of Types H3 and H4. Both Types H4 and H3 stand for the existence of slit-shaped pores.

Scanning Electron Microscopy

Scanning electron micrographs of the surface structures of 29 wt% burn-off at 1073 K and 47 wt% burn-off at 1173 K from CO_2 activation are illustrated in Figs. 3a and 3b, respectively, showing a great difference between these two activated carbons. The former has a smoother surface, while the latter displays a much more rough and irregular surface structure. This indicates a gross attack on the exterior surface and interior pore wall at high temperature and burn-off. As a result, it effectively creates new pores and increases the total pore volume and surface areas (i.e., greater adsorption capacity) as illustrated in Table 1.

CONCLUSIONS

The BET surface areas of the activated carbons obtained in this study can satisfy the commercial requirement, compared with Calgon F-400. The largest BET surface area obtained from the resulting activated carbons by CO_2 activation at 1173 K with about 71 wt% burn-off is 1705 m^2/g. In addition, the higher activation temperature has a higher potential to produce an activated carbon of greater adsorption capacity. The levels of development and widening of microporosity depend on the activation temperature, activation time, and gasifying agents. Comparison of all resulting activated carbons indicates that steam activation at 1173 K with low water flow rate can produce microporous activated carbons, while CO_2 activation at 1173 K is able to manufacture mesoporous activated carbons. From the foregoing, it is obvious that agricultural byproduct corn cob is a suitable carbonaceous precursor for the production of activated carbon by physical activation using CO_2 or steam, plus, of course, chemical activation.

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