PREPARATION OF ACTIVATED CARBON FROM FOREST AND AGRICULTURAL RESIDUES THROUGH CO_2 ACTIVATION

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Activated carbons are highly porous materials that have found numerous applications such as adsorbents, catalysts, and catalyst supports; in fact, the market for activated carbons is significant. The global consumption of activated carbons was 750,000 tons in 2002. The estimated growth of worldwide demand is 4-5% per year, with higher growth rates of 5-6% per year projected for the U.S. between 2002 and 2005. Currently, activated carbons are manufactured from a variety of starting materials, *i.e.*, precursors, including different types of wood, nutshells, grains, coal, and polymers. These precursors are usually high in carbon content.

Carbon precursors attain commercially viable surface areas almost always through physical or chemical activation. The bulk of the internal surface area is present in the micropores of the carbon. High surface areas are required for high sorptive capacities. In industrial practice, physical activation is carried out most frequently by burning off some of the raw carbon in an oxidizing environment to create micropores. The usual commercial choices of activation gas are steam, CO_2, air, or their mixtures. Activation normally takes place at temperatures between 700 and 1000 °C in steam and CO_2, and lower temperatures in air. Chemical activation was not considered in the current work, because it entails the addition of materials such as zinc salts or phosphoric acid to the carbon precursors, thereby possibly generating secondary environmental pollution during disposal.

In the present study, CO_2 was selected as the activation gas: CO_2 is clean and easy to handle. Moreover, CO_2 has been a preferred choice as the activation gas on the laboratory scale: it facilitates control of the activation process due to the slow reaction rate at temperatures around 800 °C. (Rodríguez-Reinoso, 1991). González *et al*. (1997) conducted their investigation of CO_2 activation with both vertical and horizontal furnaces. They have concluded that a horizontal furnace is advantageous for the micropore development.

Significant quantities of forest and agricultural residues are not recycled; consequently, they are wasted. The aim of this study is to investigate the conversion of some of these abundant forest and agricultural residues into high quality activated carbons that might be commercially viable. The residues that served as precursors included oak wood waste, corn hulls, and corn stover. Table 1 lists the elemental analysis of each precursor. The table reveals that these residues are high in carbon content; this indicates that they are suitable precursors for preparing activated carbons.

The residues were fed into a fluidized sand-bed reactor, operating at approximately 500 °C, with inert nitrogen as the fluidizing agent. The typical residue feed rate was 7 kg/hr. The process typifies fast pyrolysis because of the high heating rates of the rather small particles (less than 1mm). Once the residue was fed into the sand bed, it pyrolyzed; the resulting gas stream and entrained fine char exited the freeboard of the reactor and entered two heated cyclones in series. The cyclones were enclosed in a heated jacket at 450 °C. The vast majority (95%+) of the char was collected in the first cyclone. At the end of the run, the char was removed from the cyclone collection bins, weighed, and sealed in containers. The remaining hot gas flow continued through a set of condensers and exited the system. The resulting char yields from oak, corn hulls, and corn stover were 10%, 32%, and 22%, respectively. Table 1 also lists the results of elemental analysis of the resultant char obtained from each precursor. It is clear that the carbon content of char was significantly higher after carbonization, and the oxygen and hydrogen were lower. The surface areas and total pore volumes for the chars obtained were very low as listed in Table 2.

Table 1. Elemental analysis of raw materials and their chars

Elements	Weight percent of elements in the materials					
	corn hull	Corn hull char	corn stover	corn stover char	oak	oak char
C	44.100	70.330	39.980	59.360	45.610	70.840
H	6.975	3.226	5.811	3.060	6.755	3.165
O	41.109	16.733	43.517	16.936	47.209	13.225

Table 2. Properties of Char

	S_{BET} (m^2/g)	V (cc/g)
oak	92	0.1458
corn hulls	48	0.0581
corn stover	38	0.0538

S_{BET}: surface area calculated using the BET equation.

V : total pore volume estimated by converting the amount of N_2 gas adsorbed at a relative pressure of 0.99 to liquid volume of N_2

The activated carbons were obtained through physical activation of char performed in a quartz tube reactor vessel, which was contained in a horizontal three-zone laboratory tube furnace(model HTF55437C, Lindberg/Blue). The reactor's inner diameter was 6 cm, with a length of 60 cm; a quartz boat containing char was positioned centrally within the reactor. The reactor's temperature was regulated with a three-zone temperature control system (model CC58434C, Lindberg/Blue); it contained three independent microprocessor-based digital

temperature controllers. First, about 0.7 g of char was weighed to the nearest one-tenth of a milligram and placed in a thin layer in the sample boat. The boat was then centered in the furnace. The furnace was turned on after CO_2 with a purity of 99.5% purged the system for about two hours to exclude O_2. It took approximately 15 minutes for the furnace to reach the set temperature. After a specified duration for activation, the furnace was turned off. Carbon dioxide continued to flow through the system for about 2 hr until the sample cooled down. The volumetric flow rate of gas was maintained at 24 ml/min (STP) for all experiments. On completion, the resultant activated carbon was weighed to determine the burn-off of the sample. The burn-off refers to the weight difference between the original char and the activated carbon divided by the weight of original char with both weights on a dry basis, i.e.,

$$\text{burn-off} = \frac{W_o - W_1}{W_o} \times 100\% \tag{1}$$

where W_o is the weight of char; and W_1, the mass of the carbon after activation. The activation was performed at temperatures of 700 and 800 °C and activation durations of 1 hr and 2 hrs. Each experiment was replicated 3 to 5 times to ensure the reproducibility of the resultant data.

The N_2-adsorption isotherms of activated carbons at 77 K were obtained with a gas sorption analyzer, Autosorb-1-MP-LP (QUANTACHROME). Each sample's surface area, pore volume, and PSD were determined from nitrogen adsorption data and the Quantachrome software (adsorption data were obtained over the relative pressure, p/p_o, range from 10^{-6} to 1 with nitrogen adsorption at 77 K). Two minutes were allowed for each adsorption point. The samples were degassed under high vacuum at 120 °C for 8 hrs prior to measurement. The surface area, S_{BET}, was calculated using the BET (Brunauer, Emmett and Teller) equation (Yong and Crowell, 1962; Parfitt and Sing, 1976) from selected N_2 adsorption data within the range of relative pressure, p/p_o, from 0.1 to 0.3. The total pore volume, V, was estimated by converting the amount of N_2 gas adsorbed (expressed in cm^3/g STP) at a relative pressure of 0.99 to liquid volume of the adsorbate (N_2). The micropore volume, V_o, was determined according to the DR (Dubinin-Radushkevich) method (Dubinin, 1960; 1967; Dubinin and Stoeckli, 1980). Pore-size distributions were computed by the NLDFT method (Seaton et al., 1989; Lastoskie et al., 1993; 1994; Oliver et al., 1994; Russell, 1994) by minimizing of the grand potential as a function of the fluid density profile.

Table 3 lists the activation conditions, burn-off, BET surface area, total pore volume, micropore volume, and ratio of micropore volume to total pore volume of each sample. Comparison of the data in Tables 2 and 3 reveals that the activation process has a notable effect on the properties of carbons.

Blank experiments were carried out to determine the effects of heating alone. Char placed in N_2 atmosphere was heated under the same experimental conditions as those adopted for the CO_2 activation experiments. Typical results of heat treatment at 700 °C for the duration of 1 hr are listed in Table 4. As can be seen from the data, heat treatment alone led to burn-off about 20% in comparison to 30-50% with CO_2 activation. The surface area, total pore volume, and micropore volume of the resultant activated carbons were significantly lower than those of activated carbons obtained through CO_2 activation. According to Rodríguez-Reinoso et al. (1995), CO_2 can open closed pores as well as widen existing pores by the activation, thus increasing the accessibility of the small pores to the molecules of an adsorbate.

Consequently, nitrogen molecules can more easily penetrate into the interior of activated carbons where the pore structure is well-developed.

Obviously, activated carbons produced by CO_2 activation have much higher BET surface areas than those produced by heat treatment alone. For instance, the surface area for the activated carbons from corn hulls at 700 °C for 1 hr thought CO_2 activation was more than twice of that through heat treatment; the former was 977 m²/g, and the latter, 411 m²/g.

Table 3. Properties of activated carbons through carbon dioxide activation

oak						
activation temperature (°C)	activation time (hr)	burn-off (%)	S_{BET} (m²/g)	V_o (cc/g)	V (cc/g)	V_o/V
700	1	31.8	642	0.2704	0.4113	0.6574
700	2	41.8	644	0.2450	0.4040	0.6064
800	1	43.0	845	0.3212	0.6011	0.5344
800	2	51.4	985	0.3792	0.6403	0.5922
corn hulls						
activation temperature (°C)	activation time (hr)	burn-off (%)	S_{BET} (m²/g)	V_o (cc/g)	V (cc/g)	V_o/V
700	1	32.3	977	0.3352	0.8923	0.3757
700	2	37.0	902	0.3284	0.8223	0.3994
800	1	44.4	1010	0.4348	0.8341	0.5213
800	2	45.2	975	0.3792	0.6803	0.5574
corn stover						
activation temperature (°C)	activation time (hr)	burn-off (%)	S_{BET} (m²/g)	V_o (cc/g)	V (cc/g)	V_o/V
700	1	41.5	660	0.2817	0.4879	0.5774
700	2	41.7	432	0.1818	0.3329	0.5461
800	1	42.6	712	0.2849	0.5494	0.5186
800	2	50.2	616	0.2343	0.4223	0.5548

S_{BET}: surface area calculated using the BET equation.
V_o: micropore volumes determined according to the DR method.
V: total pore volume estimated by converting the amount of N_2 gas adsorbed at a relative pressure of 0.99 to liquid volume of N_2.
V_o/V: the ratio of micropore volume to total pore volume.

Table 4. Properties of Activated Carbons after Heat Treatment at 700 °C for 1 hr in the Flow of N_2

precursor	burn-off (%)	S_{BET} (m^2/g)	V_o (cc/g)	V (cc/g)	V_o/V
oak	20.7%	330	0.1712	0.2610	0.6559
corn hulls	21.2%	411	0.2657	0.4041	0.6573
corn stover	20.8%	368	0.1380	0.3452	0.3998

S_{BET}: surface area calculated using the BET equation.

V_o: micropore volumes determined according to the DR method.

V : total pore volume estimated by converting the amount of N_2 gas adsorbed at a relative pressure of 0.99 to liquid volume of N_2.

V_o/V: the ratio of micropore volume to total pore volume.

Activated carbons with well-developed microporosity and high surface areas can be manufactured from agricultural and forest residues such as corn hulls, corn stover and oak; they can be generated by CO_2 activation of the chars from these residues. The activated carbons produced had BET surface areas ranging from 400 to 1000 m^2/g, and ratios of micropore volume to total pore volume ranging from 0.38 to 0.66. The PSD's of activated carbons, calculated by the NLDFT method, are much narrower than those of the starting chars. The differential pore volume of each of these activated carbons peaks approximately at a pore diameter of 0.5 nm, thereby indicating its potential as a gas adsorbent.

Both the surface area and the nature of porosity are significantly affected by the conditions of activation, the extent of which depends on the nature of the precursors. In general, the higher the activation temperature, the greater the surface areas and micropore volumes of the resultant activated carbons. Nevertheless, various precursors are affected differently by the activation duration. For oak, the longer the activation duration, the greater the adsorption capacity of the resultant activated carbons, and vice versa for corn hulls and corn stover.

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