CHEMICAL AGENTS FOR PRODUCTION OF ACTIVATED CARBONS FROM EXTRUSION COOKED GRAIN PRODUCTS

Chi-Chin Wu, W.P. Walawender, and L.T. Fan
Department of Chemical Engineering, Durland Hall
Kansas State University, Manhattan, Kansas 66506-5102, U.S.A

Introduction

Conventional methods for producing activated carbons can be divided into two categories: physical and chemical activation [1]. In physical activation, the precursor is first carbonized in an inert gas and subsequently activated with CO_2 or steam while in chemical activation, the precursor is usually carbonized and activated simultaneously after impregnation with a chemical activation agent. Chemical activation generally requires lower activation temperature and leads to higher yields and microporosity than physical activation. The most widely used agents are H_3PO_4 and $ZnCl_2$ [1]; alkali salts, e.g., KOH have also been used [2].

This paper explores the production of activated carbons from two precursors, i.e., extrusion cooked products of whole kernels of corn (extruded corn) and wheat flour (breading) by chemical activation with various agents under similar treatment conditions. Unlike the traditional method, the precursor was carbonized at 300°C prior to impregnation with the activation agent. The pore characteristics and yields of the resultant activated carbons were determined and compared to those generated by physical activation [3].

Experimental

Materials

Extrusion cooked grain products, specifically extruded corn and breading, served as the precursors. The former, similar to puffed corn snacks, was sliced into cylindrical pieces approximately 1 cm in diameter as well as in length, and the latter was in the original form of irregularly shaped crumb of approximately 10 mesh. Three activation agents adopted were H_3PO_4, $ZnCl_2$, and KOH; the precursors were impregnated with each agent in a 50 wt % aqueous solution.

Facilities

Carbonization and activation were conducted in a tubular furnace with an I.D. of 10.16 cm and a length of 55 cm under a steady flow of N_2. A wire gauze cylindrical basket served as the sample container. Adsorption experiments were conducted with a gas sorption analyzer. The morphological features of the activated carbons were determined by SEM.

Procedure

The precursor (1-2 g) was initially carbonized at 300°C for 15 min., ground to about 100 mesh, and soaked overnight in about 50 ml of a 50 wt % solution of the activation agent. The impregnated char was filtered, dried and then activated in N_2 at a selected temperature for 10 min. The carbon product was thoroughly washed (with boiling distilled water / dilute HCl), filtered, and dried. The yield was determined as the ratio of the weight of activated carbon obtained to that of the original precursor on the dry basis.

Determination of pore characteristics

Analysis of adsorption / desorption data with N_2 at 77°K generated the values of various parameters characterizing porosity. The total surface area, S_{BET}, was calculated on the basis of the BET equation [4, 5]. The mesopore surface area, S_{meso}, was obtained using the t-method based on the Halsey equation [6]. The micropore volume, V_0, was determined by the D-R equation [7]. The total pore volume, V, was estimated at the highest relative pressure selected, which was close to 1. The pore-size distribution was evaluated from the desorption isotherm and computed by the BJH method [8].

Results and Discussion

Figure 1 shows the variations of the total surface area, S_{BET} of the carbon product with the activation temperature for each agent. Obviously, the activation with H_3PO_4 and $ZnCl$ exhibit similar trends. The microporosity rapidly rose with increasing activation temperature followed by a pronounced decline. With either agent, the maximum S_{BET} was generated approximately at 500°C. In contrast, the

microporosity increased monotonically with increasing temperature for the activation with KOH; moreover, highly microporous carbons were obtained only at high activation temperature at the expense of yield.

The S_{BET} obtained from breading was always larger than that from extruded corn at each activation temperature for every agent examined. The maximum microporosity obtained with any one of the activation agent was much larger than that obtained by physical activation (see Table 1). The yields from the activation with H_3PO_4 and $ZnCl_2$ were also much higher than those from physical activation.
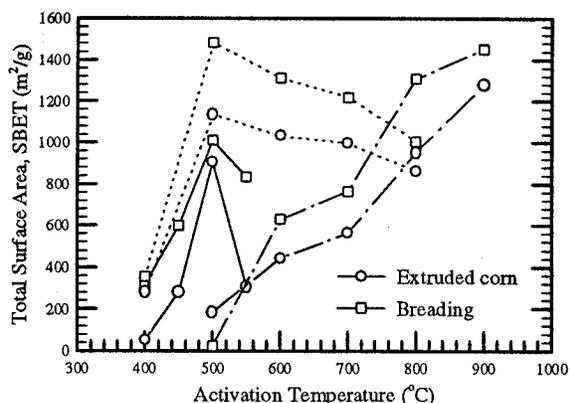

Figure 1. Total surface area, S_{BET}, vs. activation temperature: H_3PO_4 activation (———); $ZnCl_2$ activation (········); KOH activation (——·——).

Table 1. Yield and the maximum porosity of the activated carbons.

Procedure	Precursor	Yield (%)	S_{BET} (m²/g)	V_0 (cc/g)
Physical activation	Extruded corn	6	428	0.214
	Breading	15	580	0.292
H_3PO_4 activation	Extruded corn	29	905	0.333
	Breading	38	1010	0.398
$ZnCl_2$ activation	Extruded corn	30	1132	0.514
	Breading	33	1482	0.581
KOH activation	Extruded corn	9	1280	0.641
	Breading	8	1452	0.667

Conclusions

Activated carbons with S_{BET} of the order of 1,000 m²/g have been obtained from chemical activation of extruded corn with H_3PO_4, $ZnCl_2$ or KOH. With $ZnCl_2$ and KOH, the S_{BET} from breading approached 1,500 m²/g. The results show that all the activated carbons produced in the present work are superior in terms of both the development of microporosity and the yield compared to those obtained by physical activation; moreover, the activation duration is remarkably shorter. Among the activation agents investigated, $ZnCl_2$ produced activated carbons with the highest microporosity at the temperature of 500°C. With this agent, the S_{BET} was 1,132 m²/g with a yield of 30% for extruded corn, and 1,482 m²/g with a yield of 33% for breading.

References

1. Smíšek, M. and Černy, S., *Active Carbon: Manufacture, Properties, and Applications*, Elsevier, Amsterdam, 1970.
2. Marsh, H. and Yan, D. S., *Carbon*, 1984, 22 (6), 603.
3. Wu, C.C., Walawender, W. P., and Fan, L. T., *Carbon in press*.
4. Yong, D. M. and Crowell, A. D., *Physical Adsorption of Gases*, Washington, Butterworths, 1962.
5. Parfitt, G. D. and Sing, K. S. W., *Characterization of Powder Surfaces*, Academic Press, New York, 1976.
6. Halsey, G. D., *J. Chem. Phys.*, 1948, 16, 931.
7. Dubinin, M. M. and Stoekli, H. F., *J. Colloid. Sci.*, 1980, 75, 34.
8. Barrett, E,. P, Joyner, L. G., and Halender, P. P., *J. Am. Chem. Soc.*, 1951, 73, 373.