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Characterization of the Micropore Structure of Activated Carbons by Adsorptions of Nitrogen and Some Hydrocarbons

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ABSTRACT

In the present study the effects of the duration of carbonization and physical activation properties of activated carbon from vegetable materials were investigated. Peanut shells were used to obtain active carbon. These shells were activated chemically with $ZnCl_2$ and/or CO_2 for different times, and the micropore structures of these active carbons were studied by measuring the adsorption isotherms for nitrogen and some hydrocarbons such as benzene, *n*-butane, isobutane, 2,2-dimethylbutane, and isooctane. As the physical activation time was increased, the primary micropores, which were measured at 0.01 relative pressure, were reduced, and they were replaced by larger secondary and tertiary micropores which were measured at 0.15–0.01 and 0.30–0.15 relative pressures. The ratios of the mesopore volume to the micropore volume also increased as the duration of physical activation increased.

Key Words. Activated carbon; Characterization of carbons; Hydrocarbon adsorption

INTRODUCTION

Activated carbons are commonly used in industry for the purification and separation of both gases and solutes in solution. Activated carbons exhibit wide pore size distributions and are known as universal adsorbates. However, activated carbons can show molecular sieve effects like those of zeolitic molecular sieves; the size of the pores can depend on the preparation conditions.

Agricultural by-products are frequently used to prepared activated carbons because they are abundant in some Mediterranean countries, and there may be few or no other applications for these by-products (1).

The adsorption of N_2 and/or CO_2 is commonly used to characterize activated carbons (2). On the other hand, this study illustrates how the use of hydrocarbons with different molecular dimensions can provide a better understanding of the microporosity of activated carbons and the possible molecular sieving that activated carbons can exhibit (3, 4). Several of the lower alkanes have been used from time to time for surface area determination. They possess the virtue of being chemical inert toward the majority of adsorbents, and their saturation pressures are such that (apart from ethane) they can be used at convenient temperatures, usually around ambient (5).

EXPERIMENTAL

The peanut (P) shells were broken and formed into pieces with dimensions of about 2 mm. When the carbonization processes were carried out at various temperatures at a heating rate of $5°C \cdot min^{-1}$, the minimum and maximum carbonization temperatures were determined to be 723 and 1273 K from a graph of the percent weight loss vs temperature. After this pretreatment, the following processes were carried out to obtain carbon and activated carbons;

1. Some peanut shells were only carbonized for 12 hours at 1173 K in air. These activated carbons are labeled P-C.
2. i) Other peanut shells were carbonized for 12 hours and activated chemically for 6 hours (1:1 ratio w:w) with a 10% $ZnCl_2$ solution. These carbons are labeled P-0.
   ii) Other peanut shells were activated chemically for 6 hours (1:1 ratio w:w) with a 10% $ZnCl_2$ solution and then for 1, 4, 6, 8, 10, or 12 hours with CO_2 gas with a $75\ mL \cdot min^{-1}$ flow rate at 1173 K. Activated carbons obtained in this way are labeled P-1, P-4, P-6, P-8, P-10, and P-12, respectively.

The carbon and activated carbons obtained from these processes were crushed to 80 mesh.

To characterize the activated carbons, adsorption isotherms were measured for hydrocarbons such as benzene (B, 298 K), *n*-butane (n-B, 273 K), isobutane (i-B, 273 K), 2,2-dimethylbutane (2,2-DMB, 298 K), and isooctane (i-O, 298 K) (having a purity of 99%) in addition to the isotherm for N_2 (77 K) adsorption in a conventional gravimetric adsorption system using silica spring balances.

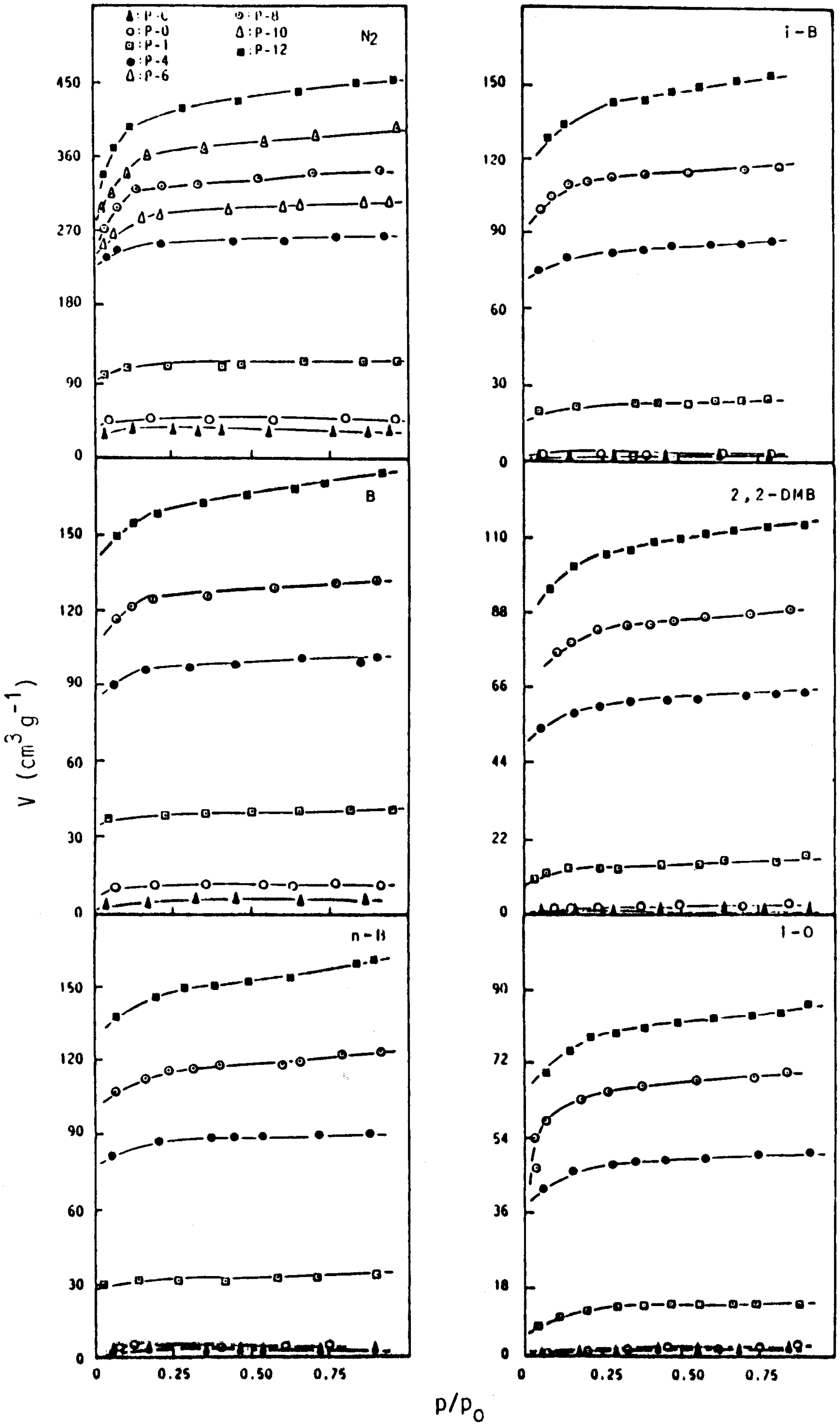

FIG. 1 Adsorption isotherms according to different adsorbates related to the active carbons.

RESULTS AND DISCUSSION

Since the active carbons are essentially microporous, their adsorption isotherms are Type I in the BDDT classification which is peculiar to microporous adsorbents. Figure 1 shows the adsorption isotherms obtained from the adsorption results with the different adsorbates and the different activated carbons prepared. If one investigates those isotherms by taking into account all the adsorbates, they are all Type I isotherms, but the detailed shapes of the isotherms are a function of the distribution of the pore sizes (6, 7). Carbon P-1 gives the Type I-b isotherm, but carbons P-4, P-8, and P-12 obey the Type I-c isotherm by not becoming parallel to the pressure axis at higher pressures; this implies the presence of mesoporosity as well as a developed microporosity. According to nitrogen adsorption on carbons P-6 and P-10, which have Type I-c isotherms, Fig. 1 shows the adsorptivity of the adsorbates used decreases in the order $N_2 > B > \text{n-B} > \text{i-B} > \text{2,2-DMB} > \text{i-O}$. This results from the differences between the minimum molecule sizes of the adsorbates (N_2: 0.30 nm, B: 0.37 nm, n-B: 0.43 nm, i-B: 0.51 nm, 2,2-DMB: 0.56 nm, i-O: 0.59 nm) (4) and from their ability to enter and adsorb on the pores of various sizes. Adsorption from the gas phase is affected remarkably by the adsorption temperature and the minimum molecule size of the adsorbent as well as the pore structure of the adsorbate. In this study the minimum dimension of the adsorbates affects the adsorption more effectively than the adsorption temperature.

Table 1 includes the pore volumes and the contributions of the activated carbons as determined by using the density 0.808 $g \cdot cm^{-3}$ for the adsorbed N_2 (77 K) (5). This table includes the volumes ($V_{0.01}$, $V_{0.15}$, $V_{0.30}$, and $V_{0.95}$) of adsorbed gases at relative pressures at 0.01, 0.15, 0.30, and 0.95, respectively,

TABLE 1
The Pore Volumes ($cm^3 \cdot g^{-1}$) and Contributions (%) at Various Relative Pressures

Active carbons	$V_{0.01}$	$V_{0.15}$	$V_{0.30}$	$V_{0.95}$	$V_{0.95} - V_{0.30}$	$\frac{V_{0.01}}{V_{0.30}}$
P-C	0.050	0.051	0.051	0.051	0.000	98.0
P-0	0.061	0.070	0.070	0.070	0.000	87.1
P-1	0.149	0.172	0.174	0.179	0.005	85.7
P-4	0.336	0.390	0.396	0.414	0.018	84.9
P-6	0.356	0.443	0.450	0.473	0.021	79.1
P-8	0.380	0.492	0.500	0.532	0.031	75.9
P-10	0.428	0.557	0.570	0.611	0.041	75.1
P-12	0.480	0.628	0.645	0.703	0.058	74.4

the micropore volumes ($<V_{0.30}$) and mesopore volumes ($V_{0.95} - V_{0.30}$), and the contributions of the primary micropores ($V_{0.30} - V_{0.01}$), the secondary micropores ($V_{0.15} - V_{0.01}/V_{0.30}$) and the tertiary micropores ($V_{0.30} - V_{0.15}/V_{0.30}$) to the total micropores at the various relative pressures (P/P_0: 0.01, 0.15, 0.30, and 0.95) [P_0 is the saturated vapor pressure of the adsorbate (6). The values of P_0 taken are as follows: 754.0 mmHg for N_2, 95.5 mmHg for B, 816.4 mmHg for n-B, 1033.1 mmHg for i-B, 318.1 mmHg for 2,2-DMB, and 50.7 mmHg for i-O]. The data were correlated by dividing micropores smaller than 1.5 nm into subgroups designated as primary, secondary, and tertiary according to the various relative pressure intervals ($<$0.01, 0.15–0.01, and 0.30–0.15) over which they were measured. Furthermore, Table 1 includes the total pore volumes ($V_{micro} + V_{meso}$) at 0.95 relative pressure by neglecting the macropore volumes corresponding to P/P_0 between 0.95 and 1.0, and the contributions of the micro- and mesopore volumes [$V_{0.30}/V_{0.95}$ and ($V_{0.95} - V_{0.30}$)/$V_{0.95}$, respectively] to the total pore volume.

Figure 2 shows the straight lines $\log^2(P_0/P)$ vs log V which are drawn by evaluating the N_2 adsorption results in the Dubinin–Raduskevich (DR) relation (Eq. 1).

$$\log V = \log V_0 - K \log^2(P_0/P) \tag{1}$$

where V_0 is the micropore volume determined from the intersection of the DR line with the ordinate axis and D is a constant related to the adsorption system.

Table 2 present values for the microp`ore volume ($V_{0.30}$) determined from the adsorption isotherms of the activated carbons for different adsorbates, and the micropore volumes (V_0) obtained by evaluating the adsorption results related to the other adsorbents such as N_2 (Fig. 2) in the DR equation.

from the Nitrogen Adsorption Results Related to the Active Carbons

$\frac{V_{0.15} - V_{0.01}}{V_{0.30}}$	$\frac{V_{0.30} - V_{0.15}}{V_{0.30}}$	$\frac{V_{0.30}}{V_{0.95}}$	$\frac{V_{0.95} - V_{0.30}}{V_{0.95}}$	$\frac{V_{0.95} - V_{0.30}}{V_{0.30}}$
2.0	—	100.0	0.0	—
12.9	0.0	100.0	0.0	—
13.1	1.2	97.2	2.8	2.9
13.6	1.5	95.7	4.3	4.5
19.3	1.6	95.1	4.9	4.7
22.3	1.8	94.0	6.0	6.3
22.6	2.3	93.0	6.7	7.2
22.9	2.7	91.7	8.3	9.0

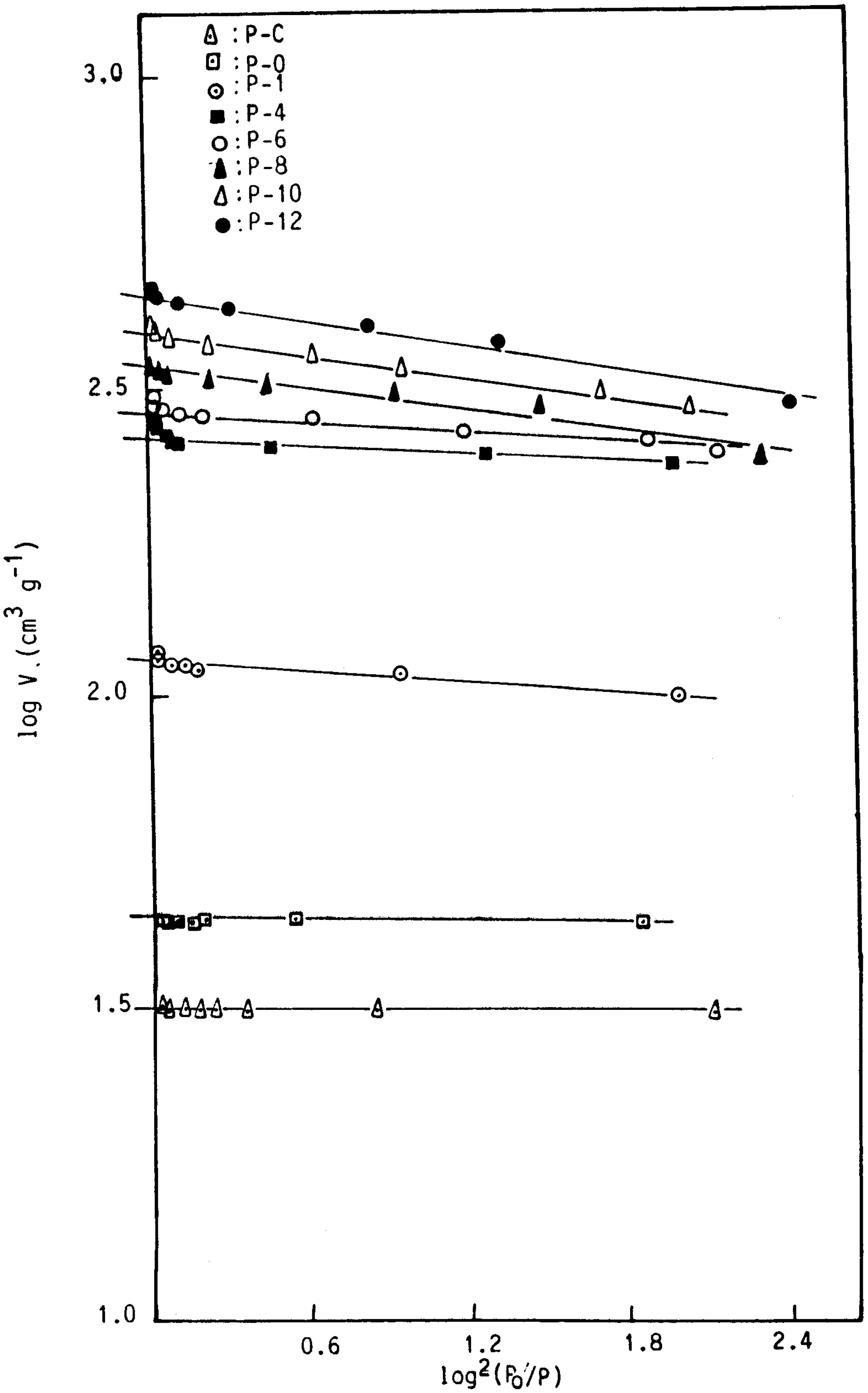

FIG. 2 DR plots of the N_2 (77 K) gas adsorption results related to active carbons.

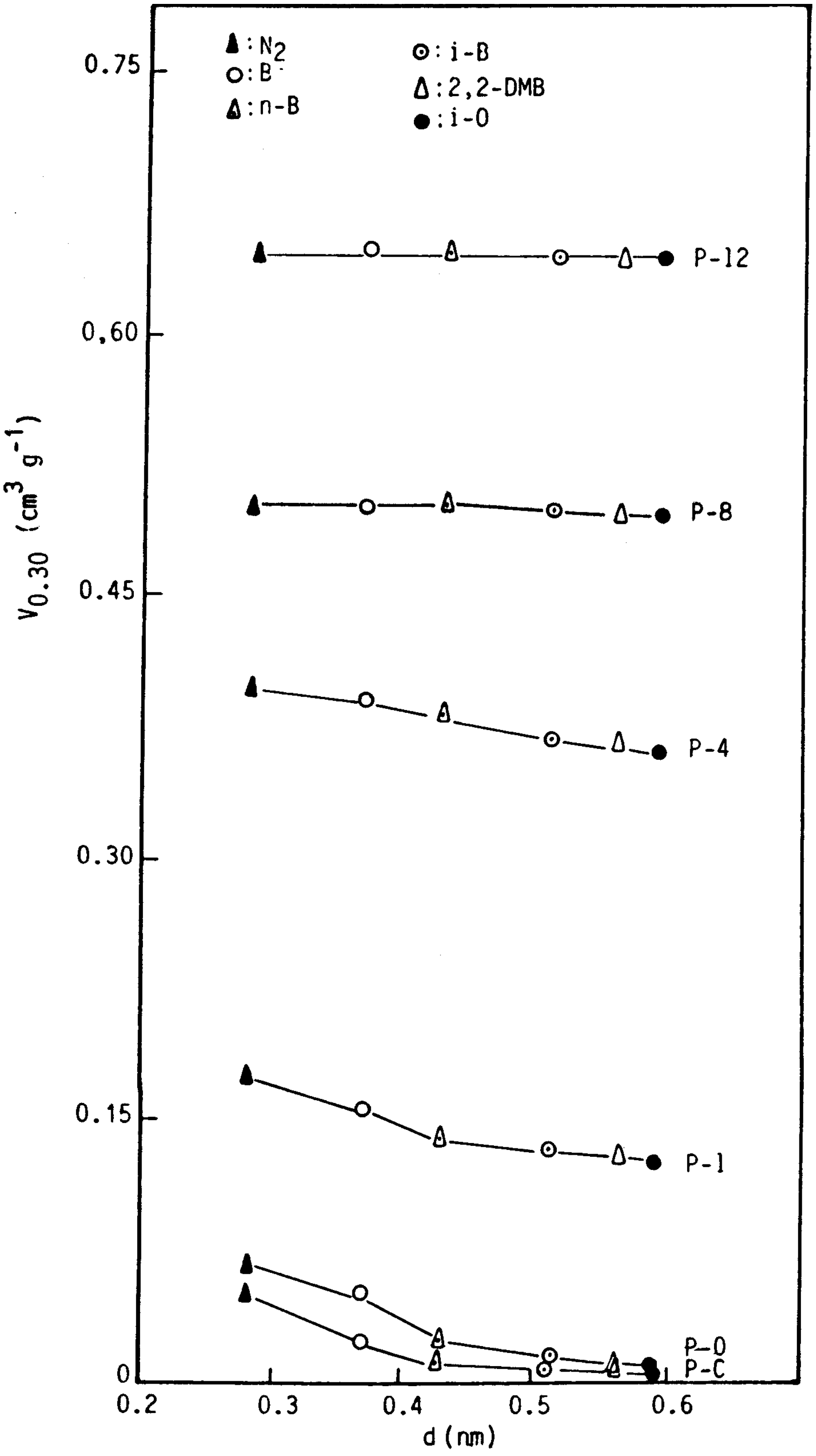

FIG. 3 Micropore volumes versus minimum molecular dimensions of the adsorbates.

TABLE 2
The Micropore Volumes ($cm^3 \cdot g^{-1}$) According

	N_2		B		n-B	
Active carbons	$V_{0.03}$	$V_{0.1}$	$V_{0.30}$	$V_{0.1}$	$V_{0.30}$	V_0
P-C	0.051	0.049	0.051	0.052	0.013	0.018
P-0	0.070	0.070	0.065	0.063	0.026	0.029
P-1	0.174	0.176	0.156	0.158	0.139	0.143
P-4	0.396	0.403	0.388	0.391	0.381	0.385
P-6	0.450	0.455	—	—	—	—
P-8	0.500	0.520	0.501	0.493	0.502	0.499
P-10	0.570	0.578	—	—	—	—
P-12	0.645	0.660	0.647	0.638	0.644	0.639

The graph showing the variation of the minimum molecule dimensions, $d_{\min}$ (nm), of the adsorbates used versus the micropore volumes ($V_{0.30}$) is given in Fig. 3.

Table 3 contains the values of the surface area (S_{N_2}) determined from N_2 adsorption for the activated carbons and values of the surface area (S_H) determined from adsorption of the hydrocarbons. These values were obtained by evaluating the values of monolayer capacity (V_m) from the inverse of the slopes of the lines from the different adsorbates and using Eq. (2):

$$S(m^2 g^{-1}) = \frac{V_m}{22{,}415}(mol \cdot g^{-1}) \cdot \sigma' \times 10^{-20}(m^2) \cdot N_A(mol^{-1}) \qquad (2)$$

TABLE 3
The Surface Areas ($m^2 \cdot g^{-1}$) and the Accessible Surface Area Ratios (%)

Active carbons	S_{N_2}	S_B	S_{n-B}	S_{i-B}	$\frac{S_{N_2} - S_B}{S_{N_2}}$
P-C	36.5	47.1	21.2	10.9	65.5
P-0	198.1	110.0	50.6	20.6	44.5
P-1	508.2	400.6	329.6	286.0	21.2
P-4	162.7	1089.8	997.0	920.6	6.3
P-6	1332.6	—	—	—	—
P-8	1521.8	1497.5	1405.5	1381.6	1.6
P-10	1737.3	—	—	—	—
P-12	1927.9	1899.5	1815.0	1795.1	1.5

to the Different Adsorbates of Active Carbons

i-B		2,2-DMB		i-O	
$V_{0.30}$	V_0	$V_{0.30}$	V_0	$V_{0.30}$	V_0
0.009	0.008	0.006	0.006	0.004	0.005
0.015	0.015	0.010	0.009	0.008	0.007
0.101	0.100	0.096	0.097	0.092	0.090
0.369	0.371	0.367	0.366	0.360	0.362
—	—	—	—	—	—
0.498	0.493	0.495	0.479	0.493	0.487
—	—	—	—	—	—
0.636	0.627	0.643	0.630	0.639	0.626

where σ' is the cross-sectional area of the adsorbed molecule. In this study the following values of σ' were used: 0.162 nm^2 for N_2 (77 K) (5), 0.39 nm^2 for B (298 K) (8), 0.405 nm^2 for n-B (273 K) (9), and 0.507 nm^2 for i-B (273 K) (10). N_A is Avogadro's number. Table 3 gives the accessible surface area ratios (S_H/S_{N_2}) and the ratio of the unaccessible surface area to the accessible surfaces area [$(S_{N_2} - S_H)/S_{N_2}$] for the adsorbates B, n-B, and i-B. All surface areas are expressed in terms of the surface area found for N_2 adsorption.

Tables 1 and 3 and Fig. 3 show that there are some differences in the pore structures of the activated carbons activated for different time intervals at constant temperature (1173 K) from peanut shells. The primary, secondary, and tertiary micropore volumes, and the total pore volumes, increase in the follow-

According to the Different Adsorbates Related to the Various Active Carbons

$\frac{S_{N_2} - S_{n-B}}{S_{N_2}}$	$\frac{S_{N_2} - S_{i-B}}{S_{N_2}}$	$\frac{S_B}{S_{N_2}}$	$\frac{S_{n-B}}{S_{N_2}}$	$\frac{S_{i-B}}{S_{N_2}}$
84.5	92.0	34.5	15.5	8.0
74.5	89.6	55.5	25.5	10.4
35.1	43.7	78.8	64.9	56.3
14.3	20.8	93.7	85.7	79.2
—	—	—	—	—
7.6	9.2	98.4	92.4	90.8
—	—	—	—	—
5.9	6.9	98.5	94.1	93.1

ing order: P-C $<$ P-0 $<$ P-1 $<$ P-4 $<$ P-6 $<$ P-8 $<$ P-10 $<$ P-12. The contributions of the primary micropore volumes and the total micropore volumes to the total pore volumes (Table 1) decrease in the following order: P-C $>$ P-0 $>$ P-1 $>$ P-4 $>$ P-8 $>$ P-12. The contributions of the secondary micropore volume, tertiary micropore volume, and the mesopore volume contributions increase in the following order: P-C $<$ P-0 $<$ P-1 $<$ P-4 $<$ P-8 $<$ P-12. The values of the surface area (Table 3) determined relative to the adsorbate increase in the following order: P-C $<$ P-0 $<$ P-1 $<$ P-4 $<$ P-6 $<$ P-8 $<$ P-10 $<$ P12. All of these results indicate that the P-C and P-0 carbons show a dominant underdeveloped primary micropore structure. The data of the pore volume obtained from these two carbons do not exhibit any remarkable difference. This is believed to result because pore gates are homogeneous small-sized pore structures, and pore gates are formed when $ZnCl_2$ is used as a chemical activator. The differences between the pore volumes and the surface areas of activated carbons P-1, P-4, P-6, P-8, P-10, and P-12 come from the role of CO_2 in making the pores wider and deeper (7). Carbon dioxide reacts with graphite carbon microcrystals in the structure, and the carbon atoms on the sides of the pores are burned and removed. These differences in activation periods result in heterogeneous pore structures and allow more adsorbates of larger sizes into the micropores. The accessable pore volumes are in the order P-C $<$ P-0 $<$ P-1 $<$ P-4 $<$ P-8 $<$ P-12 as seen in Fig. 3. The increase in the ratios of the mesopore volume to the micropore volume is shown in Table 1. The ratios $[(V_{0.95} - \mathrm{V}_{0.30})/\mathrm{V}_{0.30}]$ vary in the order P-C = P-0 $<$ P-1 $<$ P-4 $<$ P-6 $<$ P-8 $<$ P-10 $<$ P-12. The variations in the ability of different molecules to enter the pores ($S_{\mathrm{H}}/S_{\mathrm{N}_2}$) and the inaccessibility of pores to other adsorbates $[(S_{\mathrm{N}_2} - S_{\mathrm{H}})/S_{\mathrm{N}_2}]$ relative to N_2 are P-C $>$ P-0 $>$ P-1 $>$ P-4 $>$ P-8 $>$ P-10 $>$ P-12 and P-C $<$ P-0 $<$ P-1 $<$ P-4 $<$ P-8 $<$ P-10 $<$ P-12, respectively (see Table 3).

In conclusion, the volume of primary micropores as measured at $<$0.01 relative pressure increases with the duration of physical activation. Primary micropores expand to form secondary and tertiary micropores as determined at 0.15–0.01 and 0.30–0.15 relative pressure. The ratio of mesopore volume to micropore volume increases as the duration of physical activation increases. In order to characterize an activated carbon with narrow micropores by adsorption of a single hydrocarbon is not enough. Measurements using several hydrocarbons with different dimensions as well as measurements with microgen provide a more comprehensive assessment of pore structure, although the method is expensive.

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