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Introduction

The adsorptive characteristics of activated carbons change with continued activation. In a general way these changes have been associated with changes in pore structure and surface area. In this paper a closer investigation is made of the actual changes taking place in the pore structure and its effect on adsorptive characteristics.

Experimental Procedure

Three activation series were studied wherein the base or starting materials were coconut, bituminous coal and lignite. The water isotherm method (1,2) was used to determine the pore structures; the adsorption branch of the isotherm was used to calculate the pore cavity diameter distribution and the desorption branch to determine the pore constriction diameter distribution. This method covered the diameter range from \sim 7Å to \sim 2,000Å. Total pore volumes, corresponding to 100,000A pore diameter, were determined by measuring the carbon volume by helium and mercury displacements (1). Pore size distributions between 2,000Å and 100,000Å, normally measured by mercury penetrometry, were estimated in this study since they did not enter into the calculation in a significant manner. Pore structure determinations were further supported by vapor and aqueous phase iodine adsorption data (2). Effect of pore structure on acetone, carbon tetrachloride and benzene vapor adsorption was done according to procedures described in reference 3.

Experimental Results

Figures 1, 2 and 3 show families of complete pore size distribution curves for each of the base materials. The base material has a very predominating effect on the relative micro- and macropore volumes. In coconut carbons 64% of the total pore volume is micropore, while the percentage drops to about 50 for the coal base and about 20 for the lignite base. Common to all, continued activation increases the total pore volume and increases the micropore diameters, with the cavity diameters increasing at a faster rate than the constriction diameters. Table I presents calculated areas based on the constriction and cavity diameters; calculations were made by the method described in reference 2. The last column shows a decrease in cavity area/constriction area ratios for each group of carbons as activation is continued. This decrease in ratios further supports the above observation that the cavity diameters enlarge at a faster rate than the constriction diameters.

Iodine vapors adsorb in micropores, pores < 30Å dia., by pore filling accompanied by monolayer coverage of the macropores during or after the pore filling process. Figure 4 presents correlations of the theoretical adsorbed weights as a function of experimentally observed weights. The good agreement between the calculated points and the solid line, which represents a perfect correlation, supports the micropore volume measurements as derived from water adsorption data.

Iodine in aqueous phase is adsorbed by monolayer

Table I. Surface areas from pore constrictionand cavity-diameter distribution curves

Carbon	Surface area, m ² /g		Area ratio,
	Constrictions	Cavities	Cavity/Const.
1	1250	1000	0.80
2	2050	1290	0.63
3	2140	1170	0.55
4	680	640	0.94
5	940	810	0.86
6	1280	1040	0.81
7	1470	1170	0.80
8	1020	770	0.75
9	1030	790	0.77
10	1500	1080	0.72
11	1580	1090	0.69

surface coverage, hence, it is a means for determining the portion of surface area associated with pore constrictions and cavities. Figure 5 shows correlations of theoretical amount adsorbed as calculated from the constriction and cavity diameter curves when plotted as function of actual amount adsorbed. The points calculated from the cavity-diameter distribution curves are close to the solid line, representing perfect correlation. Points calculated from the constriction-diameter distribution curves deviate from the solid line with increasing divergence for carbons of increased activity. These test results show that as activation continues, the surface associated with cavities becomes the major part of the total surface area. Referring to Table I, the surface areas calculated for the cavities are then closer to the true surface area than those calculated for the constrictions.

The effect of pore structure on the carbon's ability to adsorb carbon tetrachloride, benzene and acetone is shown in Figure 6. Two sets of test results are shown, one at low relative vapor pressures and one at high relative vapor pressures, as given below:

Vapor	p/p _o	Pore dia. Å
Carbon tetrachloride	0.0005	18.6
Carbon tetrachloride	0.30	50.
Benzene	0.001	12.6
Benzene	0.25	37.3
Acetone	0.0005	14.6
Acetone	0.30	35.

In pores of the diameter being considered, adsorption proceeds by pore filling, hence, at the given p/p_{o} pores will fill with adsorbed liquid to the diameter given in the last column. The procedures for making these calculations are given in reference 3. As shown in the figure, adsorption at the higher p/p_{o} fills the micropores, while adsorption at the lower p/p_{o} fills only the smallest micropores. With continued activation the ability of the carbon to adsorb at low p/p_{o} decreases while at the higher p/p_{o} it increases.

References

- Juhola, A. J. and Wiig, E. O., J. Am. Chem. Soc. <u>71</u>, 561, 2069 and 2078 (1949)
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Fig. 2. Pore size distribution, coal carbons, constrictions ---, cavities ---.



Fig. 3. Pore size distribution, lignite carbons, constrictions ——, cavities ---.



Fig. 4. Iodine vapor adsorption, constrictionssolid points, cavities-open points.



Fig. 5. Aqueous phase iodine adsorption, constrictions-solid points, cavities-open points.



Fig. 6. Distribution of pore constriction diameters, coconut carbons.