

MEASUREMENT OF THE SURFACE AREAS OF COALS FROM
THE DYNAMIC SORPTION OF CARBON DIOXIDE

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INTRODUCTION

Dynamic-sorption apparatus has been described by Nelsen and Eggertsen¹ and refined by Daeschner and Stross² for use in the determination of the surface area of solids. The essentials of the apparatus have been incorporated in commercially available equipment (Perkin-Elmer's Sorptometer). With the apparatus, the volume of nitrogen sorbed by the sample from a nitrogen-helium gas stream is determined by thermal conductivity measurements. Other mixed-gas systems may be used for special studies. The surface area is calculated using the well-known theoretical principles of Brunauer, Emmett, and Teller³ (BET equation). Surface-area values are in close agreement with those obtained from the use of more conventional apparatus in which pressure-volume measurements are made in a static system. The dynamic-sorption apparatus, however, lends itself more readily to routine measurements, having the advantage over conventional apparatus in speed and simplicity of operation. In addition, the rate of sorption is recorded directly. This can be of value in revealing pore-size variations, particularly in microporous substances where equilibrium is slow in being reached.

It is well-recognized that nitrogen at 77° K. does not reach a large part of the internal surface of coals. This is attributable, for the most part, to activated diffusion^{4,5} although thermal contraction can not be completely ruled out as being responsible for some pore closure. Conversely, it has been concluded that carbon dioxide at 195° K. does reach most of the internal surface^{6,7,8}. Three recent papers^{9,10,11} are substantially in agreement as to the magnitude of the surface-area values obtained using carbon dioxide as the adsorbate. The values are appreciably greater than those obtainable from nitrogen adsorption and do not differ greatly from those obtained using heats of wetting in methyl alcohol^{12,13}.

The primary purposes of the work reported herein are (1) to demonstrate the applicability of continuous-flow measurements to internal surface studies of coals and (2) to report for comparative purposes the surface-area values obtained for the different coals studied. Of special significance are the values obtained for coals from the Illinois Basin. These coals are high volatile A, B, and C bituminous and, to the authors' knowledge, with the exception of the work reported by Machin, Staplin, and Deadmore¹⁴ in which nitrogen and water vapor were used as adsorbates, they have not been studied to any appreciable extent.

EXPERIMENTAL

Apparatus

The adsorption apparatus was quite similar in design and use to the original apparatus described in detail in the afore-mentioned references. Modifications included: (1) needle valves for controlling gas flow rates (2) a disc integrator (Disc Instruments, Inc., Santa Ana, California) attached to a Sargent Model MR recorder for integrating peak areas (3) a reversing switch in the bridge circuit to permit positive adsorption peaks to be recorded for integration as well as positive desorption peaks and (4) a Sorensen QB12-2 D.C. Power Supply (Raytheon Company, South Norwalk, Connecticut).

Samples

Coal samples used in the study and appropriate analytical data are given in Table I. The Illinois high volatile A, B, and C bituminous coals (3 for each rank) represent only a fraction of the total number of coals of similar rank that were studied and include those coals which yielded the extremes of the range of surface-area values found for each rank.

Samples of anatase, silica spheres, bone char, carbon black (Spheron 6), and a silica-alumina catalyst with known surface areas were used to establish the effective cross-sectional area for the carbon dioxide molecule under the given experimental conditions. These substances have been evaluated at several participating laboratories by the BET nitrogen adsorption method and are distributed by the Bone Char Research Project, Inc. (Revere Sugar Refinery, 333 Medford Street, Charlestown 29, Mass.).

Procedure

Operational details for the apparatus are clearly outlined in the work of Nelsen and Eggertsen, as is the transformation of experimental data into a surface-area determination. The conditions used for the coal studies reported here are summarized as follows: A 40 x 120-mesh sample of approximately 0.2 gram is weighed into the sample tube which is then attached to the apparatus, and the sample is outgassed at 90° C. for 1 hour under a flow of helium. A controlled gas mixture of carbon dioxide and helium is permitted to flow over the sample. A dry ice-absolute ethanol bath (approximately 195° K.) is raised into position around the sample tube and adsorption is continued for 16 hours. (The adsorption step for a few samples was conducted for 30 minutes, 2 hours, and 24 hours for comparison purposes.)

After the adsorption step is completed, the gas is desorbed from the sample by removing the dry ice-ethanol bath and quickly replacing it with another bath (glycerol here) at 150° C. The volume of desorbed gas is determined from a calibration curve (detector response versus known volumes of carbon dioxide) and it is this volume that is used for determining the surface area. The relatively high desorption temperature is necessary to remove virtually all the adsorbed carbon dioxide (less than 0.5% of the original volume is retained at this temperature) and it helps provide a sharper, symmetrical desorption peak that is more comparable with calibration data. Thus, errors which may arise from badly tailing peaks are minimized.

From the familiar BET equation, which is assumed to be applicable, a single-point plot using P/P_0 as the abscissa and $P/V(P_0 - P)$ as the ordinate, and with the intercept at 0, yields $V_m = 1/\text{slope}$. The saturation vapor pressure (P_0) used in the calculations was 1450 mm. which allows for a very slightly higher temperature than the value (1.86 atm. at 195° K.) given by Bridgeman.¹⁵ Surface area then is readily determined from V_m , from the area occupied by a carbon dioxide molecule, and from the sample weight which is more carefully determined on the dry sample after the desorption step.

Multipoint plots were used for three coal samples and for all the substances involved in the determination of the effective area occupied by the carbon dioxide molecule. The constant C of the BET equation is large for carbon dioxide as the adsorbate on coal and a multipoint plot passes practically through the origin of coordinates. This enables one to use the single-point method on a more-or-less routine basis, particularly in view of the inherent uncertainties of the BET method with coals and the necessary long adsorption periods.

TABLE I

Selected Analyses of Coals Studied

No.	Sample	Proximate Analysis				Dry, Mm-Free		Heating Value	
		Moisture, %	Moist, Mm-Free Matter, %	Volatile Matter, %	Fixed Carbon, %	Fixed Carbon, %	Moist, Mm-Free Btu per pound		
<u>Illinois hvCb</u>									
1	Madison Co. (#6 coal)	17.6	35.5	46.9	57.0	11,700			
2	Kankakee Co. (#2 coal)	15.2	41.2	43.6	51.4	12,300			
3	Vermillion Co. (#7 coal)	13.1	42.6	44.3	50.8	12,700			
<u>Illinois hvBb</u>									
4	Franklin Co. (#6 coal)	11.2	33.8	55.0	62.0	13,000			
5	Williamson Co. (#6 coal)	7.9	39.1	53.0	57.5	13,700			
6	Saline Co. (#6 coal)	7.6	37.6	54.8	59.3	13,600			
<u>Illinois hvAb</u>									
7	Gallatin Co. (#5 coal)	5.9	39.4	54.7	58.2	14,100			
8	Gallatin Co. (Lower Willis)	2.3	36.9	60.8	62.2	14,900			
9	Gallatin Co. (#6 coal)	3.2	41.7	55.1	56.8	14,600			
10	West Virginia (Pittsburgh seam)	1.7	42.7	55.6	56.6	15,200			
11	West Virginia (Sewell seam)	2.1	29.9	68.0	69.5	- - -			
12	West Virginia (Bakerstown)	2.3	17.9	79.8	81.6	- - -			
13	Utah	5.7	45.0	49.3	52.3	13,700			
14	Kentucky (#5 coal)	2.6	39.1	58.3	59.8	14,700			
15	Arkansas (Hartshorne)	1.6	17.8	80.6	81.9	- - -			
16	Pennsylvania anthracite	2.1	5.1	92.7	94.8	- - -			
17	Meta-anthracite (Leoben, Austria)	0.1	1.8 (d.a.f.)	-	98.2 (d.a.f.)	- - -			
18	Borneo (Silantek)	0.8	25.3	73.9	74.5	- - -			

RESULTS AND DISCUSSION

Molecular Area of Carbon Dioxide

Table II gives the results from which the effective cross-sectional area of the carbon dioxide molecule used as the adsorbate in the studies was established. The cross-sectional area of the nitrogen molecule was taken as 16.3 \AA^2 . The assumption is made that carbon dioxide at 195° K . should give the same surface area as N_2 at 77° K . It is seen that the values are in satisfactory agreement with the exception of that obtained for the carbon black. Slight differences are to be expected, of course, owing to the wide differences in the chemical compositions of the substances used. It would appear that the large difference is due to the presence of a micro-pore system - similar perhaps to that which exists in coals - that also is not permeated during nitrogen adsorption at 77° K .

Excluding the value obtained for the carbon black, the average effective molecular area of carbon dioxide is 22.1 \AA^2 . Calculated from this value, the surface area for Spheron 6 should be about $150\text{-}155 \text{ m}^2/\text{g}$.

Adsorption-Desorption Characteristics

The desorption curve and the portion of the adsorption curve shown in Figure 1 are typical for carbon dioxide adsorbed on coals. During adsorption, a rather sudden uptake of the gas extending over a period of 2-3 minutes is followed by very slow diffusion that may extend over a period of 16 hours. As much as one third of the total adsorption volume is adsorbed by certain high-volatile C bituminous coals during the first 2-3 minutes.

Table III gives some comparative data for various periods of adsorption. Although the table includes only a small sampling of coals, the data clearly show that adsorption is far from complete at 2 hours but also indicate that it is essentially complete somewhere between 2 and 16 hours. The 16-hour period was selected as it was found convenient to conduct adsorption overnight.

Adsorption is much too slow to enable one to use the adsorption curve for the gas-volume determination since calibration curves are practically impossible to construct for the extended removal or addition of a gas introduced at a variable rate into the mixed-gas stream. Fortunately, however, for analysis purposes, desorption is rapid and essentially complete within the first 2-3 minutes of its initiation.

Surface Areas of Coals

Table IV lists the surface-area values for the coals studied. As indicated earlier, a larger number of Illinois coals than shown were investigated and a range of intermediate values was found within the extremes shown here for each rank. Some overlap of values is present between the ranks of Illinois coals as would be anticipated. The range of values from the work of Machin et al. by classical nitrogen adsorption methods is shown for comparative and supplemental purposes.

It is seen that the values from carbon dioxide adsorption are of the same order of magnitude as values obtained from heats of wetting and, thus, also are in agreement with the more recent studies in which carbon dioxide was used as the adsorbate in static systems and to which references have been made. Values for the hvAb coals are the lowest reported thus far from carbon dioxide adsorption on coals, with the exception of meta-anthracite, but they are not any lower than values that have been obtained from heats-of-wetting methods.

Maximal and minimal values among all the coals studied are found essentially within the ranks of Illinois coals. Since the Illinois coals comprise such a narrow

TABLE II

Determination of the Effective Cross Sectional Area of the Carbon Dioxide Molecule

Adsorbent	S.A., m ² /g*		N ₂ S.A. CO ₂ S.A.	Effective Molecular Area of CO ₂ , A ²
	(N ₂ ads.)	(CO ₂ ads.)		
Anatase	10.3	7.9	1.30	22.1
Silica spheres	24.3	18.6	1.31	22.3
Bone char	69	52	1.33	22.6
Carbon black(Spheron 6)	110	117	0.94	16.0
Silica-Alumina catalyst	550	436	1.26	21.4

*Mean of accepted values from several participating laboratories.

**Assuming a cross sectional area of 17.0 A² for the carbon dioxide molecule.

TABLE III

Adsorption of Carbon Dioxide on Coals for Different Adsorption Times

Coal	Volume Adsorbed Per Gram of Sample (ml.)*			
	0.5 hour	2 hours	16 hours	24 hours
Sample 4	27.1	35.1	42.2	42.3
Sample 7	3.3	5.8	10.2	- -
Utah	14.1	17.7	28.3	28.4
Borneo	29.9	38.0	38.4	38.4

*P/P₀ differed slightly among the coals used but was the same for each coal for the different adsorption periods.

TABLE IV

Surface Areas of Coals

No.	Sample	Surface Area, m ² /g		No.	Sample	Surface Area, m ² /g	
		CO ₂ ads.	N ₂ ads.*			CO ₂ ads.	N ₂ ads.*
	<u>Illinois hvCb</u>		46.8-91.8	10	W. Virginia (Pitts. seam)		43
1	Madison Co. (#6 coal)	292		11	W. Virginia (Sewell seam)		197
2	Kankakee Co. (#2 coal)	248		12	W. Virginia (Bakerstown)		128
3	Vermilion Co. (#7 coal)	184					
	<u>Illinois hvBb</u>		7.2-16.3	13	Utah		145
4	Franklin Co. (#6 coal)	205		14	Kentucky (#5 coal)		66
5	Williamson Co. (#6 coal)	115		15	Arkansas (Hartshorne)		182
6	Saline Co. (#6 coal)	83					
	<u>Illinois hvAb</u>		1.8-4.5	16	Pennsylvania anthracite		262
7	Gallatin Co. (#5 coal)	86		17	Meta-anthracite (Leoben, Austria)		6.0
8	Gallatin Co. (Lower Willis)	57		18	Borneo (Silantek)		290
9	Gallatin Co. (#6 coal)	46					

*From work by Machin, Staplin, and Deadmore.

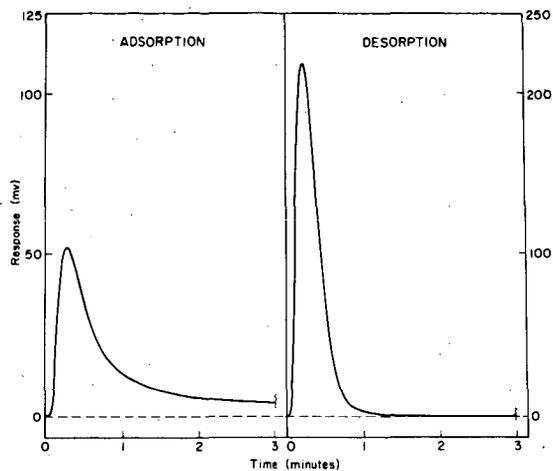


Figure 1. Typical carbon dioxide adsorption and desorption curves for coals (without integrator record)

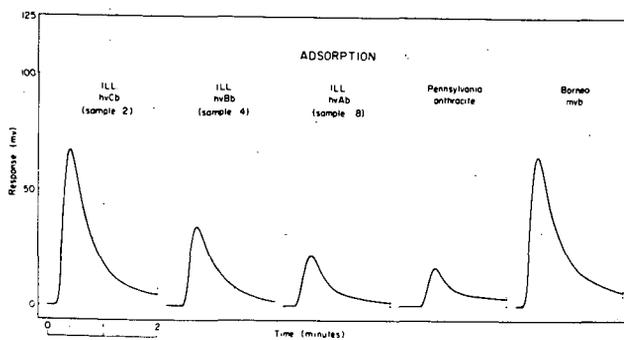


Figure 2. Initial portions of adsorption curves for 0.2-gram samples of various coals (without integrator record)

portion of the overall degree of metamorphism among coals, and since the values for the higher rank coals examined do not change in an orderly manner with increase in rank, there appears to be little basis for attempts to construct a curve relating rank and surface area.

Implications from Initial Adsorption Rates

It is significant that surface-area values for Illinois hvCb coals from nitrogen adsorption isotherms reported by Machin et al. are as high as $91 \text{ m}^2/\text{g}$. A search of the literature failed to uncover a report in which a coal sample produced a surface area this large by nitrogen adsorption. In some of our own studies using nitrogen as the adsorbate in the continuous-flow apparatus, values for sample numbers 2 and 3 were found to be 99 and $48 \text{ m}^2/\text{g}$, respectively. Indications are that a larger proportion of pores of greater diameter than a certain minimal size exists in the hvCb coals permitting greater quantities of nitrogen to permeate the structure at 77° K .

Further proof of this may be seen in a comparison of the initial adsorption rates for carbon dioxide on similar sample weights of several coals shown in Figure 2. All of the coals shown have surface-area values of over $200 \text{ m}^2/\text{g}$, with the exception of the hvAb which should not be used directly in this comparison. It is readily apparent that the rate of carbon dioxide taken up during the first 2-3 minutes differs markedly among the coals. It would appear that the greater rate of adsorption of carbon dioxide by the hvCb coal in comparison with the hvBb, hvAb, and anthracite coals coincides with a greater macropore volume of the coal and would tend to supplement the nitrogen adsorption data from this standpoint. It is tempting to say, without knowledge of the Borneo coal, that the macropore volume decreases with rank, and this appears to be true for the Illinois coals studied thus far. The large volume of carbon dioxide initially adsorbed by the Borneo coal (mvb), however, would tend to negate this concept, and yet nitrogen adsorption for this coal gives a surface-area value of only $0.8 \text{ m}^2/\text{g}$. Thus, it would appear that this coal has very little macropore volume available to nitrogen at 77° K ., and yet it has a large number of pores of sufficient size to permit carbon dioxide to permeate the structure rapidly at 195° K . making it different from anthracite or hvAb coals in this regard. This only serves to emphasize the danger in making generalities about coals from widely differing localities and perhaps formed in widely differing environments.

CONCLUSIONS

It is recognized that in the determination of the surface areas of coals no method reported thus far is completely free of criticism. In the work reported here it is assumed that the BET equation is applicable, and this in itself is subject to some criticism. The abbreviated single-point method used here, however, should be as good as any other method for obtaining useful relative data for practical comparative purposes. In addition, the ability to easily follow the initial adsorption rate should be of advantage in attempts to describe quantitatively the molecular sieve characteristics of various coals.

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