

SURFACE AND PORE PROPERTIES OF ANL AND PETC COALS.

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ABSTRACT

Surface areas, pore volumes, pore size distributions, and solid densities were measured for three ANL coals (Pittsburgh No. 8, Wyodak, and Beulah Zap Lignite), two PETC coals (Lower Wilcox, and Dietz) and a Utah Scofield coal and for chars derived from these coals. Surface areas were measured using nitrogen and carbon dioxide adsorptions; pore volumes were determined using nitrogen adsorption, mercury porosimetry, and NMR spin-lattice relaxation measurements of samples saturated with water. Solid densities were obtained using helium displacement. The results indicate that chars have larger surface areas and pores relative to coals; large fractions of the internal surfaces of coals are not penetrated by nitrogen molecules but are penetrated by carbon dioxide suggesting that the pores are mostly smaller than 1 nm.

INTRODUCTION

Coals are highly-aged biomaterials (with mineral inclusions) of high surface area and high porosity. These surface properties play an important role in their application as fuels. For example, in pulverized coal combustion the removal of volatile matter and the oxidation of the remaining char are processes the kinetics of which are governed at least in part by diffusion of materials in and out of the pores. Moreover, char oxidation rates depend upon the surface properties of the char, such as total surface area, active surface area and pore structure.

The work reported here is part of an ongoing collaborative study of the surface properties and pore structure of U.S. coals and in particular of a suite of 11 coals selected for comprehensive study by the Advanced Combustion Engineering Research Center (ACERC) of which 8 are ANL coals and 3 are PETC coals [1]. The principal objective is to correlate the surface, pore, and chemical properties of coals and chars with their rates of combustion. Ultimately these correlations will be developed into a computerized mathematical model of char oxidation which relates reactivity with structure [2].

This paper reports surface areas and pore volumes of 6 coals (3 ANL, 2 PETC, and one Utah coal) and of high temperature chars derived from three of these coals. It includes the results of studies of the precision of surface area and pore volume measurements on a given sample and on different samples by different adsorption techniques and by different laboratories. Comparisons are made of the results of this study with those reported in the literature for the same coals and similar chars derived from these coals.

EXPERIMENTAL

Materials. The coals studied are listed in Table 1 according to rank and source.

Table 1
Rank and Source of Coals Studied

<u>Coal Name</u>	<u>Rank</u>	<u>Location</u>	<u>Coal Bank Source</u>
1. Pittsburgh #8	H.V. A Bituminous	Greene Co., PA	ANL
2. Utah Scofield	H.V. C Bituminous	Scofield, UT	Valley Camp Mn
3. Dietz	Subbituminous B	Bighorn Co., MT	PETC
4. Wyodak	Subbituminous C	Gillette, WY	ANL
5. Beulah-Zap	Lignite A	Mercer Co., ND	ANL
6. Lower Wilcox	Lignite A	Titus Co., TX	PETC

Coal Preparation. The parent coals were air-classified and sieved. The lignite coals agglomerate easily and therefore, to facilitate the sieving process, they were first separated into wide size fractions using a cyclone particle classifier. The coal was processed through the separator two times. The first time, the apparatus removed the largest particles which were reground. The reground coal was then fed through the classifier again along with the smaller fraction from the first separation to remove the smallest size fraction. The larger size fraction was then classified using sieve screens to obtain the -200/+230 mesh size fraction. Sieving was performed to collect 200–300 grams of each coal using a RoTap sieve shaker; every fifteen minutes the screens were blown clean. The number of 15-minute periods for completion was greatly dependent on the individual sample, but was generally 4–6. The sieving was considered complete when the percentage passing through the 230 mesh screen remained constant. Both -325/+400 mesh (37–44 μm) and -200/+230 mesh (63–74 μm) size fractions were collected so that the effects of particle size could be studied.

Char Preparation. Details of the char preparation unit are described elsewhere [3]. The apparatus consists of a vibrating annular coal feeder, air/methane delivery system, a flat flame burner, and a cooled probe collection system. The coal feed rate is generally about 30 grams per hour. The flat-flame burner is fabricated from a ceramic monolith support (Cordierite, Corning Glass Works) with 300 square cells per square inch. The monolith is divided into two halves, and glass capillary tubes are inserted in every other hole in every other row. This arrangement gives a flame composed of many diffusion flamelets (at about 2000 K). Flows are controlled by high-accuracy rotameters and pressures are maintained constant by low-pressure line regulators to ensure a stable flame. Typical flow rates (SCFH) are: N₂ feed, 0.632; N₂ quench, 6; methane, 5.867; and air, 59.4. The collection system consists of a water-cooled, nitrogen-quenched probe, a cyclone separator, and a household vacuum. The particle residence time may be changed by varying the height of the collection probe above the burner. The cyclone separator is designed to collect 20 micron particles with greater than 90% efficiency.

Surface Area/Pore Volume Measurements. Total surface areas were measured by means of carbon dioxide adsorption at 273 or 298 K and nitrogen adsorption at 77 K, using either volumetric [4,5] or flow (Quantasorb) adsorption systems. Carbon dioxide adsorption measurements at UNM were conducted at 273 K and three relative pressures using a Quantasorb flow adsorption analyzer, after samples had been outgassed in a dry helium stream at 373 K. CO₂ adsorption measurements at BYU were conducted at 298 K and 3-7 relative pressures using either flow or static, volumetric systems on samples previously outgassed *in vacuo* for 12 hours at 378 K or outgassed in helium at 373 K. In both cases, the data were analyzed using the Dubinin-Polyani (DP) or Dubinin-Radushkevich (DR) equation using an area for the CO₂ molecule of 0.201 nm² based on good agreement between nitrogen adsorption and carbon dioxide adsorption measurements on a graphite carbon [6]. Nitrogen adsorption and desorption experiments were conducted over the relative pressure range of 0.05 to 0.99 at 77 K using

either an Autosorb-1 automated volumetric adsorption analyzer (UNM) or (at BYU) a volumetric adsorption apparatus [4,5]. Samples were outgassed *in vacuo* at either 383 K for three hours (UNM) or 378 K for 12 hours (BYU). Nitrogen isotherms were analyzed using the BET equation and an area for the nitrogen molecule of either 0.162 nm² (BYU) or 0.170 nm² (UNM) to obtain surface areas.

Pore size distributions for pores in the 1-100 nm range were obtained from extended nitrogen isotherms using the Kelvin equation. Mercury intrusion experiments were obtained (at UNM) for selected samples previously outgassed at 383 K *in vacuo* for one hour in the pressure range of 12 to 33,000 psia. The analysis of the mercury intrusion data was complicated by (i) filling of irregular-shaped voids around particles and (ii) sample compression at higher pressures necessary to fill pores smaller than 3 nm diameter [6].

NMR spin-lattice relaxation measurements of pore volume and pore size distribution were performed (at UNM) at 20 MHz and 303 K on samples saturated with water vapor. Coal and char samples were saturated by placing them in a desiccator, evacuating, backfilling with water or salt solution and allowing the samples to equilibrate with the solution vapor at a given pressure. Samples were weighed into 5 mm NMR tubes and a 180°-t-90° spin-lattice relaxation experiment was performed from which pore size distributions for pores of greater than 0.5 nm were extracted [6,7]. The surface-interaction parameter, β , was determined from measurements at different water contents [8]. Helium or "true" densities were obtained by helium pycnometry at UNM.

RESULTS AND DISCUSSION

Surface areas were measured for six coals and three chars while pore volumes, pore size distributions, and densities were also measured for three coals and three chars (two samples of one of the chars). Data obtained at BYU and the University of New Mexico (UNM) are summarized in Tables 2-4 and in Figure 1.

Table 2 summarizes the results of a repeatability study of CO₂ and nitrogen adsorptions on a Utah Scofield coal using a volumetric system to (i) define pretreatment conditions that would lead to removal of adsorbed CO₂ and allow repeatable measurements on the same sample and (ii) define the precision of CO₂ and N₂ adsorption measurements on the same sample and different samples (of about 1 g). The data (Table 2) indicate that immersing the sample cell in boiling water for five minutes, while evacuating, quantitatively removes adsorbed CO₂ and enables the adsorption measurement to be repeated with a high degree of precision (better than 7%). The data (Table 2) also indicate the precision of both CO₂ and N₂ measurements is within 7% on different samples.

Table 3 summarizes results from a similar repeatability study on high temperature Dietz chars using a flow system. They indicate that different runs on the same sample are repeatable to within 1-2% while the precision of measurements on different samples of the same preparation is 7-14% for samples sizes of 25-35 mg from a poorly-mixed preparation and 2-7% for sample sizes of 75-120 mg from a well-mixed sample. Accordingly, it is clear that the precision of surface area measurements by the flow method is significantly greater for samples larger than 50-75 mg and/or is improved by mixing the sample well. These results emphasize the importance of choosing representative samples and of conducting repeat measurements on different samples of the same preparation rather than repeating measurements on the same sample. Comparison of the data for the Dietz A and B preparations (temperature and residence time were nearly the same) indicates that large variations in surface areas (20% for CO₂ and 300% for N₂) can be obtained with only subtle variations in the preparation conditions. Similar variations are observed for Dietz Chars B and C prepared

under nearly the same conditions (Table 4). This emphasizes the need for careful temperature and residence time control in char preparation. Thus, we are presently computerizing our preparation system to enable better reproduction of gas temperature and particle residence time in our preparations.

Table 4 summarizes our measurements of total surface area, pore volume, pore volume distribution and interaction parameters from NMR measurements for the five coals and 3 chars. Wilc Chars 1 and 2 were prepared separately; the preparation of Wilc Char 2 involved a higher residence time and probably a higher degree of burnout; this is confirmed in part by the larger nitrogen BET surface area of Wilc Char 2 relative to Char 1. Wherever possible, measurements were repeated to obtain a measure of experimental precision; the listed limits of error refer to the the standard deviation for a series of 2-5 measurements.

Several significant trends in the data (Table 4) are evident: (i) CO₂ surface areas of coals are generally 50-300 and of chars 2-5 times larger than the corresponding N₂ surface areas, (ii) CO₂ and N₂ surface areas of chars are higher than those of the corresponding coals, and (iii) the fraction of pores having diameters of less than 0.5 nm is significant for both coals and chars. The first of these trends is explained by the ability of the CO₂ to penetrate micropores (of less than about 1 nm diameter) whereas N₂ is unable to penetrate; accordingly it is clear that most of the internal surface area of coals and much of that of these chars consists of micropores having diameters less than 1 nm. The larger measured surface areas of chars relative to coals is explained by a combination of the following factors: (i) the removal of strongly adsorbed molecules or functional groups from the micropores that would otherwise hinder access of CO₂ and N₂, (ii) creation of new micropores during the restructuring process involved in devolatilization, and (iii) creation of greater macroporosity as volatile materials are removed.

The data in Table 4 and Figure 1 indicate that the net result of these factors is to slightly decrease during char production the fraction of pores in the range of 0.5-1 nm, while significantly increasing the fraction of pores in the range of 1 to 10 nm and to increase pore volume measured by either nitrogen or water adsorptions. The data for the Wilc Char provide an exception to this trend; however in this case, the unexpectedly large pore volume of coal may be due to swelling as water is taken up by the lignite structure. A similar effect may also explain the unexpectedly large fraction of pores less than 0.5 nm for Wilc Char 1.

Table 5 compares surface area and pore volume data available in the literature with those determined in this study. The relatively few surface area data available are in fair to good agreement with the data obtained in this study, while the pore volume data are insufficient to enable comparison. The differences in the results from this and other studies are probably explained by differences in the pretreatments of the samples, e.g., the extent of oxidation and outgassing of the sample and by differences in the conditions of adsorption, e.g. the temperature at which CO₂ was adsorbed and the cross-sectional area used in calculating surface areas. This emphasizes the need for development of standard pretreatment conditions and methods of adsorption. To realize that goal additional studies of pretreatment effects, such as that of Deevi and Suuberg, [10], are needed. It is hoped that this continuing study will contribute to that end.

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Table 2: Repeatability Data for CO₂^a and N₂^b Adsorptions on a Utah Bituminous Coal (Scofield Mine; Deseret Coal Co.) Obtained in a Static System

Run No.	Procedure	S.A. (m ² /g)	
		CO ₂	N ₂
1.1	Outgassed; CO ₂ adsorption	129.8	
1.2	Cell immersed in boiling water for 5 min.; pumped 2 hr. to <10 ⁻⁴ torr; CO ₂ adsorption	129.3	0
1.3	Same as run #1.2	132.4	
2.1	Same as run #1.1	156.8	
2.2	Same as run #1.2	140.9	
2.3	Same as run #1.2	147.4	0
3.2	Same as run #1.2	150.8	0
3.3	Same as run #1.2	153.8	
3.4	Same as run #1.2	152.7	
4.1 & 4.2	Pumped to <10 ⁻⁴ Torr		1.72, 1.94
4.3	Same as 4.2		1.95
4.4	Same as 4.2		1.96
4.5	Same as 4.2		1.73

^a CO₂ area = 0.201 nm²; P_{CO₂} = Polynomial Fit

^b N₂ area = 0.162 nm²

Table 3: Repeatability Study in a Flow System of CO₂ and N₂ Adsorptions on Dietz Chars^a

Sample ^b	Run No. ^c	CO ₂ SA (m ² /g)	N ₂ SA (m ² /g)
A-1	1		333
	2		325
	4		327
	5		331
	6		<u>324</u>
	ave 5 runs		328 ± 3.9
B-5	5	289	
	6	296	
	7	289	
	8	293	
	9	<u>298</u>	
	ave 5 runs	293 ± 4.1	
A-1		394	328
A-2		381	322
A-3		<u>304</u>	<u>288</u>
	ave of A samples	360 ± 49	313 ± 22
B-4		301	106
B-5		293	89
B-6		293	93
B-7		307	99
B-8		<u>285</u>	<u>99</u>
	ave of B samples	296 ± 7.6	96.0 ± 5.9

a. Prepared in methane flame (gas temperature of 2000 K; residence time of about 10 ms).

b. A and B are different repeat preparations of char; A-1 to A-3 are different samples of Preparation A. A samples were 25-35 mg and not well mixed; B samples were 75-120 mg and well mixed

c. Run numbers and averages of runs are provided for samples A-1 and B-5 only

Table 4: Physical and Surface Properties of ANL, PETC & Other U.S. Coals and Chars

Sample	Surface Area (m ² /g)		Pore Volume (m ³ /g)			β^d , ^e (nm/s)	Fraction of PV < 0.5nm ^d	Density of g/cm ³
	CO ₂ ^a	N ₂ ^b	Hg	N ₂ ^c	H ₂ O ^d			
Pitt #8 (-200+230) ^f	119±17	1.3±0.1	0.43	0.012	0.031	20.4	0.35	1.39±0.01
Pitt #8 (-200+230) ^h	117±18							
Pitt #8 Char ^g	155	74.6	-	0.056	0.053	67.1	0.28	-
Wilc (-200+230) ^f	144±7	3.3	0.16	0.033	0.282	487	0.31	1.48±0.01
Wilc (-200+230) ^h	154							
Wilc Char 1 ^f	253±30	60.5	0.61	0.128	0.124	36.3	0.88	2.03±0.09
Wilc Char 1 ^h	242±35	47						
Wilc Char 2 ^g	252	124	-	0.164	0.153	226	0.22	-
Dietz (-200+230) ^g	218	3.0	-	0.012	0.257	260	0.44	-
Dietz Char A	360±49	313±22						
Dietz Char B	298±6.8	97±7.4						
Dietz Char C ^{g,j}	526±20	131	-	0.107	0.110	123	0.27	
Wyodak (-200+230) ⁱ	206	5.0±0.4						
Wyodak (-325+400) ⁱ	208	5.0±0.1						
B-Zap (-200+230) ⁱ	229±50	0.5±0.2						
B-Zap (-325+400) ⁱ	255±62	1.0±0.6						
Ut Scof (-200+230) ⁱ	153±10	1.6±0.05						
Ut Scof (-325+400) ⁱ	144±11	1.9±0.1						

^a Measured at 0° C at UNM using flow system, 25° C at BYU using static system; Calc. from DP Eqn. using CO₂ area of 0.201 nm²/molec. and P_{CO2} = 26,144.7 mm Hg at 0° C.

^b Measured at -196° C; Calc. from BET Eqn. using N₂ area of 0.170 nm²/molec.

^c From extended BET measurements

^d From NMR analysis of adsorbed water

^e Interaction parameter from NMR

^f Measured by Mr. Wayne White at UNM; SA's by flow measurement

^g Measured by UNM personnel; SA's

^h Measured at BYU by flow method

ⁱ Measured at BYU by volumetric method

^j Char C was prepared under conditions very similar to those of Char B

Table 5: Comparison of Multisource Surface Area & Pore Volume Data for ANL and PETC Coals and Chars

Samples	Surface Area (m ² /g)		Pore Vol (cm ³ /g)		Ref.	
	CO ₂	N ₂	Hg	N ₂		
Coals	Pitt #8	119	1.3	0.43	0.012	This study
		141	<1.0	-	-	9
	Wyodak	207	5.0	-	-	This study
B-Zap		308	2.6	-	-	9
		242	0.5-1.0	-	-	This study
		-	2.2-4.6	0.08-0.14	-	10
		268	<1.0	-	-	9
Chars ^a		115	1.2-2.6	-	-	11
	Wilcox (2,000 K) ^b	252	47-124	-	0.16	This study
	Wilcox (1,700 K) ^c	211	191	0.68	-	12

^a Gas temperatures shown in parenthesis

^b Prepared in a methane flat flame burner

^c Prepared in a drop tube furnace at a residence time of about 0.2 sec.

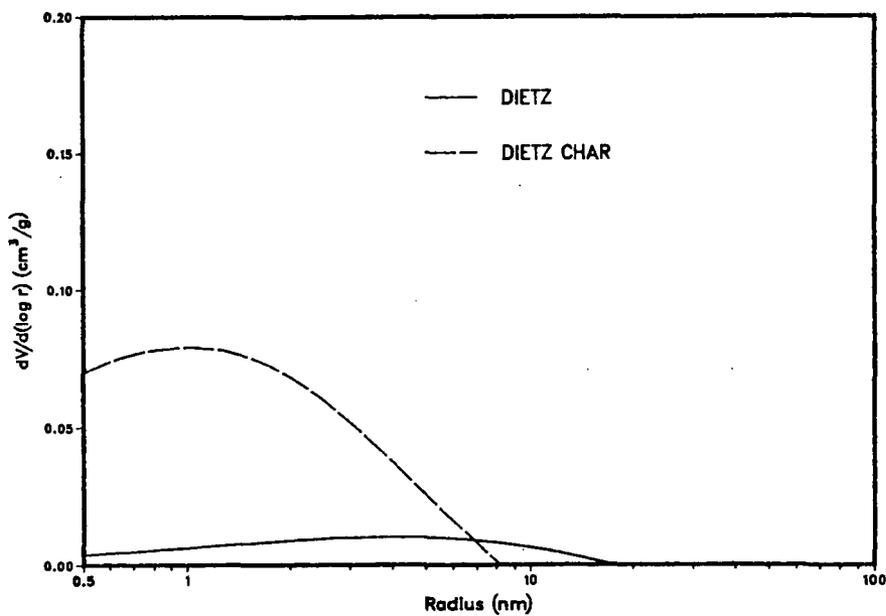
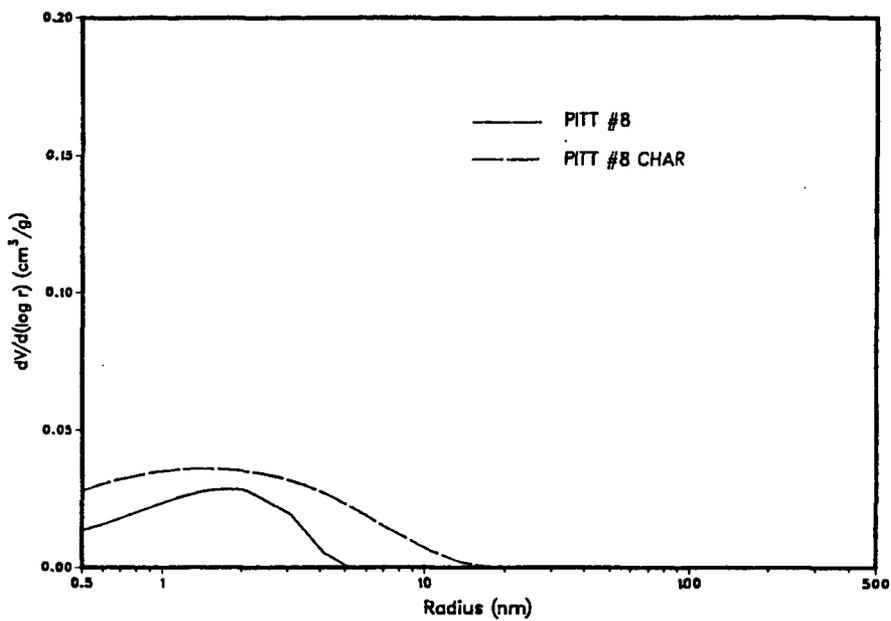


Figure 1. NMR pore volume distributions for two coal/char pairs.