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Publication Date

1978-11-01

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November 1978

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Prepared for the U.S. Department of Energy under Contract No. W-7405-ENG-48

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Change in Physical Characteristics of Roland
Seam Coal with Progressive Solvent Extraction

by

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ABSTRACT

The physical structure of Roland Seam Coal was characterized by studying the surface areas, pore volumes, and pore distributions of raw and extracted coals. BET surface areas were measured by carbon dioxide adsorption at 195°K and nitrogen adsorption at 77°K. Pore volumes were calculated by the difference in the reciprocals of measured apparent and actual densities. Distributions curves were generated by measuring mercury penetration as a function of pressure.

The data gathered suggest a micropore structure having a 3.4 nm average diameter and random constrictions of the order of 0.4 nm. Extraction generates new micropores and degrades the micropore structure, for yields in excess of 30 percent. Changes in the pore distribution and the generation of new pores indicate that resistance to extraction due to the pore structure is minimal, pore-volume data confirm the preferential liquefaction of lower molecular-weight material.

Summary Statements

1. This paper investigates the changes of raw coal with progressive extraction using six organic solvents containing nitrogen groups. This permitted the evaluation of solvent hold up in the extracted coal.
2. The coal was treated in a refluxing extraction apparatus and the dried residues were outgassed and areas measured using the Brunauer, Emmett and Teller method. The adsorbates were carbon dioxide at dry-ice acetone temperature and nitrogen at liquid nitrogen temperature. Mercury porosimeter was used to obtain the macropore structure and bulk density. Helium densities were measured to get true densities.
3. The most significant limitation in interpreting the results is the lack of knowledge of the influence of the residual solvent on the surface area of the residues.

INTRODUCTION

Coal has a highly complex internal pore system, resembling molecular sieves in this respect. In order for chemical reactions, gas adsorptions, and extraction to take place, reagents or vapors have to pass into the micropore structure of coal. Rates of mass transfer may be greatly restricted by the very small size of the openings in the coal structure. The pore framework should be maintained during extraction to allow the processing fluid to be in contact with as much of the solid coal as possible. Therefore, the pore volume and surface area should be measured as processing takes place to determine if the pore system is being utilized effectively.

Van Krevelen and Zwietering¹, using Ritter and Drake's² method of mercury porosimetry to study coal, suggested that coal contains two pore systems: a macropore system and a micropore system. Generally pores having diameters below 4 nm are described as micropores, those above 30 nm as macropore, and those in between as transitional or intermediate pores. Mercury is able to penetrate the macropore system, but even at high pressure is unable to penetrate the micropore system. However, both pore systems are accessible to helium at room temperature.

The pore size distribution can very greatly depending on the rank of coal. Gan, Nandi, and Walker³ measured the pore size distributions for a number of coals by nitrogen adsorption isotherms at 77°K in the diameter range of 3000 nm to 1.2 nm. For an Illinois No. 6 high-volatile-C bituminous coal 30.2% of the pore volume is smaller than 1.2 nm, 52.6% is between 1.2 nm and 30 nm,

and 17.2% is above 30 nm. For a low-volatile bituminous Pennsylvannia coal, 73% of the pore volume is under 1.2 nm, 0% is between 1.2 nm and 30 nm, and 27% is above 30 nm. Medeiros and Petersen⁴ recast Walker's results showing that most of the internal surface area of coal is contained in the micropores.

As already mentioned, the internal structure of coal has certain characteristics of molecular sieves. Bond and Spencer⁵ observed that the heat of wetting for any rank of coal decreases as the molecular volume of the wetting liquid increases. They obtained a relationship for the ultrafine internal surface area as a function of size, showing that the critical dimensions of ultrafine pores are 0.5 nm and 0.8 nm in approximate diameters, corresponding to wetting liquids with molecular volumes around 50 and 150 mL/mole.

Lamond and Marsch⁶ and later Medeiros and Petersen⁴ used 0.4 nm and 0.5 nm sieves to study the pore sizes in coal. Marsch observed that nitrogen at 77°K would penetrate 0.5 nm sieves but not 0.4 nm sieves, whereas carbon dioxide at 195°K has no difficulty penetrating either. Medeiros studied the microporous structure of coal using the adsorption of four gases (CO₂, CF₄, N₂, and Ar) on Wyodak Roland Seam coal, Illinois No. 6, and 0.4 nm and 0.5 nm Linde molecular sieves. He concluded that Roland Seam coal resembles a 0.4 nm sieve in its micropore structure, whereas Illinois No. 6 coal more closely resembles the 0.5 nm molecular sieves.

Booras and Petersen⁷ studied high and low temperature adsorption of CO₂ on an alumina catalyst, a synthetic sodium

mordenite and Roland Seam coal. Using experimental conditions of 195°K and room temperature. They concluded that activated diffusion was not an important factor in CO₂ adsorption at either of these temperatures, for samples having pore diameters as low as 0.67 nm.

EXPERIMENTAL

Samples

Raw Roland Seam coal was obtained from the Roland top seam of the Wyodak Mine at Gillette, Wyoming. This coal was used in this study and in the extraction studies of Grens et al.^{8,9}. The as-received coal was reduced to -28 + 150 Tyler mesh following ASTM Method D-346 and subsequently placed in a desiccator under vacuum or stored under nitrogen in friction-lid paint cans. Separate ASTM ultimate analysis were done by Commercial Testing and Engineering Co., Denver Laboratory (CT and E). The results of these tests are presented in reference 4.

The extracted coal used in the adsorption studies was obtained from Grens et al.^{8,9} wherein detailed extraction procedures and results are presented. Extraction procedures can also be found in reference 11. Dorighi and Grens⁸ used pyridine, ethylenediamine, quinoline, and piperidine as solvents, while Lindsay and Grens⁹ used pyridine, dipropylamine, and tripropylamine as solvents in a reflux liquid extraction of Roland Seam coal. Yields were varied by conducting the extraction at various temperatures and lengths of time. Yields were corrected for solvent entrainment by making nitrogen balances on the residues. However, except where noted, all runs were for 4 h. The residues (extracted coal samples) were dried at 130°C and 26.5 kPa pressure for 24 h in a nitrogen purge of 20-25 mL/min. The dried residues

were then stored in a desiccator under a vacuum of 13.3-40.0 kPa nitrogen pressure until needed.

Apparatus

A volumetric gas adsorption apparatus⁴ was used to measure nitrogen and carbon dioxide isotherms at 77°K and 195°K respectively. Samples were degassed at 130°C for 16 h at a pressure of 1.3 mPa before measuring adsorption. Adsorption isotherms were followed up to a p/p_0 value of 0.3, where p is the equilibrium pressure and p_0 is the vapor pressure of the adsorbate at the temperature of adsorption. An equilibrium time of 30 min was allowed for each adsorption. Surface areas were measured using the BET correlation¹⁰ and 4 adsorption points.

Helium densities were measured in a section of the above mentioned apparatus at room temperature. The apparatus was of the constant volume type, the pressure was recorded before and after the expansion of helium into the sample holder from a reference volume. Equilibrium time for a measurement was 2 h. Degassing procedures were the same as above.

An Aminco porosimeter was used to determine apparent densities and pore volume distributions for pores with diameters greater than 30 nm. The samples were degassed at below 6.6 Pa for 10 min at room temperature before being exposed to mercury.

RESULTS AND DISCUSSION

Coal appears to have a highly unusual structure as evidenced by the results of BET area measurements made using carbon dioxide and nitrogen and from apparent and true densities as measured using a porosimeter and helium density apparatus, respectively.

The average surface areas obtained for the samples are presented in Table 1. They were calculated from two BET measurements, using molecular surface areas of $.234 \text{ nm}^2$ and $.162 \text{ nm}^2$ for carbon dioxide and nitrogen, respectively. The variation of surface area per gram raw coal with extraction yield is shown in Figure 1. In this figure, the increased yield was obtained by extracting at higher temperatures. Temperatures used were 100, 150, 200, 250 and 300°C . The approximate trends indicate that the surface area depends primarily on the nature of the solvent and the yield. The largest area was developed using pyridine as a solvent. In all cases the absolute area of the original sample increases with extraction. The somewhat surprising result that for small yields the area is smaller than that of raw coal is believed to be due to solvent retention by the samples which reduces surface roughness. This effect applies particularly to ethylenediamine and to piperidine which exhibited the largest solvent retention. Despite solvent retention the areas increase with increasing amounts of extraction.

In Figure 1 the amount of coal sample decreases linearly with yield. The curves suggest that the specific surface area developed with extraction approaches a value obtained by an extrapolation of the dashed lines on the figure to the zero yield value. These values appear to be characteristic of the solvent.

The increase in nitrogen BET surface area with extent of extraction indicates that the micropore structure has been opened up significantly by the solvent. This will be discussed later in this paper.

Apparent and actual densities were determined by mercury and helium displacement, respectively. Pore volumes were determined by the difference in reciprocal densities. Mercury penetration experiments on the -50 + 100 Tyler mesh fraction and the -28 + 50 Tyler mesh fraction of the residue exhibited no observable size dependence. Helium densities were determined on a well-mixed sample of the residue and are assumed to be independent of particle size. Density measurements of samples extracted to high yields indicate that the residue approaches that of graphite with progressive extraction.

The porosimeter used in this work could only penetrate pores with diameters greater than 30 nm and the macropore volumes listed in Table 1 are based upon the volume of mercury penetrating pores greater than 30 nm. Assuming all of the surface area is in the micropores, the average diameter of the micropores decreases with nearly all of the extracted samples. This is interpreted to mean that there a large number of new pores are formed during extraction.

The experimentally measured total pore volume, i.e., the sum of the micropore and macropore volumes, can be expressed by Equation 1 below:

$$V_{\text{EXPERIMENTALLY MEASURED}} = \frac{V_O + \frac{Y_C}{\rho_{\text{EXT}}} - \frac{M_{\text{SOL}}}{\rho_{\text{SOL}}}}{1 - Y_C + M_{\text{SOL}}} \quad (1)$$

V_O = pore volume of raw coal, cc/g

Y_C = yield corrected for solvent retainment

V_r = volume of solvent retained, cc/g residue

$$= \frac{M_{\text{SOL}}}{\rho_{\text{SOL}}}$$

ρ_{EXT} = average density of the material extracted

M_{SOL} = mass of solvent retained per gram of original coal.

ρ_{SOL} = density of solvent,

provided the density of the solvent retained is the same as it is in the pure state. Note, however, that we can make a calculation using the density of the raw coal, in place of ρ_{EXT} in Eq. 1. That is, $V_{\text{CALCULATED}}$ can be defined as

$$V_{\text{CALCULATED}} = \frac{V_0 + \frac{Y_C}{\text{RAW COAL}} - \frac{M_{\text{SOL}}}{\rho_{\text{SOL}}}}{1 - Y_C + M_{\text{SOL}}} \quad (2)$$

Equations 1 and 2 define the ordinate and abscissa, respectively, of Figure 4. The figure shows that the density of material removed by these solvents is smaller than that of the original coal and accordingly the density of the residue increases with extraction. This of course is well-known from chemical analysis, but it is interesting to show this solely from physical measurements.

The pore volume and surface area measurements lead to interesting conjecture about the nature of the coal structure and changes in the structure as the extent extraction increases. The pore-volume and surface-area measurements on raw and extracted coals strongly suggest that Roland Seam coal has two pore systems. The macropores have large volume, small surface area, and no mass-transfer limitations, while the micropores have small volume, large surface area, and some mass-transfer limitations. The

micropores appear to have small constrictions of the order of 0.4 nm that inhibit the flow of solvent into the micropores as suggested by the following observations: 1) the surface area measurements by carbon dioxide and nitrogen are $99.3 \text{ m}^2/\text{g}$ and less than $1 \text{ m}^2/\text{g}$, respectively as shown in Table 1 and 2) unlike carbon dioxide at 195°K , nitrogen at 77°K will not penetrate a 0.4 nm molecular sieve⁴, 3) the average micropore diameter of the raw coal is about 3.5 nm.

The data on extracted coals reveal that the carbon dioxide BET surface area increases more than the nitrogen BET surface area and that in general the average micropore diameter decreases upon extraction. Therefore it would appear that new micropores must be formed during extraction.

It is consistent with all data gathered in this study to postulate that the micropores in the raw coal are reasonably large, with periodic constrictions some of which are removed during extraction. The number of constrictions removed and the extent of new pores formed appear to depend primarily on yield, solvent molecular size, and chemical nature of the solvent.

This model of the pore structure accounts for all of the known physical characteristics of raw and extracted Roland Seam coal. No attempt was made to determine the magnitude of swelling of coal by the solvent, or of thermal expansion during extraction, although both are believed to be small. An attempt was made to determine qualitatively the general shape of the pore structure such as slot shaped or rod-like from the changes in the pore volume and the surface area, but due to the complexity of the structure and to solvent entrainment the results were inconclusive.

FIGURE CAPTIONS

- Figure 1. Variation of surface area with extraction yield.
- Figure 2. Pore distribution of raw coal extracted coals.
- Figure 3. Pore distribution of extracted coals.
- Figure 4. Experimental pore volume vs calculated pore volume.

TABLE 1. SURFACE AREAS AND PORE VOLUMES OF EXTRACTED COALS.

	CO ₂ SURFACE AREA M ² /G	CO ₂ SURFACE M ² /G RAW COAL	N ₂ SURFACE AREA M ² /G	MICROPORE VOLUME CC/G	MACROPORE VOLUME CC/G	AVERAGE MICROPORE DIAMETER MANOMETERS
PYRIDINE	247	194	10	0.110	0.099	1.78
DIPROPYLAMINE	170	127	5	0.078	0.102	1.84
TRIPROPYLAMINE	172	144	4	0.077	0.088	1.79
ETHYLENE DIAMINE	195	79	44	0.228	0.603	4.68
QUINOLINE	209	152	8	0.101	0.129	1.93
PIPERIDINE	144	95	8	0.093	0.195	2.58
RAW-COAL	99	99	1	0.086	0.042	3.46

* ALL COALS LISTED WERE EXTRACTED FOR 4 HOURS AT 250°C EXCEPT DIPROPYLAMINE WHICH WAS EXTRACTED 4 HRS. AT 200°C.

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Figure 1. Variation of surface area with extraction yield.

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Figure 2. Pore distribution of raw coal extracted coals.

XBL 784-555

Figure 3. Pore distribution of extracted coals.

XBL 784-553

Figure 4. Experimental pore volume vs calculated pore volume.

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