

THE ARGONNE COALS DO NOT HAVE AN EXTENDED INTER-CONNECTED PORE NETWORK

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Keywords: pore structure, gas adsorption, surface area

ABSTRACT

The sorption of N_2 , CO_2 , ethane, cyclopropane, cyclobutane, cyclopentane, and cyclohexane has been studied on all of the Argonne premium coals. For all of the bituminous coals, the CO_2 BET surface areas are as expected and much higher than all of the other molecules studied. Plots of \log (moles adsorbate in monolayer) vs. \log (cross section area of adsorbate) are straight lines whose slopes are very steep (-5.5 to -11.6) and inconsistent with the known fractal dimensionalities of the coal pore surfaces. For Zap lignite, the CO_2 BET surface area is $274m^2/g$, while all of the hydrocarbons give lignite surface areas of $8 \pm 3m^2/g$. These data are inconsistent with adsorption in an inter-connected pore network. For bituminous coals, the dependence of the amount sorbed vs. molecular diameter is similar to the dependence of diffusivities through glassy polymers on molecular diameter. We conclude that the pores in coal are isolated from each other and can only be reached by diffusion through the solid, glassy, macromolecular coal.

INTRODUCTION

It is widely accepted that coals contain an inter-connected network of slit like pores and that the connections between pores are often bottlenecked.¹ This conclusion is based almost entirely on experimental studies of gas adsorption. We have recently completed a study of the adsorption of a series of gases on the Argonne coals and obtained results which are inconsistent with this model. Our data for Illinois #6 coal have already been published and we will here discuss our results for some of the other Argonne coals.²

Small angle X-ray studies have been carried out on all of the Argonne coals and demonstrate that the pore surfaces are well behaved fractals.³ Being surfaces, their fractal dimensionalities are constrained to lie between 2 and 3. Fractal dimensionalities can also be obtained by determining the dependence of measured surface area on the size of the adsorbate molecule.⁴ Fractal dimensionalities obtained in this way should agree with those obtained by other techniques. The basis of the measurement is that small molecules will follow a rough surface more precisely than will larger molecules and thus report a larger surface area. The difference between the surface areas reported by a small and a large molecule will increase with the degree of surface roughness, that is with the fractal dimensionality. The fractal dimensionalities calculated from adsorption measurements carried out using ethane, cyclopropane, cyclobutane, cyclopentane, and cyclohexane

are reported in Table 1. The dimensionalities do not lie between 2 and 3 demonstrating that the process under investigation cannot be a simple equilibrium surface adsorption.

Perhaps the most impressive feature of these data are the great size of the calculated "fractal dimensionalities". They vary from 11 to 23. The amount of gas adsorbed varies with the cross sectional area raised to at least the 5th power. Stated another way, the amount of gas sorbed by these coals exhibits an extraordinarily steep dependence on gas molecular size, that dependence being between the 5th and 12th power of the cross sectional area. Any model for coal structure must rationalize this extraordinary fact.

This enormous sensitivity to molecular size is rare. Diffusivities through glassy polymers are known to have similar and even greater sensitivities to molecular size.⁵ We propose that the process occurring here is not gas adsorption on the surface, but rather diffusion of the gases through a glassy polymer to reach an internal pore surface. We are suggesting that the BET surface areas measured using these gases are not equilibrium values, but are controlled by the rate of diffusion of these gases through the glassy coal. This was confirmed by following the uptake of ethane by Illinois No. 6 coal at 177°K which had not reached equilibrium after 5.5 days.

We look to the surface areas measured using the individual gases for confirmation of the idea that it is diffusion through glassy polymers which is occurring, not diffusion through a more-or-less rigid pore network. We have already pointed out for Illinois No. 6 coal that we were unable to rationalize the reported surface areas based on diffusion through a interconnected network.² Figure 1 contains the data for Bruceton coal and the results are similar. CO₂, which is known to swell coals, has a ready diffusion pathway and reports a high surface area.⁶ Ethane, which differs in size from CO₂ by only 16% and which has a similar cylindrical shape, reports a much lower surface area. It is hard to rationalize this difference if both materials are diffusing through a rigid pore network. Cyclopropane has the same surface area as ethane, but a significantly different shape. It is hard to believe that two materials, one planar and the other cylindrical, would pass equally through a rigid pore system and report the same surface area. Similar results have been obtained for all of the other Argonne bituminous coals. These data support the notion that the coals do not have an interconnected pore network, but rather isolated pores like bubbles in a solid which are reached only by diffusion through the solid coal.

Finally, we consider the surface area measurements for ZAP lignite shown in Figure 2. Hydrocarbon gases should be essentially insoluble in this high oxygen, highly polar low rank coal. If the pore structure is a rigid network, this should have no effect on the surface areas measured. The data are shown in Figure 2 and reveal that within experimental error, all of the hydrocarbon gases report the same surface area, 8 ± 3 m²/g. This is to be contrasted with the CO₂ area which is 274 m²/g. We are unable to rationalize these data using a pore network structure. They are nicely consistent with a pore model which involves

isolated pores which can be reached only by diffusion through the solid.

We conclude that the pore structure of these coals is isolated pores which can be reached by diffusion through the coals and that an interconnected pore network which provides access to a large internal surface by pore diffusion does not exist. This structure model has a number of consequences, a few of which can be elaborated here. The first is that CO₂ surface areas are approximately correct. Because it is somewhat soluble in coals, CO₂ has a rapid diffusion pathway and can quickly reach all of the pore surfaces where it is adsorbed as it would be on any surface. These reported surface areas are undoubtedly somewhat in error because of the amount of CO₂ dissolved in the coal. We believe these errors are small compared to the fundamental uncertainties of the measurement. Likewise, we believe that helium densities give accurate pore volumes. Diffusion rates vary inversely with molecular size and helium is small enough to have reasonably rapid passage through the coal and reasonable equilibrium times. Because coal surface areas depend on the diffusion rate of the molecules used to probe it, measured surface areas will depend on the nature of the molecular probe. This would be true in any case because the surfaces are fractal, but we are concerned with a much greater sensitivity to molecule size and polarity. Molecules which interact with coals (are soluble in them) will have a rapid diffusion pathway and will report much greater surface areas than will non-polar hydrocarbons and other molecules which do not interact specifically.

EXPERIMENTAL

Complete experimental descriptions of all procedures used may be found in the Ph.D. thesis of Patrick Wernett.⁷

ACKNOWLEDGEMENTS

This work was supported by the U. S. Department of Energy Contract #DE-AC22-38PC89757. We gratefully acknowledge this support. Numerous discussions with Dr. Peter Hall played an important role in the development of our ideas and we are grateful to him.

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Table 1. Fractal Dimensionality of Argonne Coal Surfaces Measured by BET Adsorption of Ethane, Cyclopropane, Cyclobutane, Cyclopentane, and Cyclohexane

Coal	%C dmmf	Dimensionality	Correlation Coefficient
Pocahontas #3	91.8	12	0.998
Upper Freeport	88.1	11	0.995
Lewiston-Stuchton	85.5	15	0.942
Pittsburgh No. 8	85.0	16	0.987
Blind Cargon	81.3	14	0.990
Illinois No. 6	80.7	23	0.999
Wyodak	76.0	11	0.867

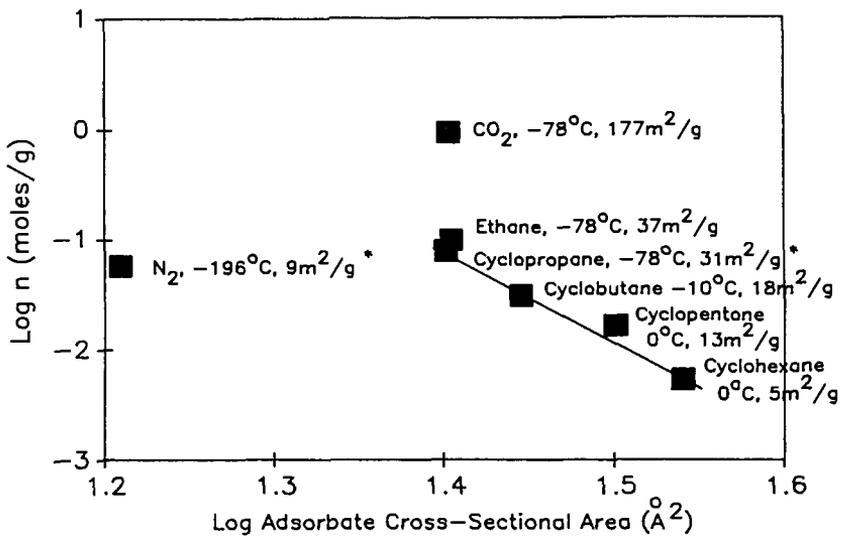


Figure 1. Fractal Analysis of the Cyclic Hydrocarbon Gas Adsorption on Argonne Pittsburgh No. 8 Coal (n is the Number of Moles Required for Monolayer Surface Coverage Obtained from the BET Equation). The Adsorbate Gas is Given Followed by the Adsorption Temperature and the Measured BET Surface Area.

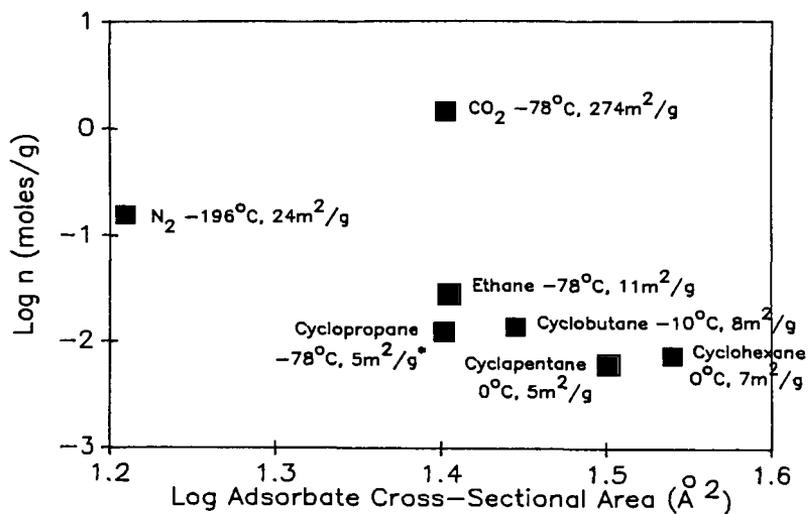


Figure 2. Fractal Analysis of the Cyclic Hydrocarbon Gas Adsorption on Argonne Beulah Zap Lignite (n is the Number of Moles Required for Monolayer Surface Coverage Obtained from the BET Equation). The Adsorbate Gas is Given Followed by the Adsorption Temperature and the Measured BET Surface Area.