

Reprinted from Vol 49 1970

# **FUEL**

**the science of  
fuel and energy**

Iliffe Science and Technology Publications Ltd

## Letter to the Editor

### Surface areas of coals from carbon dioxide adsorption at 298°K

P. L. WALKER, JR. and R. L. PATEL

Previously, Walker and Kini concluded that the surface area of coals calculated from carbon dioxide adsorption isotherms measured at 298°K, using the BET equation, most closely represents the total surface area, of any approach yet used<sup>1</sup>. In order to calculate surface areas from the BET equation, it is necessary to have adsorption data in the relative pressure range 0.05 to 0.30. Since the vapour pressure of carbon dioxide at 298°K is 63.5 atm, a high pressure apparatus is required to obtain the necessary adsorption data.

Marsh and Siemieniowska have suggested the use of the Dubinin-Polanyi (DP) equation to calculate surface areas of coals from carbon dioxide adsorption data at 298°K<sup>2</sup>. The interesting point about this equation is that surface areas can be calculated from adsorption measurements made in a conventional vacuum apparatus (i.e. for adsorption below 1 atm pressure) if a linear extrapolation of the data to the volume axis can be assumed. Thus it was of interest to compare surface areas calculated by the BET and DP equations from adsorption results measured in two different pieces of apparatus.

Table 1 Analyses of samples

Sample	Tyler mesh size	Proximate analysis moisture free (%)			
		Ash	VM	FC	Sulphur
St. Nicholas, Pa.	100 × 150	8.4	4.5	86.4	0.5
Loree, Pa.	100 × 150	7.1	5.4	87.0	0.6
885, Pa.	100 × 325	5.4	37.6	57.0	0.8
No. 6, Illinois	200 × 325	7.6	45.4	—	2.7
Elkhorn, Kentucky	40 × 70	3.8	35.4	58.7	0.6
C Seam, Kentucky	50 × 70	2.0	33.1	63.6	0.3
No. 1 Block, Indiana	40 × 60	14.3	34.2	51.5	0.7
HT155	38 × 48	20.0	4.1	74.1	1.7
HT135	28 × 48	20.3	5.0	69.8	4.8
HT141	28 × 48	19.1	4.8	71.9	3.9

Table 1 presents analyses for the samples studied. Samples designated as HT were chars. HT155 was produced by the partial hydro-gasification of a high volatile bituminous coal at *ca* 870°C to 66% weight loss. Samples HT135 and 141 were produced by the partial gasification and combustion of high volatile vituminous coals at *ca* 980°C to *ca* 50% weight loss.

Prior to adsorption measurements, samples were normally degassed at 110°C for at least 4 h down to a pressure of  $10^{-6}$  mm Hg. Variations in degassing temperature between 110 and 155°C had no detectable effect on subsequent adsorption. Equilibration time for each adsorption point was 30 min in all cases. The molecular area of carbon dioxide at 298°K was taken as  $25.3 \text{ \AA}^2$  ( $0.253 \text{ nm}^2$ )<sup>1</sup>.

Table 2 Surface areas from CO<sub>2</sub> adsorption at 298°K

Sample	Surface area (m <sup>2</sup> /g)	
	DP	BET
St. Nicholas, Pa.	238	226
Loree, Pa.	274	273
885, Pa.	133	132
No. 6, Illinois	144	139
Elkhorn, Kentucky	86	80
C Seam, Kentucky	89	85
No. 1 Block, Indiana	100	97
HT155	371	375
HT135	360	360
HT141	425	425

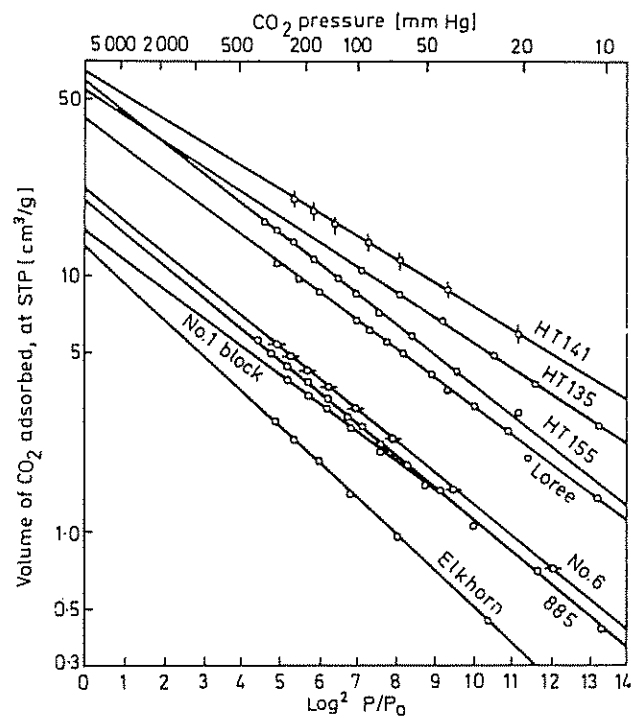
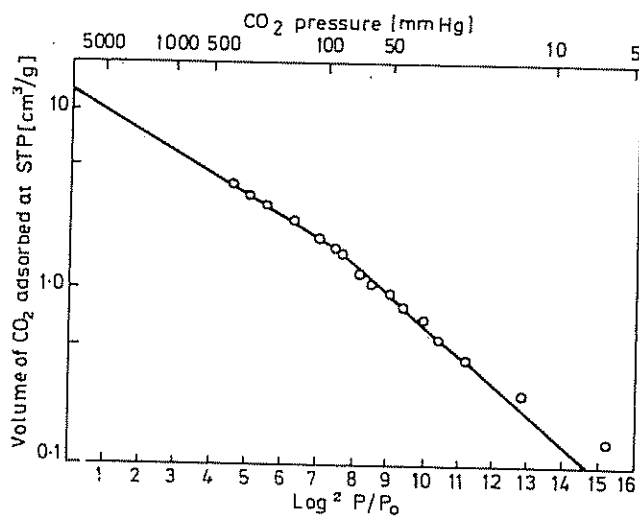


Fig 1 Dubinin-Polanyi plots for CO<sub>2</sub> adsorption at 298°K on selected coals and chars. (Note their excellent linearity).

Surface area results are summarized in *Table 2*. Agreement between the areas calculated from the BET and DP equations is very good in all cases. This is as expected for solids which have almost all of their surface area located in pores of molecular dimensions, where uptake due to capillary condensation will be negligible<sup>3</sup>. Excellent linear DP plots, with no breaks, were obtained in all cases with the exception of the C seam, Kentucky sample. This made their extrapolation to the ordinate to obtain the volume of carbon dioxide adsorbed in a monolayer straightforward. Some typical plots are shown in *Fig 1*.

*Fig 2* shows the DP plot for the C seam sample. The plot has two linear regions with a distinct break at a pressure of *ca* 81 mm Hg. Extrapolation of the linear region of lower slope to the ordinate yields a micropore surface area of 89 m<sup>2</sup>/g, in good agreement with the BET area. No reason can be given at this time for the break in the plot. Such breaks have been observed previously, however, for carbon dioxide adsorption at 298°K on zeolite molecular sieves<sup>3</sup>.



*Fig 2* Dubinin-Polanyi plot for CO<sub>2</sub> adsorption at 298°K on bituminous coal from C seam, Kentucky. (Note that the plot consists of two distinct linear regions).

These results show that there is no necessity to use a high pressure apparatus to measure the surface areas of microporous solids by carbon dioxide adsorption at 298°K. As recommended previously<sup>2</sup>, adsorption can be measured in a conventional vacuum apparatus and areas calculated using the DP equation.

ACKNOWLEDGEMENT

This study was supported by the Office of Coal Research, U.S. Department of the Interior on Project No. 14-01-0001-390.

*Department of Materials Science  
Pennsylvania State University,  
University Park, Pa. 16802  
USA*

*(Received 29 October 1969)*

REFERENCES

- 1 Walker, P. L. Jr. and Kini, K. A. *Fuel, Lond.* 1965, 44, 453
- 2 Marsh, H and Siemieniowska, T. *Fuel, Lond.* 1965, 44, 355
- 3 Lamond, T. G. and Marsh, H. *Carbon*, 1964, 1, 281