

ACCESSIBLE SURFACE AREAS OF COALS

THE accessible surface areas of bituminous coals lie in the range of 40–200 m.²/gm. when estimated from their methyl-alcohol adsorption isotherms or from heats of wetting in liquid methyl alcohol¹. Recently, Lecky, Hall and Anderson² and Malherbe³ have measured the surface by nitrogen or argon adsorption, using the Brunauer–Emmett–Teller method, and have obtained very much lower figures, in the range 0.4–11 m.²/gm., and Zwietering, Oele and van Krevelen⁴ have confirmed these low figures. In explanation of the discrepancy, they have suggested that the polar nature of methyl alcohol and water enables these substances to penetrate regions of coal inaccessible to inert gases, that is, the apparent surface is in effect created by imbibition of the polar molecules leading to incipient peptization. Lecky, Hall and Anderson have drawn a parallel with the behaviour of polymers and proteins, and suggest that coals possess very little permanent internal surface.

The samples used and their method of preparation were substantially similar in all these investigations, and there can be little doubt that the almost hundred-fold discrepancy between the two groups of surface area estimates is physically real, and does not arise from errors in interpretation (except, possibly, the neglect by Malherbe³ of the prolonged uptake of argon and nitrogen), or the use of a restricted range of coals. The purpose of this and the following communication is to discuss the evidence in support of the higher values and the reason for so large a difference. Minor variations, such as those due to surface oxidation, will not be considered at this stage.

There are many reasons for believing that the interaction of methyl alcohol with coals is predominantly physical and non-specific in nature:

(1) Reproducible and definite figures, in the region of 5–20 per cent w/w, for saturation adsorption of methyl alcohol¹, water⁵ and *n*-hexane⁴ are obtained even on low-rank coals, which are the most reactive and polar in their nature. The polymers the behaviour of which was cited by Anderson *et al.*² lose their rigidity at high relative pressures, and tend, on the contrary, to yield very high values for the saturation adsorption.

(2) The surface area estimated by the Brunauer–Emmett–Teller method from the isotherm of *n*-hexane⁴ on low-rank coal at 25° C. agreed closely with the figure obtained with methyl alcohol in spite of the non-polar nature of the hexane.

(3) The heat of wetting of low-rank coals in methyl alcohol is liberated in a few minutes, that is, as rapidly as the heat liberated when comparatively rigid adsorbents such as charcoal and carbon black are wetted; a slow peptization process is therefore unlikely to contribute appreciably to the value obtained.

(4) Bangham and Maggs⁶ calculated an elastic modulus from the linear expansion of coal during adsorption of methyl alcohol and of hexane vapours. The figures obtained were nearly equal, and this result is consistent with their assumption that the expansion was a physical effect resulting from the lateral pressure of the adsorbed film.

(5) The value of the factor used for converting the heats of wetting in methyl alcohol to surface areas,

10 m.²/cal., was derived *for coal* by dividing areas estimated from methyl alcohol and hexane isotherms by the corresponding heats of wetting. Figures closely comparable with the value for low-rank coals have been obtained for carbon black⁷, charcoal⁸, graphite¹ and high-rank coals¹, all of which undergo but slight expansion on wetting and are unlikely to enter into a specifically polar interaction with methyl alcohol.

There is thus considerable evidence—neglected by those who take the view that the nitrogen adsorption area is correct—substantiating the higher values for the surface areas of coals. In the following communication further support for this view is given, and the possible reasons why low values might be obtained from nitrogen isotherms are discussed.

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¹ Griffith, M., and Hirst, W., Proc. Conf. Ultrafine Structure of Coals and Cokes, 80 (Brit. Coal. Util. Res. Assoc., 1944). Maggs, F. A. P., *J. Inst. Fuel*, 17, 49 (1943).

² Lecky, J. A., Hall, W. K., and Anderson, R. B., *Nature*, 168, 124 (1951).

³ Malherbe, P. le R., *Fuel*, 30, 97 (1951).

⁴ Zwietering, P., Oele, A. P., and van Krevelen, D. W., *Fuel*, 30, 203 (1951).

⁵ Maggs, F. A. P., Bond, R. L., and Griffith, M., Disc. Faraday Soc., No. 3, 29 (1948).

⁶ Bangham, D. H., and Maggs, F. A. P., see ref. 1, p. 118.

⁷ Bond, R. L., and Maggs, F. A. P., *Fuel*, 28, 169 (1949).

⁸ Bangham, D. H., and Razouk, R. I., *Proc. Roy. Soc., A*, 166, 572 (1938).

COMPARISON of lump or particle densities of low-rank bituminous coals with densities measured by the displacement of the inert gas helium shows^{1,2} that 10–15 per cent of the particle volume consists of pore space in the complete absence of swelling or peptizing action. If this porosity is compared with a typical surface area measured by low-temperature nitrogen or argon adsorption^{3,4}, then, whatever the shape of the pores, their average diameter must be in the region of 0.1 μ; and any appreciable volume of really fine pores would be incompatible with so high an average. This conclusion conflicts with the observation that coals act as molecular sieves¹, being in some cases impermeable to molecules only a few angstroms in diameter.

Recent studies of the mechanism of solvent extraction of coals⁵ tentatively support the view⁶ that there exist in low-rank bituminous coals compact units some hundreds of angstroms in diameter, surrounded by pores of much smaller diameter than above calculated, and giving coal an internal surface of the order of magnitude estimated from measurements with methyl alcohol⁷.

Malherbe⁴ showed that adsorption of argon was still proceeding after 1,500 hr.; but when plotting his isotherms he arbitrarily selected the period of 10 min., at the end of which the initial very rapid adsorption was complete. This procedure must have a considerable effect on the estimated areas. But a more important point seems to have been overlooked: with a thermolabile substance such as coal, measure-