

Microporosity - Its Measurement, Structure and Utility.

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The time is opportune to examine and assess our knowledge of microporosity in coals and immediately related materials. In the United Kingdom we are witnessing the cessation of the British Coal Utilisation Research Association (BCURA) as a Research Association⁽¹⁾, this organisation being responsible for much of our detailed knowledge of the organic and physical chemistry of coals. Such occasions give rise to a response incorporating analysis and appraisal.

Historically, it is interesting to note the parallelism of theories of adsorption with those of coal structure giving now a measurement of microporosity, i.e. a volume parameter, or effective surface area which has been evaluated relatively thoroughly ranging from about 0.04 to 0.12 cm³ g⁻¹, the minimum occurring with the coking coals⁽²⁾. What is not so definite is the detail of the structure of microporosity and the mechanism(s) of change which occur on heat treatment of coals. This is essentially a multi-variant problem if extremes of fusibility with rank and the composition of coking blends are considered.

This problem of the structure or characterisation of microporosity in coals and carbons is intractable. Classical adsorption theory, in the sense of the BET or Langmuir approach helps little. It is just conceivable that the Dubinin-Radushkevich (D-R) approach and the consequences of its applicability may give some insight into the structure of microporosity. These consequences take one into the realm of statistical distributions and it may be possible to say something of the frequency distribution of micropore size (measured unfortunately not in units of length).

The D-R approach, which is not based upon a theoretical model of adsorption processes, but has a semi-empirical origin, in utilising some of the Polanyi adsorption potential theory, postulates a rectilinear relationship between $\log V$ (V is amount adsorbed) and $(\Delta G)^2$ (ΔG is the free energy of adsorption). Whereas it is impossible to anticipate, a priori, how such a relationship is related to an adsorption process it is possible to be more pragmatic and analyse the consequences. These tell us that the frequency distribution of micropore volume filling at specific values of ΔG has formulation in the Rayleigh distribution, which is a distribution describing some natural phenomena. This suggests that over the entire micropore volume there is a natural, progressive distribution of size of micropore. The specificity of this Rayleigh distribution is reasonably established. Other distributions which describe natural phenomena, such as Poisson, Gaussian and log-normal distributions, have been used to 'synthesise' D-R graphs, and except in one case (a unique selection of constants in the Poisson distribution) the D-R graphs are all non-linear. Although such a conclusion is not dramatic, it suggests that the size distribution of microporosity is random with formulation which is a step forward in the creation of possible theoretical isotherms which must take such matters into account using summations of atom-atom interactions.

The detailed picture of how micropores of different size are interconnected and of any relationship between the ordered and disordered carbon atoms (not begging the question at this stage) still remains obscure. However, high resolution electron microscopy^(3,4) is now available and it would be pleasant to have these problems solved to some extent by direct visual inspection.

The successful description of micropore volume hinges upon the realisation that rates of adsorption are temperature dependent — that for coals adsorption temperatures of about 298°K must be used and that the adsorbate molecule must not be too large. The successful description hinges also upon the method of interpretation of the isotherm obtained at 298°K. Again, the use of Dubinin-Radushkevich theory appears sensible, but it has its critics. One way to obviate the problems of interpretation of gas phase adsorption at 298°K is to attempt adsorption from solution at 298°K. Immediately one meets the difficulty of assessing the extent of adsorption of solvent as opposed to solute (adsorbate). Results will be presented which illustrate (for microporous carbons) that a worthwhile procedure must incorporate analysis at low relative concentrations, C/C_s , (equivalent to p/p_0) and that one of the simplest of suitable adsorbates is p-nitrophenol. Iodine is still under investigation. Adsorption of nonane at 298°K⁽⁵⁾ appears to give reliable micropore volumes for cokes or carbons (coals perhaps not). In this latter technique, nonane is adsorbed on outgassed carbons at 298°K for 24 hours, followed by desorption at 298°K for a further 24 hours. Appreciable quantities of nonane are retained under these conditions, the nonane molecule evidently entering the microporosity and being retained there by reason of multiple adsorption sites per molecule. With ultra-microporosity molecular sieve action is apparent. The micropore volumes are evaluated from volume of nonane adsorbed and compared with micropore volumes obtained from CO₂ isotherms using the D-R approach and from N₂ isotherms (77°K) made prior and subsequent to adsorption of nonane. The agreement between these three methods is good but obviously limited by our lack of precise knowledge of densities of adsorbed phases.

An interesting question, for non-graphitic, non-graphitising carbons, (not carbon blacks) is the exact mechanism of development of microporosity by chemical activation (gasification with H₂O or CO₂). A review of available evidence leaves much to be desired in terms of the theory of preferential gasification of 'disordered' as opposed to 'ordered' carbon atoms. Other factors such as impurity content, chemical surface heterogeneity, etc., may be more important.

A considerable investment has been put into the analysis of microporosity in coals. What are the areas of applicability of this knowledge? Safety in mines is relevant where maximum methane content and rates of diffusion of methane out of microporosity are important. Spontaneous combustion must not be overlooked. There are the uses of coal as an adsorbate, but for coal itself probably what is more important are the changes occurring on carbonisation (particularly during the plastic stage) to produce the metallurgical coke etc., or the precursor for active carbons and for carbons used as catalysts or catalyst supports. Control of these changes may possibly influence coke quality — there is yet to be acquired an understanding of the improvements in coke resulting from the preheating of coals prior to carbonisation. Is there an unexplored field of "catalytic carbonisation" in which a scientific attempt is made to influence the chemistry of carbonisation with amelioration of product? Mechanisms of burning of pulverised fuels (rates of internal combustion) are clearly relevant. Is further investment of effort worthwhile into the extraction of organic materials from coal, or will it not be more economical to use coal as a source of carbon for synthesis of organic molecules?

References

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