#809

FUEL

the science and technology of fuel and energy

Published by IPC Science and Technology Press Ltd

2 Shah, Y. T., Cronauer, D. C., McIlvried, H. G. and Paraskos, J. A. *Ind. Eng. Chem. Process Des. Dev.* 1978, **17** (3), 288

3 Whitehurst, D. D. and Mitchell, T. O. *Am. Chem. Soc., Div. Fuel. Chem., Prep.* 1976, **21** (5), 127

4 Weller, S., Pelipetz, M. G. and Friedman, S. *Ind. Eng. Chem.* 1951, **43**, 1572; 1951, **43**, 1575

5 Thomas, M. G. and Traeger, R. K. 'A Low Temperature Reaction Path for Coal Liquefaction', paper presented at the 178th National Meeting of the Am. Chem. Soc. Div. Fuel, Washington, DC, September 1979

6 Traeger, R. K., Bickel T. C. and Curlee, R. M. 'Preheater Studies in Coal Liquefaction,' Sandia Laboratories Report SAND-79-0150, May 1979

7 (a) 'Catalyst Characterization in Coal Liquefaction,' First Quarterly Report, Sandia Laboratories Report SAND-79-0303, March 1979; (b) 'Catalyst Characterization in Coal Liquefaction,' Second Quarterly Report, Sandia Laboratories Report SAND-79-1537, in press

Pore system in coal chars. Implications for diffusion parameters and gasification

P. L. Walker, Jr.

The Pennsylvania State University, Department of Materials Science and Engineering, University Park, Pennsylvania 16802, USA

(Received 18 February 1980)

As has been shown by Gan *et al.*[1] and others, coals contain a polymodal pore size distribution. Most of the surface area in coals is contributed by pores of molecular dimensions (super micropores). Superimposed on this pore system are pores exhibiting one or more distributions, in some cases up to micron size.

When non-caking coals are pyrolysed in an inert atmosphere and converted to chars, the chars retain the polymodal pore size distribution. The extent of change in the mean pore sizes of these distributions depends upon a balance between the liberation of volatiles increasing the sizes and particle shrinkage decreasing the sizes. Simons and Finson[2] conclude that the pore system in chars resembles an ordinary river or tree system with small pores feeding into increasingly larger pores until eventually all pores lead into main trunks. It is of interest to consider whether the pore system of molecular dimensions or a pore system of larger size controls the rates of such processes as gas diffusion into and out of char particles and char gasification. Further, might control change from one pore system to another as char gasification, and hence increase in average pore size, occurs?

When unsteady-state diffusion measurements of gases into or out of particles of coal chars (before their gasification) are made, it is invariably found that the diffusion parameter $D^{1/2}/L$, where L is the diffusion distance, shows an Arrhenius-type dependence on temperature. That is, the rate-controlling transport step is activated diffusion through the pore system of molecular dimensions. As discussed by Walker and co-workers,[3] this activated diffusion of gases in microporous carbons (chars) probably occurs between pseudo-graphitic basal planes. Using the Lennard–Jones (6–12) potential to estimate interaction between gas molecules and the surface, they estimate that activated diffusion commences when planes approach each other more closely than the sum of the kinetic diameter of the diffusing species and 0.16 nm. Considering that the repulsive potential varies inversely with the twelfth power of distance in the Lennard–Jones potential, small changes in slit thickness will clearly produce very large changes in activation energy for diffusion, and hence in the magnitude of the diffusion coefficient or parameter. For example, activated diffusion is expected for methane, which has a kinetic diameter of 0.38 nm, if the slits are closer together than about 0.54 nm. Conversely, at distances slightly greater than 0.54 nm, methane diffusion is expected to be in the Knudsen regime, $D_k \approx 2r\bar{V}/3$, where $2r$ is the slit width and $\bar{V}$ is the mean molecular gas velocity. The dependence of D_k on temperature is small ($T^{0.5}$). Thus, over less than 0.1 nm change in slit width, diffusion can go from activated to Knudsen in the supermicropores with a very large increase in the value of diffusion coefficient over the temperature range of our interest.

Gasification of coal chars removes carbon atoms from the structure, enlarges slit sizes, and would be expected to convert the rate-controlling process for transport of gases within the particles from activated diffusion to Knudsen (or bulk) diffusion. Patel and co-workers[4,5] showed this to be the case for the diffusion of methane through anthracite char between 298–343 K as shown in *Figure* 1. For burn-off in oxygen less than 6.9%, unsteady-state diffusion of methane through 42 × 65 mesh particles of anthracite char, first prepared by heating in N_2 at 1223 K, was too slow to be measured. After burn-off at 6.9% and 8.0%, the rate-controlling process for methane transport through the particles was still activated diffusion in the super micropores, but the activation energies for diffusion had been reduced sufficiently so that diffusion parameters could be measured in a convenient time span. Following a burn-off of 9.1%, the rate-controlling process close to room temperature was clearly no longer activated diffusion; it had changed to Knudsen diffusion.

Once the limiting process for diffusion of gas within a coal char particle is in the Knudsen regime, it is probable that diffusion in the super micropore system is no longer rate controlling. That is, for a given gas at constant temperature if the ratio of pore length to pore radius is a constant (see Reference 2 for a discussion on this point) the diffusion parameter for pores of differing size (r) in Knudsen diffusion can be approximated by

0016-2361/80/110809-02$2.00

$$\frac{D^{1/2}}{L}=\frac{\xi(r^{1/2})}{r}=\frac{\xi}{r^{1/2}} \qquad (1)$$

where ξ is a constant. Then assuming that a coal char resembles a tree system and that a significant fraction of the total pore volume resides in the super micropore system (this is a very good assumption for anthracite char[6] and a reasonable assumption for most other coal chars), it follows that the rate of gas transport into and out of the particles will be limited by diffusion in a feeder pore system of larger average pore size than that contained in the super micropore system.

It is now interesting to consider whether the super micropore system will enter diffusion control first, that is Zone II,[7] as the temperature for gasification of coal chars is increased. We take the equation of Thiele for single pore utilization during carbon gasification for a first order reaction,[7-9] that is

$$f=(1/h)\tanh(h) \qquad (2)$$

where f is the fraction of total area available in the pore which is utilized for gasification and h, the dimensionless parameter, is given by

$$h=L\sqrt{2k/rD} \qquad (3)$$

where L is the pore length, k is the reaction rate constant for gasification, r is the pore radius, and D is the diffusion coefficient of gas through the pore. The larger h is, the smaller must f be, and hence the greater will be the diffusion limitation on gasification.

Assuming that: (1) transport of the gaseous reactants and products through the pore systems is by Knudsen diffusion; (2) the ratio of pore length to pore radius is a constant; and (3) k is independent of pore size, we obtain for a given gasification reaction and coal char at a given temperature, the following:

$$h=\frac{\varphi r}{\sqrt{r^2}}=\varphi \qquad (4)$$

where φ is a constant. Thus h and consequently f are independent of pore size for *single* pores. However, in coal chars possessing a river or tree system, many super micropores branch off from larger feeder pores. Therefore, reactant concentration down the feeder pores will not only be depleted by gasification of carbon atoms from their surfaces (as just considered) but also by diffusion into the super micropores. Hence, during gasification of coal chars, Zone II should be entered first by a feeder system of larger pore size *once* sufficient gasification has occurred to convert transport in the super micropore system from the activated diffusion regime into the Knudsen regime. Simons and Finson come to a similar conclusion.[2]

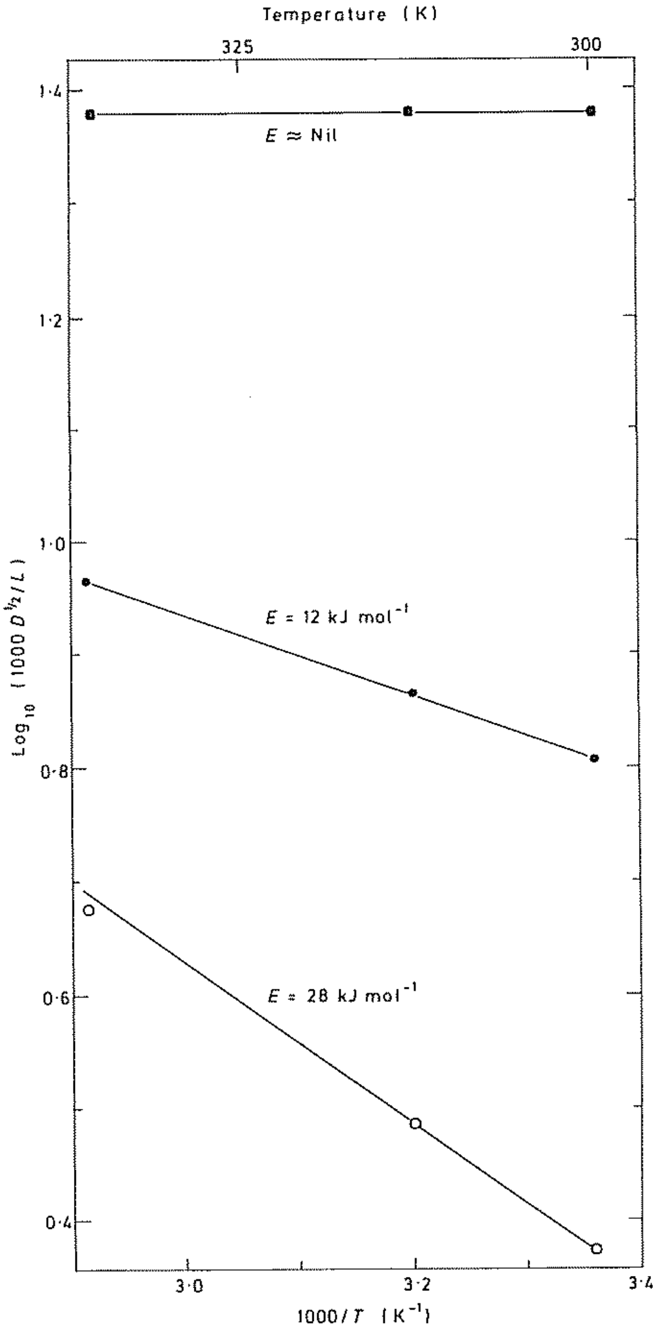

Figure 1 Diffusion parameters for methane flow into 42 x 65 mesh anthracite char as a function of diffusion temperature and anthracite burn-off: ○, 6.9%; ●, 8.0%, △, 9.1%[4]

ACKNOWLEDGEMENT

Research on fundamentals of char gasification is supported by the US Department of Energy on Contract No. DE-AC02-79ER10488.

REFERENCES

1 Gan, H., Nandi, S. P. and Walker, P. L., Jr. *Fuel* 1972, **51**, 272
2 Simons, G. A. and Finson, M. L. *Combust. Sci. Tech.* 1979, **19**, 217
3 Walker, P. L., Jr., Austin, L. G. and Nandi, S. P. 'Chemistry and Physics of Carbon' (Ed. P. L. Walker, Jr.) Vol. 2, Marcel Dekker, New York 1966, 257
4 Patel, R. L., Nandi, S. P. and Walker, P. L., Jr. *Fuel* 1972, **51**, 47
5 Walker, P. L., Jr. and Mahajan, O. P. 'Analytical Methods for Coal and Coal Products' (C. Karr, Ed.) Vol. 1, Academic Press, New York 1978, 163
6 Kawahata, M. and Walker, P. L., Jr. Proceedings Fifth Carbon Conference Pergamon Press, Oxford 1963, 251
7 Wheeler, A. 'Advances in Catalysis' (W. G. Frankenburg, V. I. Komareswsky and I. K. Rideal, Eds.) Vol. 3 Academic Press, New York 1951, 249
8 Walker, P. L., Jr., Rusinko, F., Jr. and Austin, L. G. Advances in Catalysis (D. D. Eley, P. W. Selwood and P. B. Weisz, Eds.) Vol. 11, Academic Press, New York 1959, 133
9 Thiele, E. W. *Ind. Eng. Chem.* 1939, **31**, 916