Franzen, P., "Strömungskanal mit veränderlichem Kreisquerschnitt als Modell für Zufallsschüttungen gleich großer Kugeln," *Rheol. Acta*, **16**, 548 (1977).

Gadala-Maria, F., "The Study of a Model for the Flow of Viscoelastic Fluids through Porous Media," Department of Chemical Engineering, Princeton University (1973).

James, D. F. and D. R. McLaren, "The Laminar Flow of Dilute Polymer Solutions through Porous Media," *J. Fluid Mech.*, **70**, 733 (1975).

Kamblowski, Z. and M. Dziubiński, "Resistance to Flow of Molten Polymers through Granular Beds," *Rheol. Acta*, **17**, 176 (1978).

Kuo, You-Ti, "The Determination of Second Normal Stress Difference in Viscoelastic Flows," Brown University, Ph.D. Thesis (1973).

Laufer, G., Ch. Gutfinger and N. Abuaf, "Flow of Dilute Polymer Solutions through a Packed Bed," *Ind. Eng. Chem. Fundamentals*, **15**, 77 (1976).

Laun, H. M. and H. Münstedt, "Elongational Behavior of a Low Density Polyethylene Melt," *Rheol. Acta*, **17**, 415 (1978).

Marshall, R. J. and A. B. Metzner, "Flow of Viscoelastic Fluids through Porous Media," *Ind. Eng. Chem. Fundamentals*, **6**, 393 (1967).

Metzner, A. B., "Improved Oil Recovery by Surfactant and Polymer Flooding," D. O Shah and R. S. Schechter, ed., Academic Press, New York, 439-451 (1977).

Payatakes, A. C., Chi Tien and R. M. Turian, "Numerical Solution of Steady State Incompressible Newtonian Flow through Periodically Constricted Tubes," *AIChE J.*, **19**, 67 (1973).

Schowalter, W. R., "Mechanics of Non-Newtonian Fluids," Pergamon Press, London (1978).

Vaughn, R. D. and P. D. Bergman, "Laminar Flow of Non-Newtonian Fluids in Concentric Annuli," *Ind. Eng. Chem. Proc. Des. Devel.*, **5**, 44 (1966).

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Reaction Regimes in Coal Oxidation

A series of seven coals were oxidized in a fixed bed reactor to determine the controlling reaction regimes during mild coal oxidation. The effects of coal porosity and particle size, reactor temperature, and oxygen partial pressure were evaluated. The results show that coal-oxygen reactions are controlled by the rate of internal gaseous diffusion for most coals, and by the rate of chemical reaction for the most porous coal of the set tested. Particle size effects also suggest internal diffusional control. Determinations of cumulative oxygen deposition indicate that surface areas several orders of magnitude greater than the superficial surface can participate in oxidation reactions, putting in doubt the applicability of the model previously derived by Kam et al. (1976a) for external mass transfer control.

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SCOPE

The rates at which a variety of coals undergo mild gas phase oxidation were measured in a fixed bed reactor for various reaction temperatures (150 to 300°C), coal particle sizes (−6 + 50 U.S. mesh), and oxygen concentrations (16 to 35 mol percent). Total oxygen consumption, CO_2, CO, and H_2O production, and oxygen deposition rates were determined from gas chromatographic analysis of reactor effluent gases. The experiments identify conditions under which oxidation rate is determined by the rate of gaseous diffusion within the coal particle, or the intrinsic rate of chemical reaction.

CONCLUSIONS AND SIGNIFICANCE

As a result of kinetic studies on seven coals, the oxidation rate was found for most coals to be controlled by internal diffusion, and in the extreme case where rate is independent of particle size, chemically controlled. The earlier model by Kam et al. (1976a) was based on the expectation of very small diffusion rates for gases in coal. As expected for gas-solid reactions, the activation energy for a coal oxidized in a regime of chemical control was found to be almost double the values obtained for coals in the regime of internal diffusional restrictions. At constant reaction conditions, oxidation rate increases linearly with total porosity, but is not proportional to superficial surface area. A significant portion of the internal surfaces of the coals contributes to the overall reaction rate, since cumulative oxygen adsorption during reaction covers an equivalent monolayer surface area orders of magnitude greater than the superficial surface area of the coal. The apparent order of reaction for gaseous oxygen is in the range of 0.70 and does not change significantly with the controlling regime.

Under the mild conditions of oxidation used to reduce a coal's caking propensity, the rate of oxidation depends on the unique combination of chemical composition and physical structure of each individual coal. In the chemically-controlled regime, in the absence of gaseous transport and diffusion limitations, chemical composition and/or the number of reactive sites on the coal surfaces may be expected to greatly influence reactivity; however, because many caking coals are of limited porosity, the physical structure determines the accessibility of these reaction sites to gaseous oxygen. As in any gas-solid reaction, the pore volume distribution of a coal determines the intra-particle diffusional resistance to reactant oxygen and product gases, and therefore the rate of reaction on

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TABLE 1. REPORTED VALUES OF DIFFUSIVITIES IN COAL

Source	Diffusing Gas	$\mathcal{D}$, cm^2/s
Zwietering et al. (1956)	CH_4	10^{-12}
Sevenster (1959)	H_2O vapor, O_2	10^{-11} to 10^{-13}
Nandi et al. (1970)	CH_4	10^{-12} to 10^{-14}
Nandi et al. (1975)	Ch_4	10^{-7} to 10^{-10}

internal surfaces of the porous coal. This is of particular importance when most of the effective surface area is located within the particle.

In applying these ideas to the coal oxidation system one finds that many authors report extremely small values for diffusivities in coals, as summarized in Table 1. This suggests that the rate of coal oxidation under the mild conditions employed in pretreatment would take place only on the superficial surface, and would be limited by the rate of external mass transfer. Indeed, Sevenster (1959) concluded that coal is almost impermeable to gases, and Kavlick and Lee (1967) concluded that oxidation reactions are primarily limited to the coal superficial surface. In response to these prior arguments, Kam et al. (1976a) based their oxidation model on the assumption that reaction was limited to the superficial surface area of the coal particles.

In contrast to these ideas, Karn et al. (1975) reported methane flows in coal as high as 10^{-8} to 2 cm^2/s atm, the higher rates associated with the more porous coals having increased accessibility of internal surface area. Gan et al. (1972) showed in their gas adsorption experiments that the adsorption was a diffusion-limited process: nitrogen surface areas measured at -195°C were orders of magnitude less than the CO_2 surface areas measured at 25°C. Since these latter findings raise questions concerning the earlier focus on external mass transfer as the controlling mechanism, and because coal can vary considerably among sources and types, the research reported here was undertaken to examine internal gaseous diffusion and reaction as well as the external steps in gas-solid reactions of coal.

As is well known reactions of a porous solid with a gas may be divided into three kinetic regimes, according to whether the overall process is controlled by: (1) the rate of external mass transfer from the bulk gas to the solid surface; (2) the rate of gaseous diffusion within the porous solid; or (3) the intrinsic rate of chemical reaction. Some reacting systems must be characterized as being between regimes because of changes in physical and chemical structure or in reaction conditions. Reactions controlled by external mass transfer are usually limited to superficial surface area. Since chemical reaction is fast relative to mass transfer, gas concentrations within the solid and on the superficial surface are close to zero. The apparent activation energy is only a few kcal/mol (ca. 2×10^4 J/mol), because the overall rate of reaction is determined by the mass transfer coefficient and the concentration difference between bulk gas and exterior surface, neither of which is very temperature sensitive.

Reactions in regime 2 are characterized by more porous solids with higher effective diffusivities for the reactant gas. The chemical reaction is slower relative to diffusion, allowing gaseous oxygen to diffuse into the coal particle before reacting. Gas concentration near the superficial surface approaches bulk concentration and a concentration profile within the solid is established. In regime 3, when overall oxidation rate is limited by intrinsic chemistry for solids of very high diffusivity, gaseous reactant will diffuse deeply into the solid creating a gas concentration profile which is effectively constant throughout and equal to the bulk gas concentration. In this case overall rate does not depend on particle size.

EXPERIMENTAL

Seven coals from various sources were obtained from the DOE Coal Bank at Pennsylvania State University and referred to here by the PSOC designations of the coal bank. The samples include one lignite (PSOC 87), five bituminous coals (PSOC 4, 127, 135, 190, 197), and one anthracite (PSOC 80), with chemical compositions ranging from 65 to 84% carbon, 3 to 20% oxygen, 1 to 28% moisture, and total porosities from 0.033 to 0.232 cm^3/g. Additional details of chemical analyses and porosity data are available in the report of Avison et at. (1979).

The seven coals were oxidized under various conditions to examine the effects of coal porosity, particle size, and superficial surface area, as well as temperature from 150 to 300°C, and bulk gas oxygen concentration from 16.1 to 35.3 vol. %. Various particle size fractions were obtained by standard sieves in the range $-6 + 50$ U.S. Mesh sizes. The stainless steel reactor, 711 mm in length and 19 mm OD, was fitted with top and bottom thermocouples and an effluent line to a gas chromatograph. A charge of 45 g of sieved coal and gas flow rate of 2.20 L/min at STP per kg of coal produced a bed height of approximately 30 cm and a residence time of about 8 sec. Each sample was heated under an inert nitrogen atmosphere at a rate of 5°C/min to the oxidation temperature. It was dried for 12 to 16 hours under these conditions. Further details of experimental equipment and procedure are provided by Kam et al. (1976b) and Karsner (1980).

Total oxygen consumption and carbonic gas production rates were calculated from measured flow rates and gas chromatographic analyses of reactor effluents. Water production was measured by weight gain of anhydrone driers placed in the reactor effluent line. Oxygen deposition was calculated as the difference between total oxygen consumption and oxygen consumed to produce CO_2, CO, and H_2O.

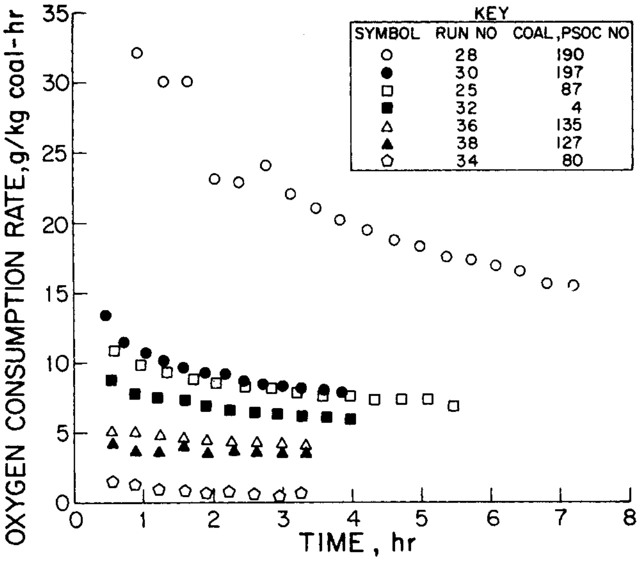

Figure 1. Oxygen consumption rates for seven different coals; mesh size: $-6 + 16$; air flow: 100 cm^3/min; temperature: 200°C.

RESULTS AND DISCUSSION

To examine the effect of coal porosity on overall rate, each of the coals was oxidized under the same conditions of temperature (200°C) and particle size ($-6 + 16$ U.S. mesh), using the standardized air flow rate. Comparable oxygen consumption rates expressed per weight of coal before drying are shown in Figure 1 for the seven coals tested. Replicate runs for selected samples were within ±5%. Although the reaction rates vary by a factor of 20 between the least reactive (PSOC 80) and most reactive (PSOC 190) coals, the rates all decay in a similar manner. Several longer runs of up to 16 hours duration suggest an approach to a non-zero asymptotic limit, as did also the long time result of Kam et al. (1976b) for yet another bituminous coal. This constant rate period must ultimately end as the coal is consumed, but there was no indication of such high conversions in this study.

The effects of coal pore structure may be examined by relating the oxidation rates in Figure 1 to the corresponding pore volume distributions for the several coals, using for convenience the three size ranges reported by Gan et al. (1972): greater than 300Å, between 12 and 300Å, and less than 12Å in diameter. To compare the coals on a common basis where the amount

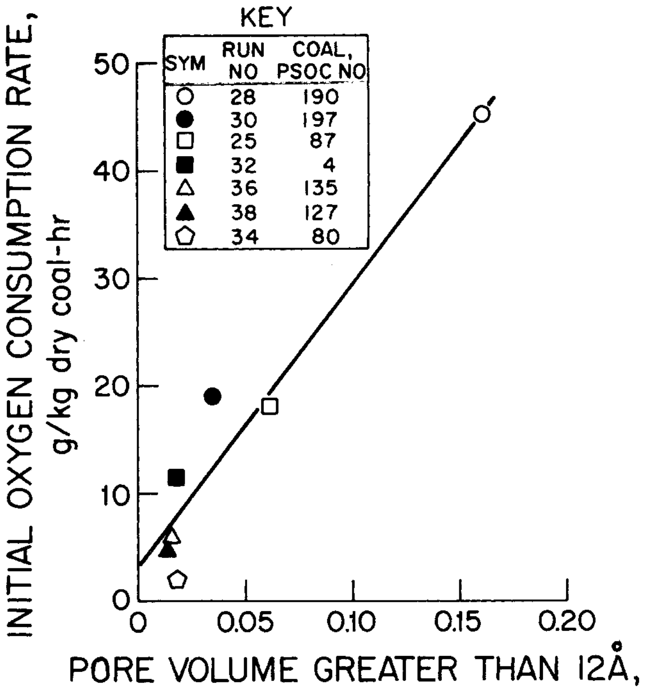

Figure 2. Correlation of initial oxidation rate with pore volume > 12A; mesh size: −6 + 16; air flow: 100 cm³/min; temperature: 200°C.

of coal consumed is negligible, initial rates of oxygen consumption were determined to within ±10% by extrapolation. The initial oxidation rates determined in this manner were each put on a dry coal basis to account for the weight changes caused by the drying procedure that preceded each oxidation run. The adjusted initial oxidation rates are correlated to different degrees with total pore volume, pore volume greater than 12Å, and pore volume greater than 300Å. The degrees of fit may be expressed in terms of correlation coefficients, as follows:

Coal Porosity Range	Correlation Coefficient
Pore volume > 12Å	0.96
Total pore volume	0.93
Pore volume > 300Å	0.59

The rates correlate well with either total porosity or the sum of porosities in the macro (greater than 300Å) plus transitional sizes (12 to 300Å). The degree of fit that corresponds to the latter correlation is shown in Figure 2.

It should be noted that no fundamental linearity relationship can be concluded from this merely statistical fit; nevertheless, the relatively high coefficients of the first two correlations show that oxidation is not limited to the macropores with surface openings greater than 300Å, since there are substantial interactions with pore mouths of diameters significantly smaller. Although Avison et al. (1979), suggested that pore volume greater than 300Å is a good indicator of relative reactivity, these results show that total porosity is a much better measure. The most reactive coal (PSOC 190), for example, is twice as porous as the next porous coals (PSOC 197, 87) and has a consumption rate

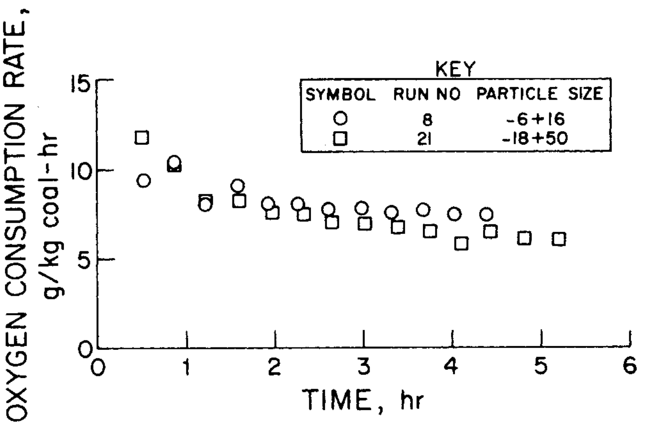

Figure 3. Effect of particle size on oxygen consumption rate at 150°C; coal: bituminous HVC, PSOC 190; air flow: 100 cm³/min.

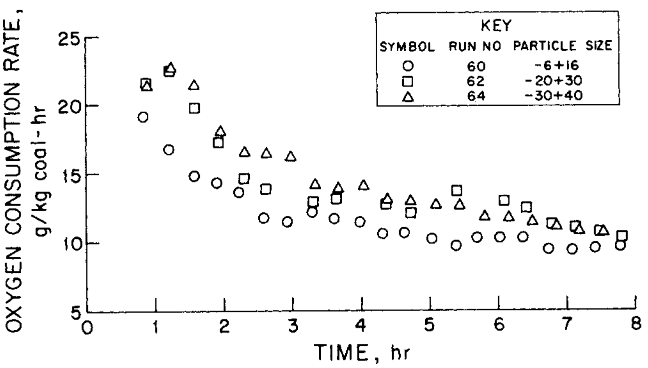

Figure 4. Effect of particle size on oxygen consumption rate at 175°C; coal: bituminous HVC, PSOC 190; air flow: 100 cm³/min.

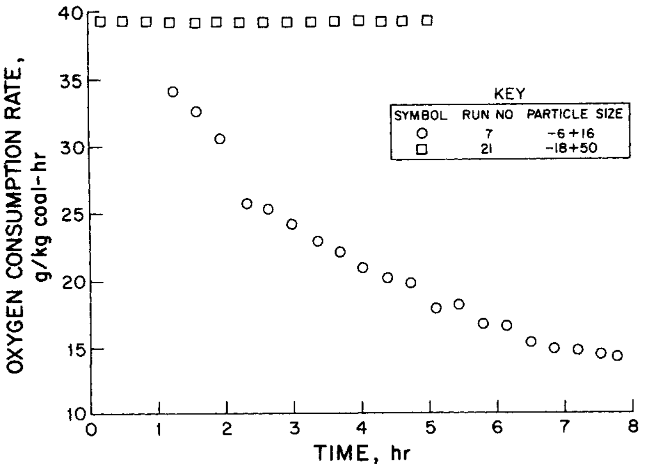

Figure 5. Effect of particle size on oxygen consumption rate at 200°C; coal: bituminous HVC, PSOC 190; air flow: 100 cm³/min.

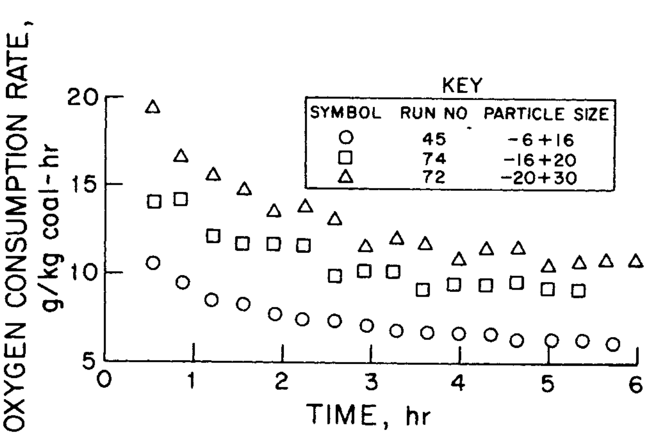

Figure 6. Effect of particle size on oxygen consumption rate at 200°C; coal: lignite, PSOC 87; air flow: 100 cm³/min.

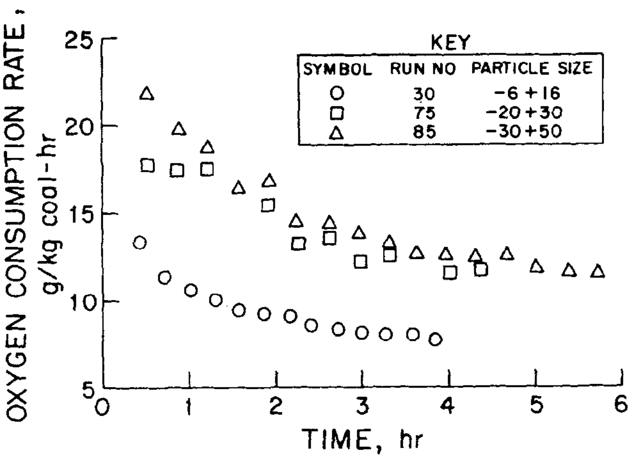

Figure 7. Effect of particle size on oxygen consumption rate at 200°C; coal: bituminous HVB, PSOC 197; air flow: 100 cm^3/min.

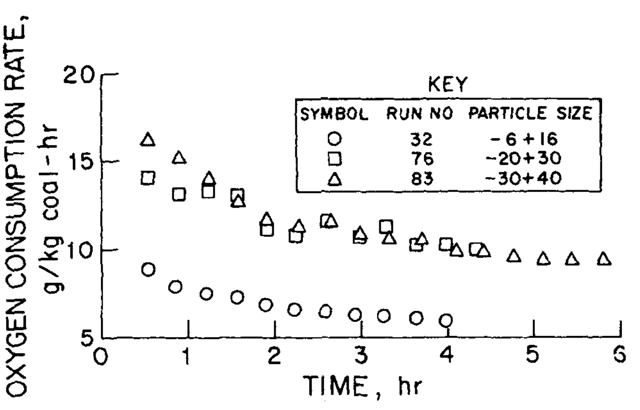

Figure 8. Effect of particle size on oxygen consumption rate at 200°C; coal: bituminous HVA, PSOC 4; air flow: 100 cm^3/min.

twice as high. The reaction rates and total porosities of PSOC 197 and 87 are similar to one another.

The degree of scatter in Figure 2 does not permit a meaningful numerical estimate of the rate at zero pore volume; however, extrapolation does give an intercept close to the origin, suggesting that most of the coal reaction surface is within the coal particle and not on the exterior surface. Such a result is consistent with the expectation of a chemically-controlled rate. Further support for this conclusion may be found in a comparison between superficial and gas adsorption surface areas. Gan et al. (1972) found CO_2 adsorption areas for these coals in the range from 96 to 408 m^2/g, whereas calculation of superficial surface area by the method ofNeedham and Hill (1935) for the particle size range in this study (−6 + 50 U.S. mesh) is orders of magnitude lower: 10^{-3} to 10^{-2} m^2/g.

Particle Size

To determine the operating regime for each coal undergoing an oxidation pretreatment, a series or runs were performed varying temperature and particle size on four coals. The effect of changing particle size on the oxidation rate of the most porous and reactive coal used (PSOC 190) is shown in Figures 3 to 5 at three levels of temperature. At 150°C the oxygen consumption rate is virtually independent of particle size, indicating that internal diffusion is rapid enough for this porous coal to allow overall chemical control at this low temperature. Since the additional superficial surface area exposed by crushing the coal to a smaller particle size does not increase the oxygen consumption rate, the coal's internal surface area must already have been accessible to gaseous oxygen at these reaction conditions. At 200°C oxidation of a smaller particle size material results in substantial increases in rate, suggesting that diffusional resistance limits the overall rate for the larger particles. The constant oxidation rate evidenced by the smaller particle size at 200°C (Figure 5), is the result of complete oxygen consumption in the fixed bed reactor and would be still larger if the system were not starved for oxygen. At 175°C there is a slight increase in oxidation rate as particle size is reduced, evidently an intermediate case. For this coal the rate of oxidation changes from chemical control (regime 3) to diffusion control (regime 2) at successively higher temperatures. At the lower temperatures, the rate is limited by neither external mass transfer nor intraparticle diffusion.

The particle size effects for a less porous lignite (PSOC 87) are shown in Figure 6 for oxidation at 200°C. The oxygen consumption rate increases with smaller particle size due to diffusional limitations in this less porous coal. Similar effects were observed at the lower temperatures of 150 and 175°C. The fact that the rate of oxidation of the lignite is diffusionally controlled at 150°C whereas that of the bituminous PSOC 190 is chemically controlled at this same temperature may be attributed to the larger pore volume and therefore more easily accessible internal surface of the latter coal. The effect of particle size on oxidation rate at 200°C for two additional coals (PSOC 197 and 4) are given as Figures 7 and 8. These less porous coals also show diffusional effects as evidenced by the inverse relationship between oxidation rate and particle size.

TABLE 2. EFFECT OF PARTICLE SIZE ON INITIAL REACTION RATE

Coal, PSOC No.	Temperature, °C	Particle Size Range, U.S. Mesh	Average Particle Diameter, mm	Initial Reaction Rate, g O_2/kg coal-h	$\frac{R_2}{R_1}$	$\frac{D_1}{D_2}$
190	150	−6 + 16	2.31	12	1.00	1.00
190	150	−18 + 50	0.75	14	1.17	3.09
190	175	−6 + 16	2.31	25	1.00	1.00
190	175	−20 + 30	1.02	30	1.20	2.27
190	175	−30 + 40	0.73	32	1.28	3.18
87	150	−6 + 16	2.31	5	1.00	1.00
87	150	−18 + 50	0.75	8	1.60	3.09
87	175	−6 + 16	2.31	9	1.00	1.00
87	175	−20 + 30	1.02	12	1.33	2.27
87	175	−30 + 40	0.73	15	1.67	3.18
87	200	−6 + 16	2.31	13	1.00	1.00
87	200	−16 + 20	1.41	17	1.31	1.64
87	200	−20 + 30	1.02	21	1.61	2.27
197	200	−6 + 16	2.31	16	1.00	1.00
197	200	−20 + 30	1.02	22	1.38	2.27
197	200	−30 + 50	0.64	26	1.63	3.64
4	200	−6 + 16	2.31	11	1.00	1.00
4	200	−20 + 30	1.02	17	1.55	2.27
4	200	−30 + 40	0.73	19	1.73	3.18

TABLE 3. EFFECT OF COAL PARTICLE SIZE ON OXIDATION RATE

Coal, PSOC No.	Temperature, °C	Total Pore Volume, cm^3/g	β
190	150	0.232	0.14
190	175	0.232	0.22
87	150	0.105	0.42
87	175	0.105	0.43
87	200	0.105	0.57
197	200	0.105	0.40
4	200	0.033	0.49
*4	225	0.033	0.41
*80	250	0.076	0.45
*127	225	0.052	0.54
*135	225	0.042	0.31

*Computed from Avison (1977) and Avison et al. (1979).

TABLE 4. COAL SURFACE AREAS*

Coal, PSOC No.	N_2-Surface Area, m^2/g	CO_2-Surface Area, m^2/g
80	7	408
87	<1	268
127	<1	253
135	<1	214
4	<1	213
190	83	96

*From Gan, Nandi, and Walker (1972).

TABLE 5. ESTIMATED EXTERNAL SURFACE AREAS FOR COAL

Particle Size Range, U.S. Mesh	Avg. Particle Diameter, mm	Equivalent Surface Area for Spheres m^2/g	Estimated Surface Area Based on Needham and Hill (1935), m^2/g
−6 + 14	2.5	7.4×10^{-5}	3.3×10^{-3}
−14 + 18	1.6	1.2×10^{-4}	5.4×10^{-3}
−18 + 50	0.75	3.5×10^{-4}	1.5×10^{-2}

Superficial Surface Area

For reaction rates limited by external mass transfer the overall rate is proportional to the product of the superficial surface area of the solid and the gas concentration difference across the corresponding fluid boundary layer. For fixed concentrations rates per unit mass may therefore be expected to vary as the area to volume ratio. For spherical particles this leads to an inverse dependence on diameter:

$$\frac{R_2}{R_1} = \frac{D_1}{D_2} \tag{1}$$

Deviations from this simple inverse relationship may arise from non-spherical particle geometry or from a change to a different controlling regime. When this is the case Eq. 1 may be modified by including an empirical exponent $\beta \neq 1$:

$$\frac{R_2}{R_1} = \left(\frac{D_1}{D_2}\right)^{\beta} \tag{2}$$

This relationship between oxidation rate and particle size may be tested empirically by comparison of initial reaction rates, obtained for individual runs by extrapolation to zero time. Results on four coals are listed in Table 2, where the particle size −6 + 16 U.S. mesh was taken as a reference for each case.

The exponents β evaluated for each coal and temperature are listed in Table 3, ranging from 0.1 to 0.2 for the extremely porous type PSOC 190 to approximately 0.5 for four coals having porosities less than 0.08 cm^3/g. The value is appreciably less than unity in all cases, indicating that external mass transfer is not the controlling mechanism. Analysis of experiments by Avison (1977) and Avison et al. (1979) shows that β varied from 0.31 to 0.54 for a series of four small pore coals. It may be noted that the oxidation rates for more porous coals, which contain a larger pore volume in the greater than 12Å range, are not as dependent upon average particle diameter, presumably because the diffusion rates for these coals are higher, allowing increased accessibility of internal surface area for reaction. The less porous coals apparently have lower diffusion rates, and as a result oxidation rates are more dependent on particle size. Further support for the same view may be found in the work of Kam et al. (1976b), who showed that the oxidation rate of their HVA bituminous coal was proportional to superficial surface area to the 0.14 power. Schmidt (1945) showed for another coal that rate is proportional to superficial surface to the 0.33 power. Carpenter and Sergeant (1966) also concluded from their investigations that considerable penetration occurs of gaseous oxygen into coal particles.

Another method to evaluate the effect of external mass transfer requires an estimate of the mass transfer coefficient for packed beds, as for example from Wilson and Geankoplis (1966) correlation for low Reynolds number flows:

$$\frac{k_x\, D}{C_{\text{avg}}\mathscr{D}} = 1.09\,(\text{Re})^{-2/3}\,(\text{Sc})^{-1/3} \tag{3}$$

If the reaction were in fact controlled by external mass transfer, the rate would be:

$$R = k_x(C_B - C_s) \tag{4}$$

Combining Eqs. 3 and 4 predicts an inverse dependence of rate on particle diameter to the 0.67 power. Since the experimental rates produce values of β appreciably smaller than 0.67 for even the least porous coals listed in Table 3, external mass transfer is not the controlling factor. Eliminating external mass transfer control as a possible controlling regime in these tests, the occurrence of particle size effects on rate must be attributed to an internal diffusional mechanism. In the limiting case where rate is unaffected by changes in particle diameter, as observed for PSOC 190 at 150°C (Figure 3), rate is controlled by intrinsic chemical reaction rate.

Monolayer Surface Coverages

Since oxidation rates are highly dependent upon the internal surface area which is accessible to oxygen, it is of importance to estimate the extent of this area. To this end the cumulative oxygen adsorbed may be converted to an equivalent monolayer surface coverage by using an average specific surface area of 16.6 Å²/oxygen molecule (Spackman et al., 1977). It may be noted that the monolayer surface coverages corresponding to the CO_2-surface areas reported by Gan et al. (1972) and listed in Table 4 represent a potential weight gain in the range of 3 to 13% due to oxygen deposition. Kam et al. (1976b) calculated the superficial surface areas of irregularly shaped coal particles by the method of Needham and Hill (1935). These calculated areas are shown in Table 5 together with superficial surface areas for spherical coal particles. Although the superficial areas calculated for irregularly shaped coal particles are one to two orders of magnitude larger than those calculated for spherical particles, these superficial areas represent less than 0.01% of the 96 to 408 m^2/g surface areas measured by Gan et al. (1972). These several surface areas may be compared to the monolayer surface coverages obtained in the current experiments.

Cumulative oxygen depositions are presented in Table 6 for a series of experiments on the several coals. For each run, the cumulative deposition has been converted to an equivalent monolayer surface coverage. In every case the adsorbed oxygen represents a cumulative monolayer surface coverage orders of magnitude greater than the superficial surface areas for these particle sizes given in Table 5. The surface coverage for coal type PSOC 190 is significantly larger than for any of the less porous coals, yet another indication that most of the internal surface area of PSOC 190 is accessible to gaseous oxygen. Some runs, such as numbers 60, 62, and 64, result in coverage in excess of the CO_2 surface area. This may signify that: (1) multilayer oxygen deposition occurs or (2) the accessible surface area to gaseous oxygen at elevated temperatures is greater than the areas measured by Gan et al. (1972) with a larger CO_2 molecule at lower temperature. In this connection, Ignasiak et al. (1974) reported that at a lower temperature of 100°C some of the deposited oxygen on the coal is physically adsorbed rather than chemisorbed in a monolayer.

As a result of these experiments it may be concluded that for these coals most of the oxidation occurs within the coal pore

TABLE 6. SURFACE COVERAGE OF CUMULATIVE OXYGEN DEPOSITION

Coal PSOC No.	Run No.	Particle Size Range, U.S. Mesh	Temp., °C	Duration of Run, h	Cumulative Oxygen Deposition, g O_2/kg coal	Equivalent Monolayer Coverage, m^2/g	% of CO_2-Surface Area Covered
190	21	−18 + 50	150	5.2	25.0	78.1	81
	60	−6 + 16	175	7.8	59.2	185.0	193
	62	−20 + 30	175	7.8	77.6	242.2	252
	64	−30 + 40	175	7.5	79.3	247.4	258
87	24	−18 + 50	150	3.7	10.6	33.0	12
	26	−6 + 16	175	3.8	9.1	28.4	11
	66	−20 + 30	175	1.9	8.0	25.0	9
	68	−30 + 40	175	4.7	14.1	44.2	16
	45	−6 + 16	200	5.7	8.6	26.8	10
	74	−16 + 30	200	5.3	21.4	67.0	25
	72	−20 + 30	200	6.0	29.9	93.4	35
4	32	−6 + 16	200	4.0	16.1	50.4	24
	76	−20 + 30	200	4.3	36.8	114.8	54
	83	−30 + 40	200	5.8	42.0	131.0	62
135	36	−6 + 16	200	3.3	8.7	27.2	13
127	38	−6 + 16	200	3.3	7.2	22.6	9
80	34	−6 + 16	200	3.3	1.5	4.6	1

structure. Coal oxidation is not limited to superficial surface using either the areas calculated by assuming spherical geometry or the method of Needham and Hill (1935). Measurements of cumulative oxygen deposition converted to equivalent surface areas surpass N_2-surface areas and in some instances approach CO_2-surface areas.

Oxidation Temperature

The experiments on the effects of coal porosity, particle size, and surface area have already shown that the oxidation rate may be limited by either internal gaseous diffusion or intrinsic chemical reaction. A study of the dependence of rate on temperature may also be used to identify which regimes control oxidation under various circumstances. As an example, the effect of temperature on the total oxygen consumption rate of PSOC 87 is presented in Figure 9. Similar results were obtained for PSOC 190, 197 and 4. An apparent activation energy may be estimated from the usual Arrhenius variation in the rate constant:

$$k = k_o e^{-E/\mathscr{R}T} \tag{5}$$

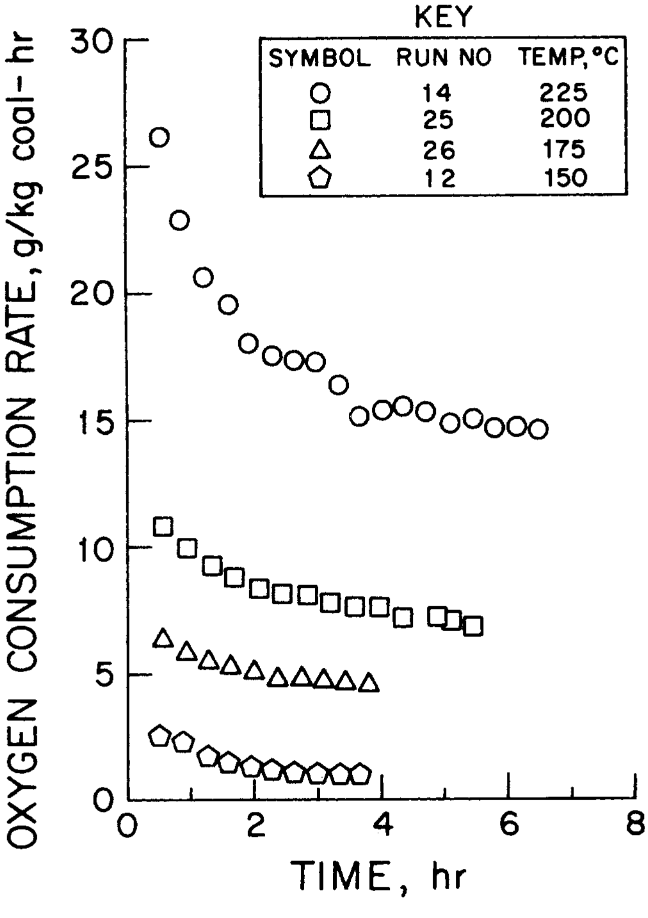

Figure 9: Effect of temperature on oxygen consumption rate; coal: lignite, PSOC 87; particle size: −6 + 16 U.S. mesh; air flow: 100 cm³/min.

If the reaction kinetics are of the form:

$$R = kC_s^n C_o^m \tag{6}$$

where C_s is the concentration of reacting species on the coal solid, C_o is the gaseous oxygen concentration and n and m are orders of reaction, then combination with Eq. 5 gives:

$$R = k_o C_s^n C_o^m e^{-E/\mathscr{R}T} \tag{7}$$

Comparison of runs at the same levels of C_s and C_o allows direct calculation of activation energy from the rate data. To compare oxidation rates at the same level of C_s, initial reaction rates are needed where virtually no solid has yet been consumed. These initial oxidation rates were determined as before by extrapolation of the rate curves to zero time.

Equation 7 may be re-written for initial rate as:

$$\ln R^\circ = -\frac{E}{\mathscr{R}}\frac{1}{T} + \ln[k_o C_s^n(0) C_o^m] \tag{8}$$

showing how the activation energy for each coal may be calculated from the slope of an appropriate graph. Applying Eq. 8 to

TABLE 7. APPARENT ACTIVATION ENERGIES

Coal, PSOC No. or Code	Particle Size Range, U.S. Mesh	Apparent Activation Energy, J/mol × 10^{-4}	
		Based on Initial Rates	Adjusted for O_2 Concentration
190	−6 + 16	4.3 ± 1.0	6.3 ± 0.67
87	−6 + 16	4.1 ± 1.8	4.9 ± 2.8
87	−20 + 30	3.9	5.0
197	−6 + 16	2.8 ± 0.71	3.9 ± 1.4
4	−6 + 16	3.0 ± 0.71	4.2 ± 1.7
K*	−14 + 18	3.2 ± 0.88	4.5 ± 1.4

* Data from Kam et al. (1976b).

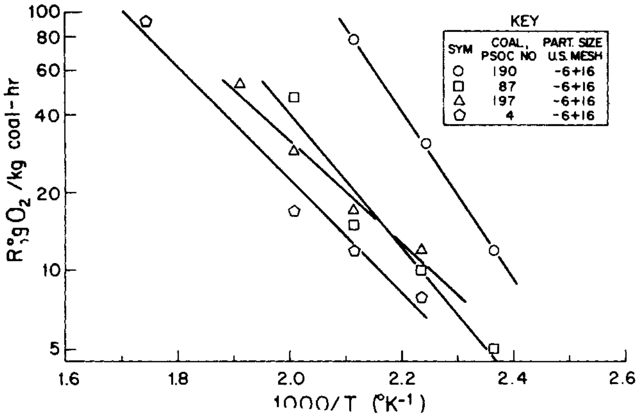

Figure 10. Arrhenius correlation for initial rates adjusted for initial oxygen concentration.

the data in this study yielded the apparent activation energies listed in Table 7 with corresponding standard deviations. The values all fall in the relatively narrow range of 2.8 to 4.3 × 10^4 J/mol, the data of Kam et al. (1976b) included. Two separate determinations are given for PSOC 87 to show that the apparent activation energy is virtually independent of particle size, differing only about 3% over a two-fold change in size.

Because conversion of the gaseous oxygen feed varies among the several runs between 10 and 90%, the initial oxygen concentration C_0 varies with position in the fixed bed reactor even if fed at a constant concentration level. For this reason the apparent activation energies listed in Table 7 can only be approximate, including as they do the effects of changes in the average initial oxygen concentration $C_0(0)$. In general, the oxygen concentration is lower at higher temperatures since oxygen consumption rates are higher. Better estimates of activation energy can be obtained by adjusting each initial reaction rate to the same bed-average initial gas concentration by means of a first-order assumption. The corrected initial oxidation rates were used for preparing Figure 10. The adjusted activation energies are also listed in Table 7.

The most porous coal PSOC 190, whose rate is determined by intrinsic chemical reaction at low temperatures, has an activation energy of 6.3 × 10^4 J/mol. All the less porous coals, including that of Kam et al. (1976b) have apparent activation energies in the narrow range of 3.9 to 5.0 × 10^4 J/mol, smaller as expected in a partly diffusional regime (Levenspiel, 1972). Since the smaller pore coals have activation energies in excess of 3.1 × 10^4 J/mol (half the true activation energy for PSOC 190), these results give added support to the conclusion that oxidation rates for smaller pore coals are limited by diffusional resistance and not by external mass transfer. Rates limited by external mass transfer would have shown activation energies of only a few kcal/mole, definitely less than 3.1 × 10^4 J/mol.

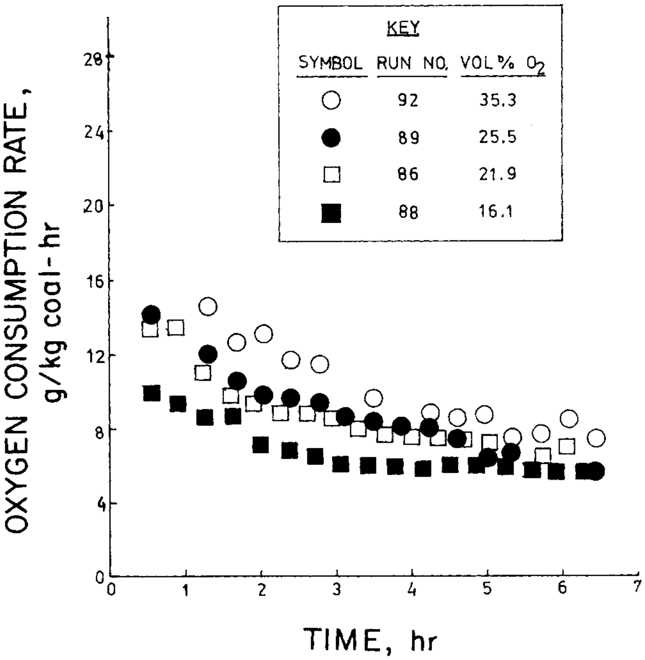

Figure 11. Effect of feed oxygen concentration on oxygen consumption rate; coal: bituminous HVC, PSOC 190; mesh size: −6:16; temperature: 160°C.

TABLE 8. OXIDATION CONDITIONS FOR PARTIAL PRESSURE STUDY

	This Study	Reference Study (Kam et al., 1976b)
Coal Type	Bituminous HVC PSOC 190	Bituminous HVA Pittsburg Seam
Particle Size Range, U.S. Mesh	−6 + 16	−18 + 50
Temperature, °C	160	225
Range of Feed Oxygen Concentration, Vol. % O_2	16.1 to 35.3	9.7 to 28.6

Order of Reaction

To determine the effect of oxygen concentration on the rate of coal oxidation, a series of runs were performed oxidizing HVC bituminous PSOC 190 at four different levels of feed oxygen-concentration. Oxidation conditions are listed in Table 8, together with those on four similar experiments by Kam et al. (1976b). The latter group of runs were performed under more

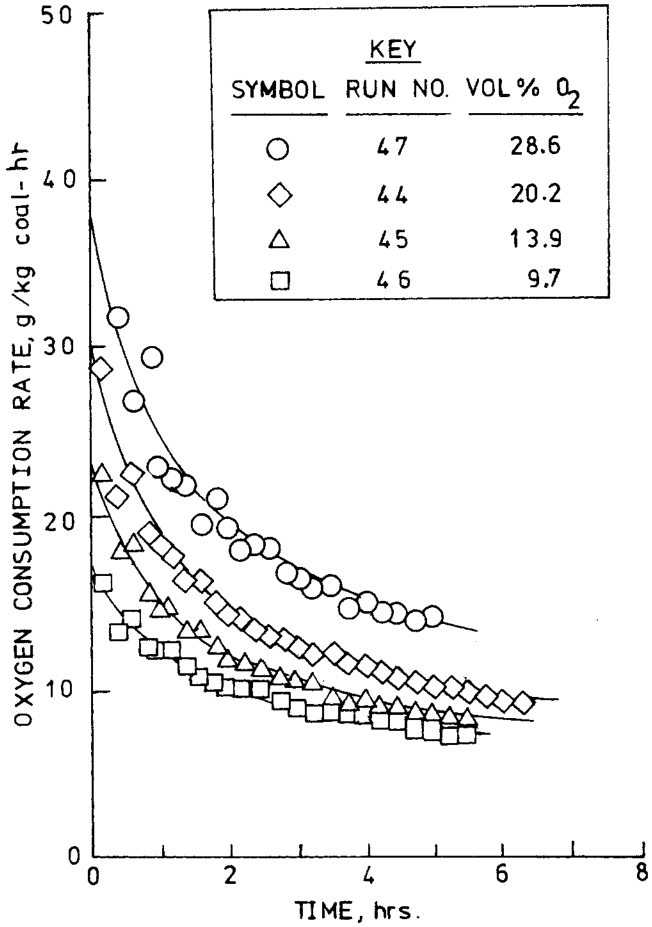

Figure 12. Effect of feed O_2 concentration on oxygen consumption rate (Kam et al., 1976b); coal: Pittsburgh seam HVA bituminous; mesh size: −18 + 50; temperature: 225°C.

TABLE 9. KINETIC ORDERS FOR SEVERAL REACTIONS

	Reaction Order, m	
	This Study	Reference Study (Kam et al., 1976b)
Oxygen Consumption	0.70 ± 0.22	0.74 ± 0.10
Oxygen Deposition	0.87 ± 0.28	0.76 ± 0.15
CO_2 Production	0.81 ± 0.30	0.91 ± 0.24
CO Production	0.87 ± 0.40	0.66 ± 0.43
H_2O Production	0	0.75 ± 0.12

severe conditions, on a smaller coal particle size, and at a higher temperature. The rates for total oxygen consumption in the two studies are presented in Figures 11 and 12.

The reaction order with respect to bulk gas concentration may be tested empirically by assuming the isothermal reaction kinetics to follow the form of Eq. 6. As before, initial rates must be compared to assure a constant site concentration. Under such conditions, Eq. 6 becomes:

$$R^\circ = k' C_o^m(0) \qquad (9)$$

and the order of reaction m may be determined from an appropriate slope.

Initial rates were obtained by extrapolation of the appropriate rate curves to time zero, and reaction orders for consumption, deposition, and product formation were estimated by the method of least squares. The results are given in Table 9 together with appropriate 95% confidence intervals. With the exception of water formation which was zero order in the current study, the orders of reaction vary over a narrow range of 0.7 to 0.9. The orders of reaction for total oxygen consumption (0.70 and 0.74) are well within the range of reported literature values. For comparison, Van Krevelen (1961) reported that oxygen consumption rate is first order with respect to oxygen concentration, but Carpenter and Giddings (1964) concluded that consumption rate increases with the square root of oxygen concentration and suggest that this is due to the dissociation of oxygen molecules into atoms prior to chemisorption. In their oxidation studies in the temperature range of 30 to 170°C, Banerjee et al. (1970) assumed the reaction to be first order.

In comparing the two columns of Table 9 it should be recalled that the controlling regime for the oxidation of the coal in this study is different from that applicable to the prior study. As already argued from the results reported in Figures 3 and 4 the oxidation rate of PSOC 190 at 160°C is chemically controlled. In contrast, the oxidation rate in the prior work of Kam et al. (1976b) is controlled by diffusion, since rate varies inversely with particle size and the activation energy is slightly in excess of one half the energy calculated for chemical reaction control (Table 7). For the case where diffusion rates are limiting, Eq. 11 is often modified to include an effectiveness factor (Levenspiel, 1972), and the apparent order of reaction differs from that for chemical control, except for the special case of first-order reaction. This is approximately the case for the two coals reported on in Table 9. The reaction orders are in ranges close to unity and do not change appreciably with controlling regime in comparison with the confidences ranges shown.

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NOTATION

C_{AVG} = average of bulk and surface oxygen concentrations
C_o = concentration in reactor feed
C_B = bulk gas concentration
C_s = gas concentration at solid surface
D = particle diameter
$\mathcal{D}$ = diffusivity
E = activation energy
k = reaction rate constant
k_o = pre-exponential factor
k' = lumped reaction rate constant
k_x = mass transfer coefficient
m, n = orders of reaction
R = reaction rate
R^o = reaction rate at time zero
$\mathcal{R}$ = gas constant
T = temperature
β = empirical exponent
Re = Reynolds number
Sc = Schmidt number

LITERATURE CITED

Avison, N. L., "A Study of the Kinetic Regimes in the Mild Oxidation of Coal," Master's Thesis, University of Pennsylvania (1977).

Avison, N. L., R. M. Winters, and D. D. Perlmutter, "On the Kinetics of Coal Oxidation", *AIChE J.*, **25**, 773 (1979).

Banerjee, S. C., B. D. Banerjee and R. N. Chakravorty, "Rate Studies of Aerial Oxidation of Coal at Low Temperatures," *Fuel*, **49**, 324 (1970).

Carpenter, D. L. and D. G. Giddings, "The Initial Stages of the Oxidation of Coal with Molecular Oxygen II—Order of Reaction," *Fuel*, **43**, 375 (1964).

Carpenter, D. L. and C. D. Sergeant, "The Initial Stages of the Oxidation of Coal with Molecular Oxygen III—Effect of Particle Size on Rate of Oxygen Consumption," *Fuel*, **45**, 311 (1966).

Gan, H., S. P. Nandi, and P. L. Walker, "Nature of the Porosity in American Coals," *Fuel*, **51**, 272 (1972).

Ignasiak, B. S., A. J. Szladow and N. Berkowitz, "Distribution of Chemisorbed Oxygen in Mildly Oxidized Caking Coals," *Fuel*, **53**, 229 (1974).

Kam, A. Y., A. N. Hixson and D. D. Perlmutter, "The Oxidation of Bituminous Coal—I. Development of a Mathematical Model," *Chem. Eng. Sci.*, **31**, 815 (1976a).

Kam, A. Y., A. N. Hixson and D. D. Perlmutter, "The Oxidation of Bituminous Coal-II. Experimental Kinetics and Interpretation," *Chem. Eng. Sci.*, **31**, 821 (1976b).

Karn, F. S., R. A. Friedel and A. J. Sharkey, Jr., "Mechanism of Gas Glow Through Coal," *Fuel*, **54**, 279 (1975).

Karsner, G. C., "The Kinetics of Coal Drying and Oxidation: A Study of Physical and Chemical Parameters," Ph.D. Thesis, University of Pennsylvania (1980).

Kavlick, V. J. and B. S. Lee, "Coal Pretreatment in Fluidized Bed," *Advan. Chem. Ser.*, **69**, 8 (1967).

Levenspiel, O., *Chemical Reaction Engineering*, John Wiley and Sons, New York, New York (1972).

Nandi, S. P. and P. L. Walker, Jr., "Activated Diffusion of Methane in Coal," *Fuel*, **49**, 309 (1970).

Nandi, S. P. and P. L. Walker, Jr., "Activated Diffusion of Methane from Coals at Elevated Pressures," *Fuel*, **54**, 81 (1975).

Needham, L. W. and N. W. Hill, "The Shape and Specific Surface of Coal Particles," *Fuel*, **8**, 222 (1935).

Schmidt, L. D., "Chemistry of Coal Utilization," 627, Wiley, New York (1945).

Sevenster, P. G., "Diffusion of Gases Through Coal," *Fuel*, **38**; 403 (1959).

Spackman, W., A. Davis, P. L. Walker, H. L. Lovell, R. H. Essenhigh, F. J. Vastola and P. H. Given, "The Characteristics of American Coals in Relation to Their Conversion into Clean Energy Fuels," *Quarterly Technical Progress Report*, Coal Research Section, The Pennsylvania State University (January-March, 1977).

van Krevelen, D. W., *Coal*, Elsevier, Amsterdam (1961).

Wilson, E. J. and C. J. Geankoplis, *Ind. Engg. Chem. Fund.*, **5**, 9 (1966).

Zwietering, P., J. Overeem and D. W. van Krevelen, "Chemical Structure and Properties of Coal XIII—Activated Diffusion of Gases in Coal," *Fuel*, **35**, 66 (1956).

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