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On the Kinetics of Coal Oxidation

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A series of seven coals of different ranks and from various locations were heated in air under relatively mild conditions to measure the rates of oxidation and the production of carbonic gases in the effluent stream. The gas flow rate, coal particle size, and reactor temperature were changed as independent variables. Each sample was exposed for from 6 to 9 hr under atmospheric pressure at temperatures in the range of 200° to 250°C. The results show two kinds of rate behavior depending primarily on the relative porosity of the coal under study. The small pore coals followed the expectations of the earlier Kam-Hixson-Perlmutter (KHP) model, but the large pore coals gave rates sensitive to transport effects. Correlations were also obtained on the ratio of carbon dioxide and carbon monoxide produced and on the relationship between the carbon content of an exposed coal and its heating value.

SCOPE

The rates at which a variety of coals undergo mild gas phase oxidation were measured in a fixed-bed reactor under a range of flow rates and for various particle sizes. Seven coals from different sources were tested at three temperatures. The coals pretreated in this manner were analyzed for chemical composition and heating value changes, and the oxidation off-gases were analyzed for carbonic gas content. Correlations were prepared in terms of an earlier KHP model and exceptional behavior noted for specific coals.

CONCLUSIONS AND SIGNIFICANCE

As a result of experimental oxidation tests on seven coals from different sources, it has been found that not one but two models are needed to distinguish between large and small pore coals. The earlier KHP model, which was based on the expectation of very small diffusion rates for gases into coal, remains valid for the largest group of coals tested but has to be modified for at least two of the coals. When the coals had relatively large pore volumes in the size range greater than 300Å, the oxidation rate was found to be sensitive to particle size, gas flow rate, and reaction temperature, in a manner indicating significant transport effects. Correlations of the carbon dioxide to carbon monoxide ratio obtained from runs under varying conditions also support the applicability of the KHP model. The heating values among the various coal samples changed upon oxidation in a manner dependent primarily on the changes in carbon content of the coal.

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Coal PSOC No.	Source location and rank	Dry analysis, wt %						Volatile matter, wt %	Water content, wt %
		C	H	N	O	S	Ash		
87	North Dakota Lignite	65.42	4.82	0.51	20.44	0.64	8.17	49.76	28.07
190	Illinois HVC Bituminous	69.15	4.89	1.00	13.42	3.05	8.49	34.70	16.14
197	Ohio HVB Bituminous	69.15	4.63	1.45	11.35	1.07	12.36	36.82	9.88
4	Kentucky HVA Bituminous	82.10	5.67	1.52	7.78	0.86	2.07	37.51	2.48
135	Alabama MV Bituminous	84.01	4.68	0.24	5.50	0.61	4.96	23.62	0.71
127	Pennsylvania LV Bituminous	84.47	4.72	0.94	3.40	0.78	5.69	19.44	1.38
80	Pennsylvania Anthracite	78.18	2.25	0.66	4.42	0.55	13.94	5.77	2.51

* Analyses supplied by Penn State-ERDA Coal Bank.

TABLE 2. PORE DISTRIBUTION IN COALS*

PSOC number	Rank and source location	Pore volumes, cm^3/g			
		Greater than 300Å	From 12 to 300Å	Less than 12Å	Total
Large pore coals					
87	Lignite North Dakota	0.062	0.000	0.043	0.105
190	HVC Bituminous Illinois	0.040	0.122	0.070	0.232
Small pore coals					
197	HVB Bituminous Ohio	0.022	0.013	0.070	0.105
4	HVA Bituminous Kentucky	0.017	0.000	0.016	0.033
135	MV Bituminous Alabama	0.016	0.000	0.026	0.042
127	LV Bituminous Pennsylvania	0.014	0.000	0.038	0.052
80	Anthracite Pennsylvania	0.009	0.010	0.057	0.076

* Taken from Gan, Nandi, and Walker (1972).

The oxidation of coal under relatively mild conditions is of interest for both its fundamental and technologic results. As a basic study of heterogeneous reaction, it provides a probe of the surface chemistry between oxygen and the complex structure of coal. More practical and immediate is the effect on the so-called plastic properties: the tendency of many bituminous coals to soften and agglomerate as they are heated. Mild oxidation is well known to inhibit this caking behavior and is used as a pretreatment step in the preparation of coal for subsequent gasification reactions under more severe conditions.

A report by Kam, Hixson, and Perlmutter (1976*a*) summarized the more pertinent background on the kinetics and chemistry of this subject and used the available evidence to develop a descriptive model. The most important implications were tested experimentally in a series of fixed-bed oxidation runs on a high volatile type A bituminous coal, varying such process parameters as temperature, gas flow rate, particle size, and oxygen partial pressure (Kam, Hixson, and Perlmutter, 1976*b*). The caking propensity of the coal was correlated with an oxidation parameter that took into account the distribution of the products resulting from the oxygen reactions (Kam, Hixson, and Perlmutter, 1976*c*).

One essential shortcoming of these prior studies is their total focus on a single coal. Since coal can vary considerably among sources and types, the research reported here was undertaken to extend the range of materials and to test the Kam-Hixson-Perlmutter (KHP) model on several coals for which it would be likely to find application. In particular, the effects of porosity and of rank were to be examined, as well as the geographic origins of a group of bituminous coals.

EXPERIMENTAL

For the purposes of this study, samples of the seven coals listed in Table 1 were obtained from the ERDA—Penn State Coal Bank. The PSOC designations are by the coal bank, and the analyses given are from the same source. Details of experimental equipment and procedure followed those given in the reference article (Kam, Hixson, and Perlmutter, 1976*b*). The only major change in apparatus was the inclusion of a Hewlett Packard Model 5830A gas chromatograph for greater precision in effluent analysis.

Air oxidation tests were run at atmospheric pressure on each of the various rank coals over the following range of conditions:

Parameter	Range covered
Temperature, °C	200 to 250
Gas flow rate, SCCM/kg (standard cm^3/kg of coal)	1 000 to 3 500
Particle size, USS mesh	-6 to $+50$

Each sample was analyzed in an independent commercial laboratory both before and after oxidation for ultimate and proximate composition and heating value.

RESULTS AND DISCUSSION

Among the seven coals of different rank and from diverse sources that were studied to delineate their similarities and differences with respect to moderate temperature oxidative kinetics, the most striking single result is the finding that the coals tested may be classified in two categories, according to whether or not the rate of oxidation monotonically falls during the 4 to 7 hr of a test. Most of the coals tested behaved under oxidation as was expected from the prior study; however, two of the coals demonstrated a constant rate period during which virtually all the feed oxygen was consumed. An interpretation of these disparate results may be obtained from the pore volume information in Table 2. In this table, where the several coals are placed in the order of their pore volumes of relatively large diameter (>300Å), the list can conveniently be divided into two subsets, as in the discussion which follows.

Oxidation of Small Pore Coals

Although the specific reaction rates differ between coals and depend on particle size, temperature, and oxygen partial pressure, all the data obtained from runs on

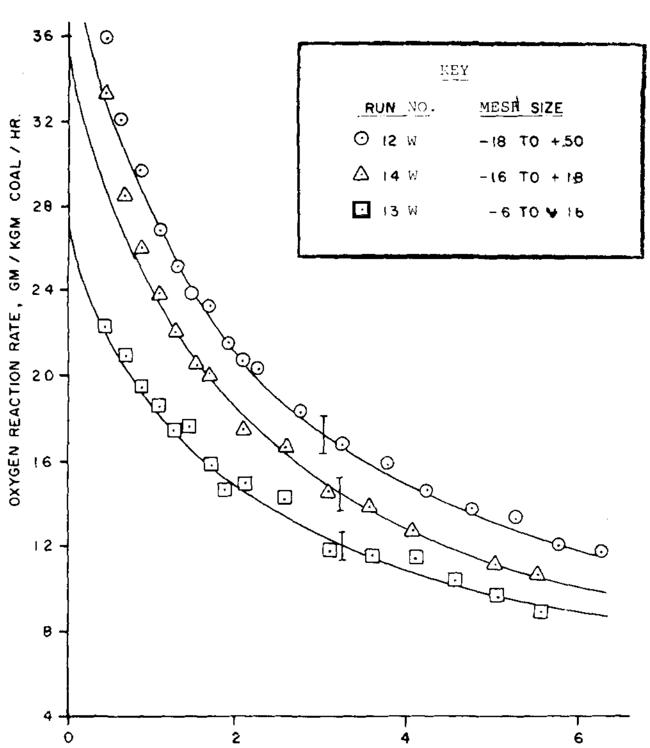

Fig. 1. Effect of particle size on oxygen reaction rate at 225°C and 100 SCCM. Coal: HV bituminous B, PSOC 197. Lines are for data fit to model. Bars show experimental error.

the small pore coals gave similar results with respect to the shape of the reaction rate curves. Typical results are presented in Figures 1 to 4 from which, with allowance for some degree of experimental scatter, it may be concluded that the behavior patterns conform to the essential features of the KHP model. More specifically, since this model predicts time dependent rates of the form

$$[1/R_i - 1/R] = [1/R_i - 1/R_o] \exp(-k_4 t) \qquad (1)$$

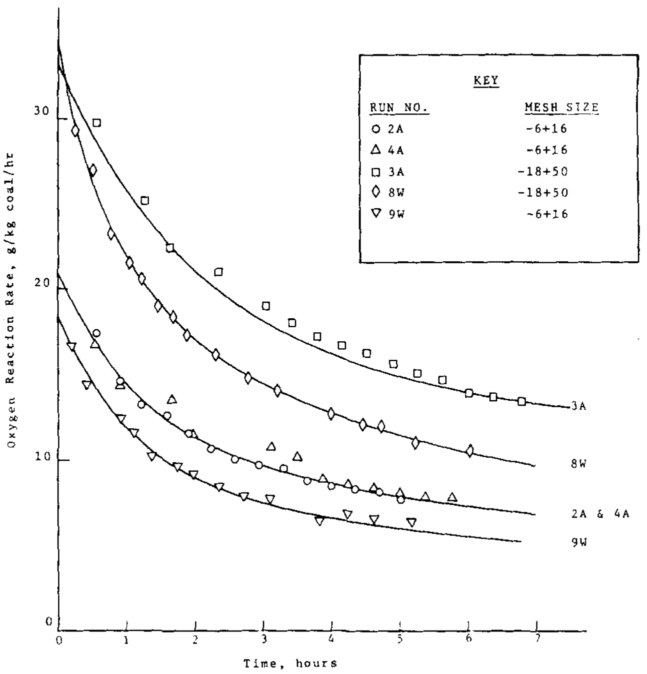

Fig. 2. Effect of particle size on oxygen reaction rate at 225°C and 100 SCCM, with replication. Coal: HVA bituminous, PSOC 4. Lines are for data fit to model.

for temperatures below 230°C and of the form

$$R - R_i = (R_i - R_o) \exp(-k_4 t) \qquad (2)$$

at higher temperatures, the oxidation data can be tested for linearity on semilog coordinates as in Figures 5 to 8. The straight and parallel lines are entirely consistent with the expectations of the KHP model, and the values of initial rate, asymptotic rate, and rate constant can be estimated from the appropriate slopes and intercepts. The computed values are given in Table 3, from which it may be noted that the k_4 values for these coals are close to one another and differ only slightly between the tests run by different investigators on the same coal. These values

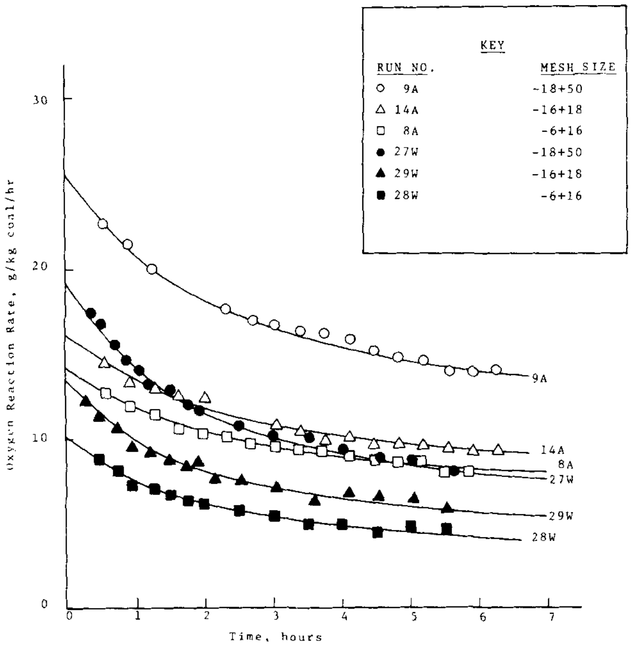

Fig. 3. Effect of particle size on oxygen reaction rate at 225°C and 100 SCCM, with replication. Coal: LV bituminous, PSOC 127. Lines are for data fit to model.

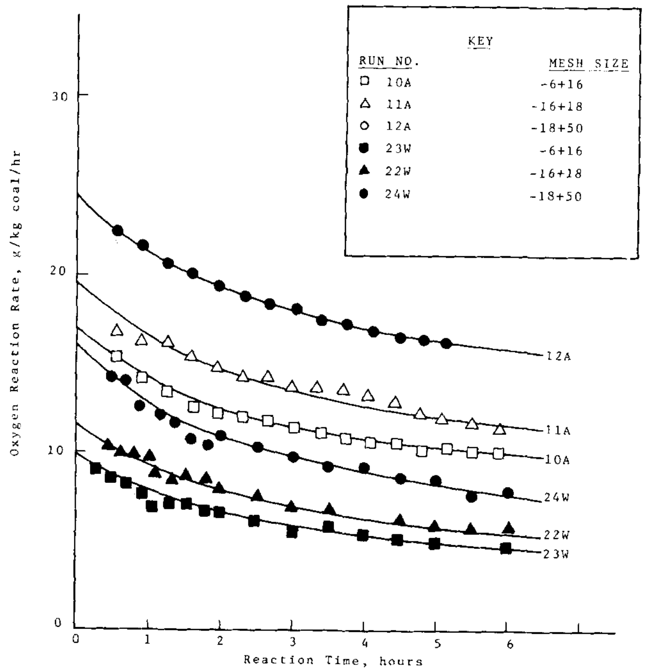

Fig. 4. Effect of particle size on oxygen reaction rate at 225°C and 100 SCCM, with replication. Coal: MV bituminous, PSOC 135. Lines are for data fit to model.

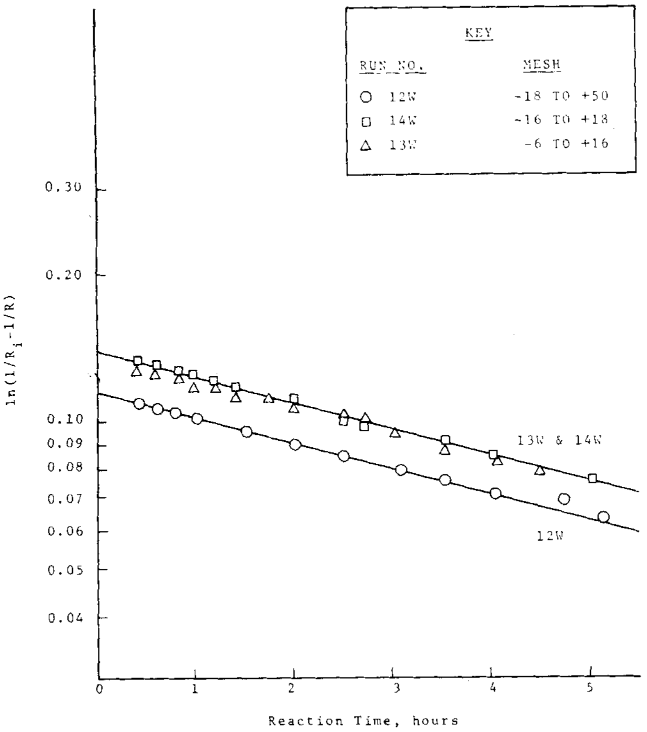

Fig. 5. Linearity test following Equation (1). Coal: HVB bituminous, PSOC 197.

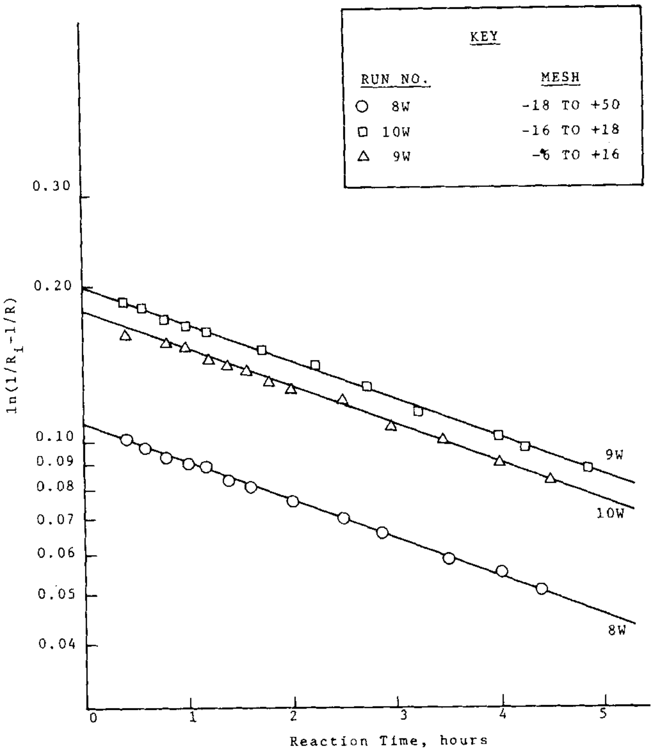

Fig. 6. Linearity test following Equation (1). Coal: HVA bituminous, PSOC 4.

also compare well to the results of the careful temperature study of Kam, Hixson, and Perlmutter (1976*b*), who report $k = 0.23$ hr^{-1} and $k = 0.60$ hr^{-1} at 225° and 250°C, respectively. These numbers can be used to estimate an activation energy in the range of approximately 17 kcal/mole.

Oxidation of Large Pore Coals

The samples of Lignite (PSOC 87) and high volatile C bituminous coal (PSOC 190) oxidized in this study had appreciably larger pores and greater chemical activity than the prior samples. The results presented as Figures 9 and 11 show extended periods of high activity during which the oxidation rates were determined by the limiting oxygen reactant. When the most reactive surface or pore available sites were used up, measured rates dropped as diffusional mechanisms began to play a limiting role.

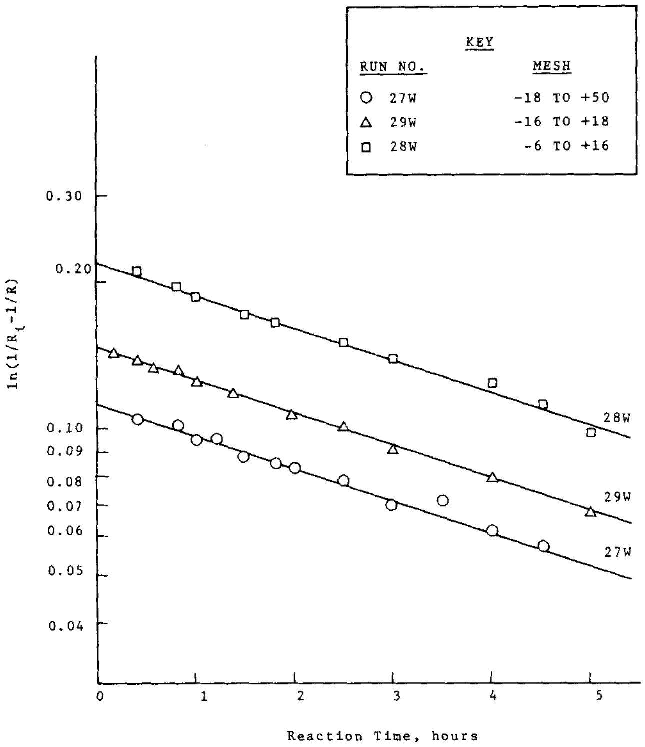

Fig. 7. Linearity test following Equation (1). Coal: LV bituminous, PSOC 127.

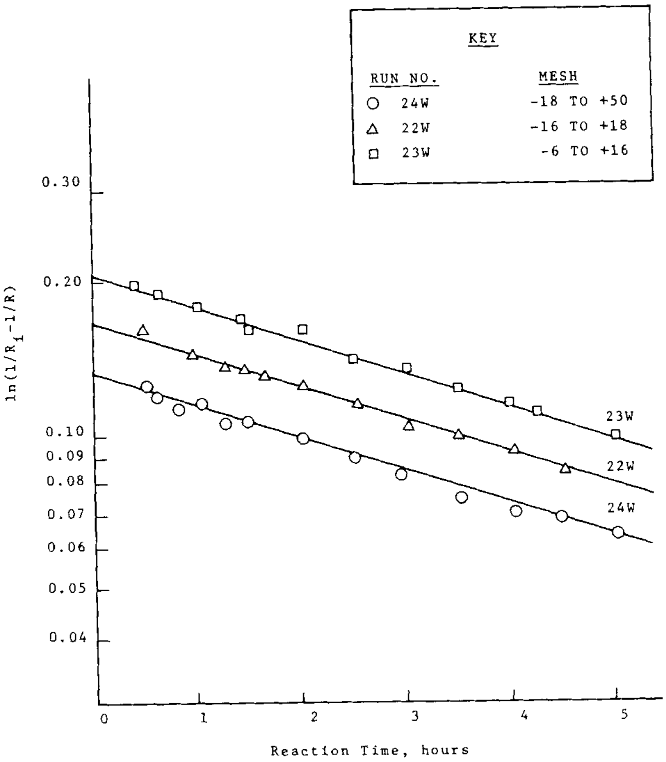

Fig. 8. Linearity test following Equation (1). Coal: MV bituminous, PSOC 135.

TABLE 3. CALCULATED VALUES FOR THE PARAMETERS OF THE OXYGEN REACTION RATE EXPRESSIONS

Run No.	Coal PSOC No.	Temp. (°C)	Initial rate, R_0 (g/kg coal/hr)	Asymptotic rate, R_i (g/kg coal/hr)	Rate constant, k_4 (1/hr)
2A	4	225	20.9	5.0	0.15
3A	4	225	33.0	9.7	0.15
4A	4	225	20.9	5.0	0.15
8W	4	225	34.2	7.5	0.17
9W	4	225	18.4	4.0	0.17
10W	4	225	22.2	4.6	0.16
19A	80	225	10.6	3.0	0.29
24A	80	250	6.4	3.1	0.64
25A	80	250	14.2	5.0	0.63
26A	80	250	10.5	4.4	0.62
27A	80	250	6.4	3.7	0.58
8A	127	225	14.1	7.0	0.21
9A	127	225	25.4	12.0	0.22
14A	127	225	16.0	8.0	0.22
27W	127	225	19.1	5.9	0.17
28W	127	225	10.1	3.1	0.17
29W	127	225	13.4	4.2	0.17
10A	135	225	17.0	8.5	0.21
11A	135	225	19.5	10.0	0.21
12A	135	225	24.1	14.0	0.21
22W	135	225	11.5	3.8	0.13
23W	135	225	9.8	3.2	0.13
24W	135	225	16.0	5.3	0.13
12W	197	225	42.2	7.1	0.12
13W	197	225	26.2	5.5	0.12
14W	197	225	38.2	6.0	0.12

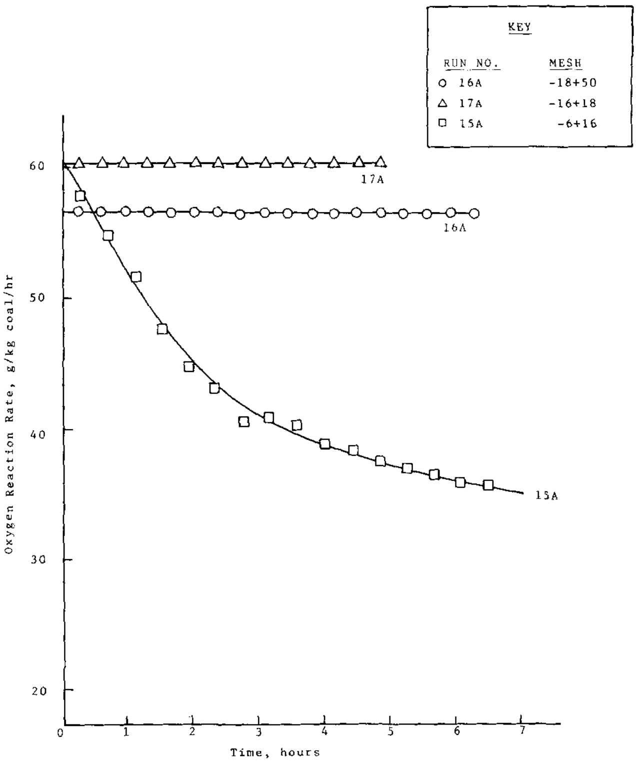

Fig. 9. Effect of particle size on oxygen reaction rate at 225°C. Coal: lignite, PSOC 87.

Figure 9 shows, for example, that no diffusional resistance is significant for small particles (−16 + 18 and −18 + 50 mesh) but that rates fall sharply when larger particles (−6 + 16) are used. Similar results are reported in Figure 10 for another coal type, where, in addition, the duration of the constant rate period is shortened with larger particles. Yet other results that follow the same pattern are given in Figure 11, but here the arguments are further supported by the changes in flow rate (reactant residence time) and temperature. As expected for a diffusion-limited process, the particle resistance is noticeably greater as the temperature is lowered. The effect of halving the flow rate is to half the oxidation rate, since only half the reactant is available to be totally consumed in any given period of time.

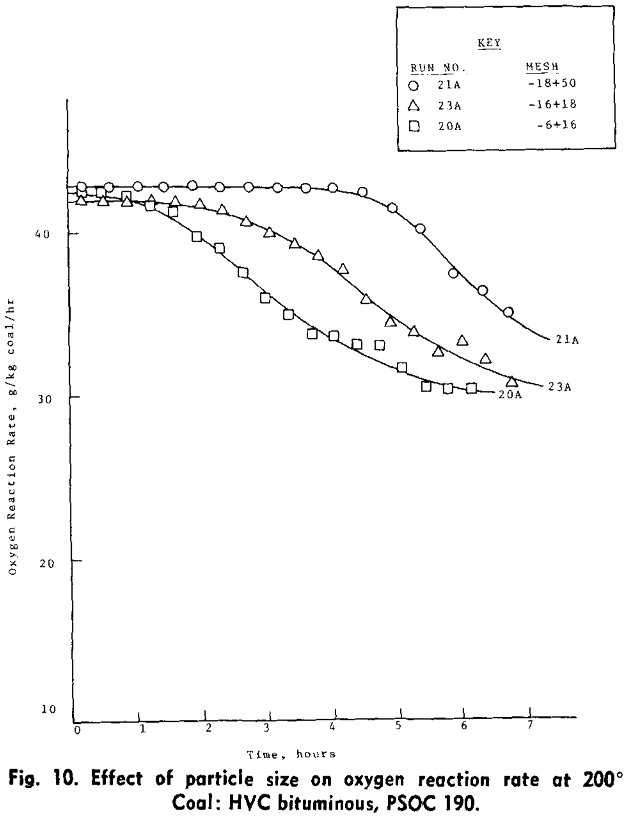

Fig. 10. Effect of particle size on oxygen reaction rate at 200°C. Coal: HVC bituminous, PSOC 190.

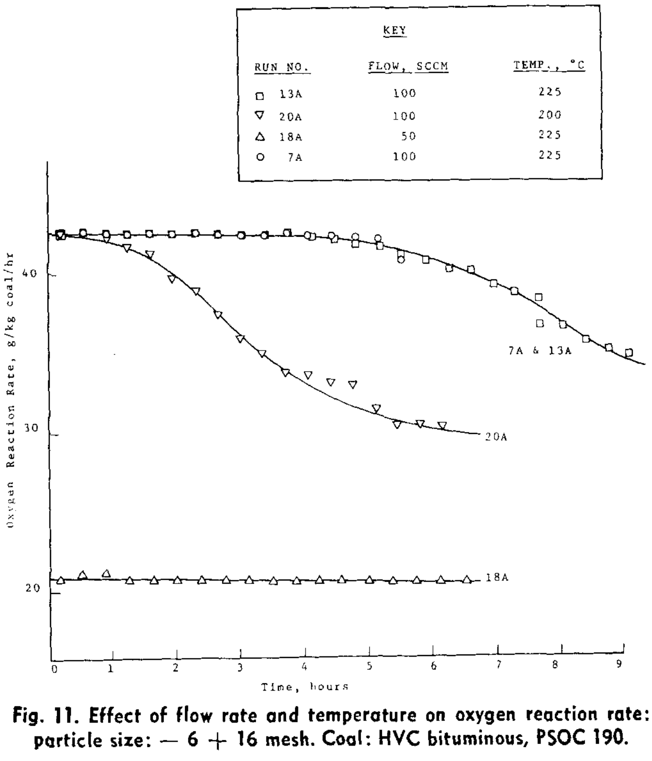

Fig. 11. Effect of flow rate and temperature on oxygen reaction rate: particle size: — 6 + 16 mesh. Coal: HVC bituminous, PSOC 190.

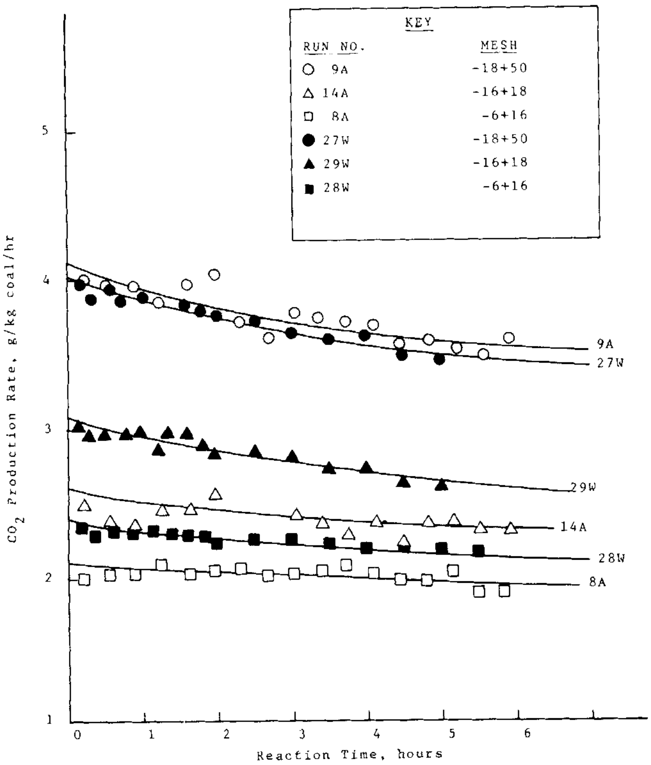

Fig. 12. Effect of particle size on carbon dioxide production rate at 225°C and 100 SCCM, with replication. Coal: LV bituminous, PSOC 127. Lines are for data fit to model.

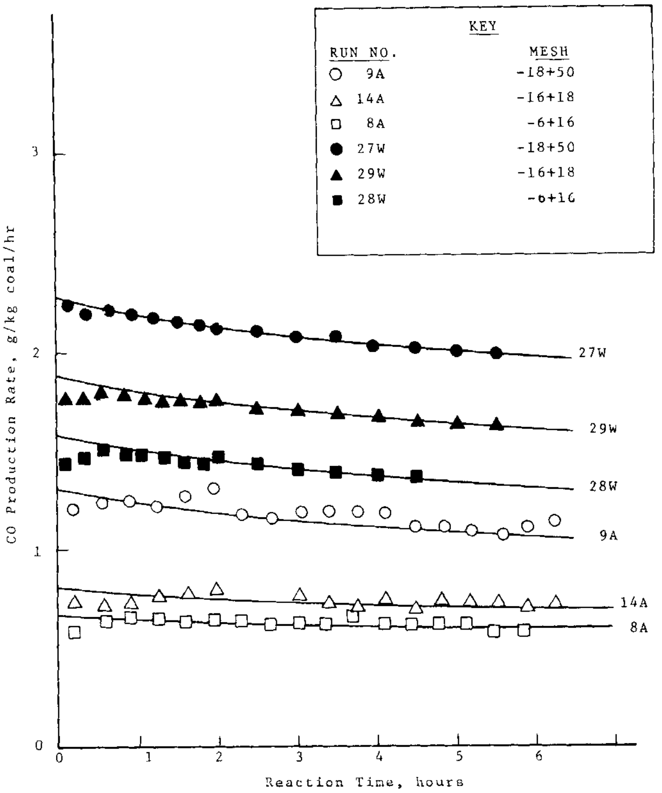

Fig. 13. Effect of particle size on carbon monoxide production rate for different samples of the same coal at 225°C and 100 SCCM. Coal: LV bituminous, PSOC 127. Lines are for data fit to model.

Production of Carbonic Gases

The chromatographic analysis run on each sample of reactor effluent provided a record of carbon dioxide and carbon monoxide production to match the rates of oxida-

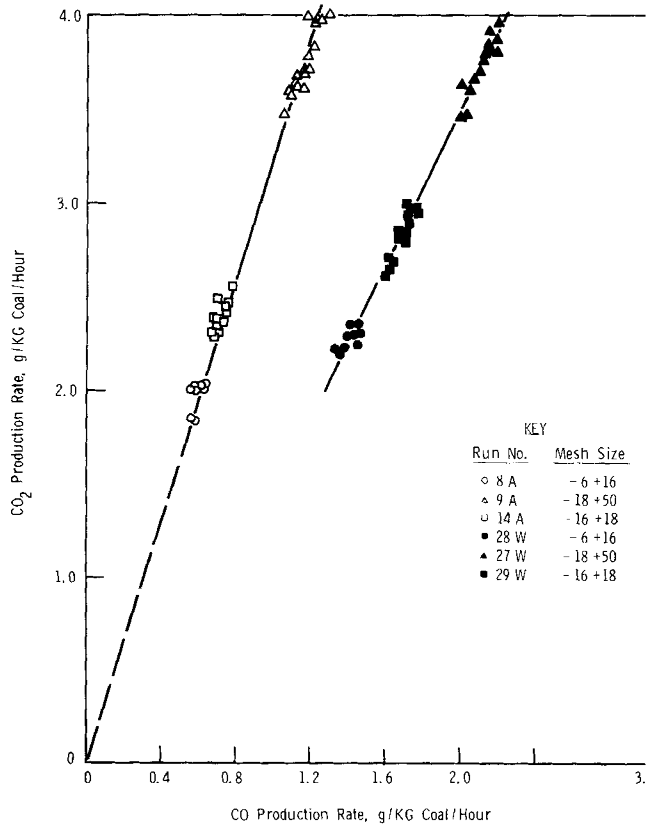

Fig. 14. Relative carbon dioxide and carbon monoxide production rates. Coal: LV bituminous, PSOC 127.

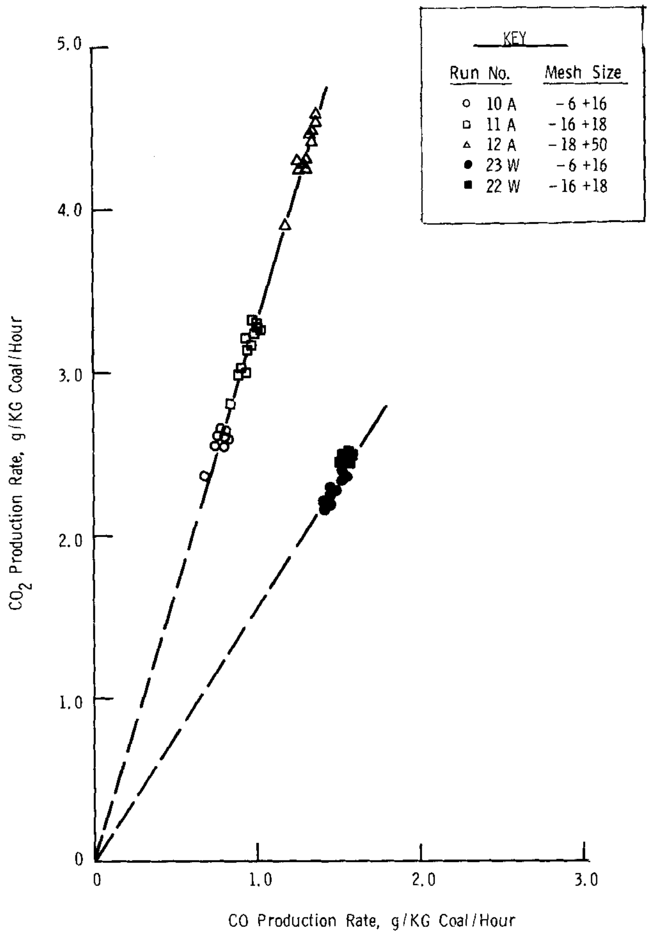

Fig. 15. Relative carbon dioxide and carbon monoxide production rates. Coal: MV bituminous, PSOC 135.

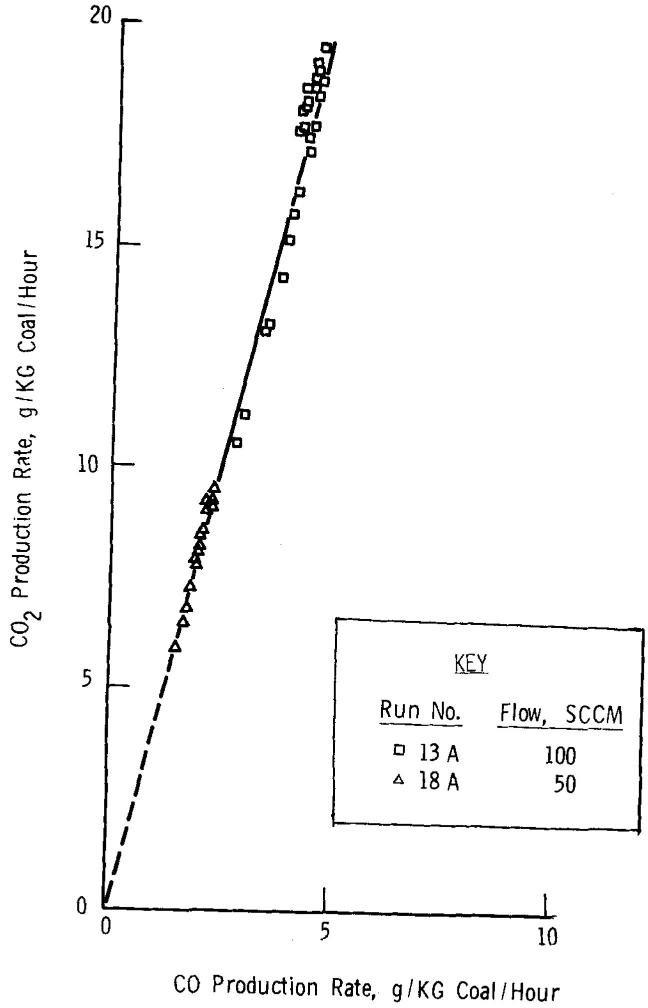

Fig. 16. Relative carbon dioxide and carbon monoxide production rates. Coal: HVC bituminous, PSOC 190.

TABLE 4. COMPARISON OF REACTION AND MASS TRANSFER RATES

Coal PSOC No.	Runs being compared	Relative reaction rates measured	Relative mass transfer rates calculated	Percent deviation
4	8W to 9W	1.9	1.87	−2
4	8W to 10W	1.6	1.45	−9
4	10W to 9W	1.2	1.30	+8
4	2A to 3A	1.6	1.87	+17
80	25A to 26A	1.4	1.45	+4
80	25A to 27A	2.2	1.87	−15
80	26A to 27A	1.6	1.30	−19
127	9A to 8A	1.8	1.87	+4
127	9A to 14A	1.6	1.45	−9
127	14A to 8A	1.1	1.30	+18
127	28W to 27W	1.9	1.87	−2
127	27W to 29W	1.4	1.45	+4
127	29W to 28W	1.3	1.30	0
135	12A to 10A	1.4	1.87	+34
135	12A to 11A	1.2	1.45	+20
135	11A to 10A	1.2	1.30	+8
135	24W to 23W	1.7	1.87	+10
135	24W to 22W	1.4	1.45	+4
135	22W to 23W	1.2	1.30	+8
197	12W to 13W	1.4	1.87	+33
197	14W to 13W	1.2	1.45	+21
197	12W to 14W	1.2	1.30	+8

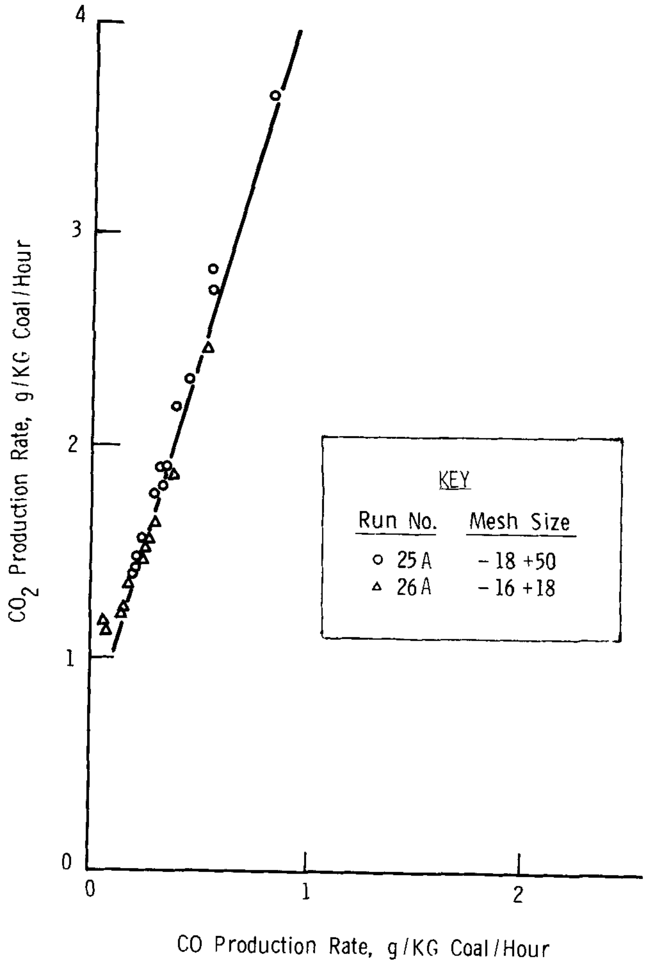

Fig. 17. Relative carbon dioxide and carbon monoxide production rates. Coal: anthracite, PSOC 80.

tion. Typical results are shown in Figures 12 and 13, agreeing in their forms with the findings and correlating equations of the earlier study by Kam, Hixson, and Perlmutter (1976*b*).

A further implication of the KHP model may be tested by examining the relative production of the two carbonic gases. Since the model makes no distinction between the mechanisms of their formation, it is to be expected that the ratio of carbon dioxide to carbon monoxide should be constant with time and independent of particle size. Cross plots are presented as Figures 14 to 17 to illustrate the linearity and to demonstrate that the correlations for the various coals do indeed persist as flow rate, particle size, and conversion vary. In several cases, the linear relationship extends to the origin, suggesting that the two gases are always produced in the same ratio; in other examples, the correlating line does not pass through the origin, indicating that some change in mechanism of carbonic gas production may occur over a wide enough range of conversion.

Mass Transfer

Another expectation of the KHP model is that a mass transfer boundary layer effect will be dependent on particle size according to a square root of Reynolds number correlation. A straightforward test of this formulation can be performed by comparing the reaction rates of pairs of runs differing only in particle size. If two such rates are indeed different because of a mass transfer limitation, the ratio of reaction rates should be approximately the same as the ratio of transfer coefficients, which should in turn

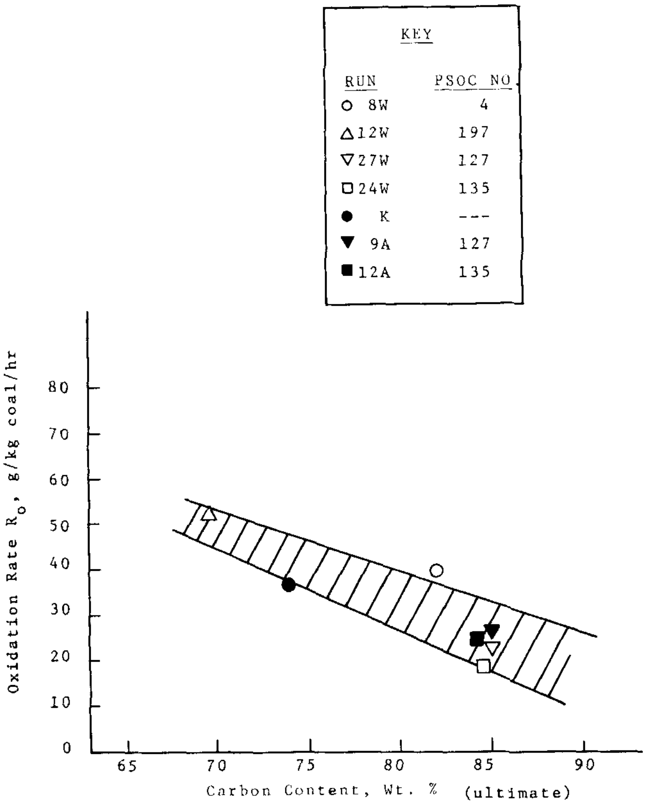

Fig. 18. Effect of coal carbon content on initial oxidation rate for − 18 + 50 mesh particles at 225°C, 100 SCCM.

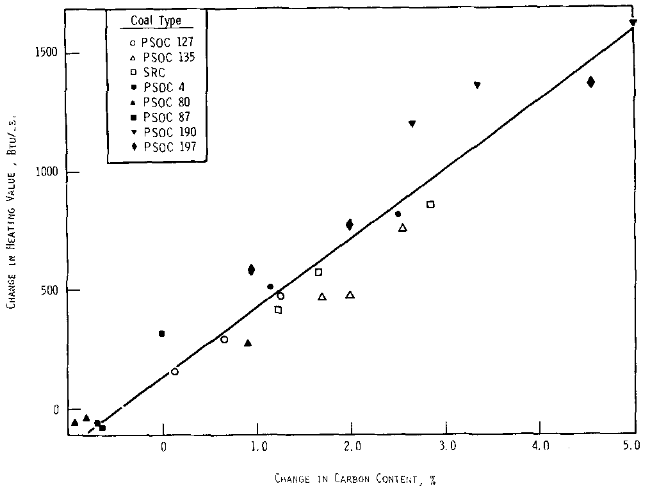

Fig. 19. Correlation between change in heating value and change in carbon content of oxidized coals.

be the same as the inverse ratio of the square root of particle size. The results of such a test are given in Table 4. Nineteen of the twenty two values compared deviate by 20% or less, and the other three are within 34%, indicating that most of the particle size effect is attributable to a boundary layer. In this connection, it is interesting to note that the largest deviations arose for the HVB bituminous coal (PSOC 197) that has the largest pore volume of any coal in the small pore group and for the MV bituminous coal (PSOC 135) which is the next one in pore volume. It would appear that the properties of these coals are close to those of the large pore group.

TABLE 5. ULTIMATE ANALYSES AND HEATING VALUES OF COAL SAMPLES*

Run No.	Mesh size	Coal PSOC No.	Dry analysis, wt % C	H	O	N	S	Ash	Heating value Btu/lb
As received		4	81.40	5.24	8.55	1.61	0.75	2.45	14 435
As received		127	84.34	4.55	3.15	1.20	0.61	6.15	14 631
As received		135	86.31	4.78	3.48	1.68	0.89	2.86	15 215
As received		80	81.68	2.31	2.40	0.74	0.58	12.29	12 994
As received		197	71.59	4.95	12.67	1.43	1.17	8.19	12 533
As received		87	63.09	4.35	22.58	0.93	0.82	8.23	10 412
As received		190	69.49	4.81	14.11	1.21	2.85	7.53	12 151
2A	−6 + 16	4	80.25	4.88	10.09	1.58	0.96	2.24	13 198
3A	−18 + 50	4	78.91	4.88	12.73	1.59	0.74	1.15	13 616
4A	−6 + 16	4	79.71	4.96	10.41	1.56	0.71	2.65	13 939
8A	−6 + 16	127	84.22	4.35	4.67	1.19	0.65	4.92	14 473
9A	−18 + 50	127	83.02	4.24	6.22	1.22	0.80	4.44	14 153
14A	−16 + 18	127	83.69	4.26	5.33	1.19	0.72	4.81	14 335
10A	−6 + 16	135	84.62	4.70	5.54	1.67	0.67	2.80	14 746
11A	−16 + 18	135	84.34	4 62	6.46	1.66	0.60	2.32	14 743
12A	−18 + 50	135	83.76	4.49	6.74	1.67	0.61	2.73	14 449
19A	−18 + 50	80	80.97	2.25	3.03	0.77	0.61	12.37	12 825
24A	−6 + 16	80	81.89	2.20	2.45	0.77	0.55	12.14	12 724
25A	−18 + 50	80	80.77	2.15	3.25	0.77	0.61	12.45	12 865
26A	−16 + 18	80	82.60	2.19	2.97	0.78	0.63	10.83	13 046
27A	−6 + 16	80	82.49	2.17	2.89	0.78	0.54	11.13	13 030
13W	−6 + 16	197	70.65	4.70	15.17	1.38	1.15	6.95	11 944
14W	−16 + 18	197	69 57	4.29	15.72	1.40	1.12	7.90	11 755
12W	−18 + 50	197	67.05	3.77	16.85	1.36	1.16	9.81	11 159
15A	−6 + 16	87	63.11	3.68	21.95	1.00	0.76	9.50	10 097
16A	−18 + 50	87	63.76	4.02	19.90	1.05	0.84	10.43	10 472
17A	−16 + 18	87	63.71	3.95	20.05	1.02	0.82	10.45	10 489
7A	−6 + 16	190	67.50	3.78	17.72	1.28	2.60	7.12	11 111
13A	−6 + 16	190	64.22	3.50	21.12	1.19	2.58	7.39	10 271
18A	−6 + 16	190	68.52	4.10	15.99	1.24	2.63	7.52	11 421
20A	−6 + 16	190	66.83	3.74	17.79	1.21	2.64	7.79	10 945
21A	−18 + 50	190	64.48	3.50	18.91	1.16	2.72	9.23	10 530
23A	−16 + 18	190	66.14	3.61	19.18	1.24	2.65	7.18	10 787

* *Analysis by Smith, Rudy & Company.*

Replication

Results of replicate oxidation runs on high volatile A bituminous coal (PSOC 4) show in Figure 2 that reaction rate is reproducible for the same type of coal and particle size, usually to within the experimental precision, but never exceeding a deviation of 5% for any given point. In all the figures, runs marked with a letter A were obtained with the newer apparatus; those labeled with a W are from the earlier set. Comparisons of the newer data with the similar runs from the previous operator and other gas chromatograph show somewhat greater differences, but this is probably to be attributed to the new analysis procedure. The new chromatograph is significantly more sensitive, especially in detecting the relatively smaller peaks of the carbonic gases. It is notable in Figure 2 that the replicate runs 2A and 4A from the same equipment gave results that were indistinguishable from one another. Further confirmation of reproducibility may be found in Figure 11 for runs 7A and 13A on a coal of the large pore volume group (HVC bituminous, PSOC 190).

Effect of Coal Rank

By using the carbon content of a coal sample as a convenient index of its rank, it is possible to detect trends in oxidative reactivity. One such correlation is presented in Figure 18, where the initial oxidation rates are shown for all the coals tested under the same conditions of gas flow, particle size, and temperature. Also included on the same figure is a result obtained by Kam, Hixson, and Perlmutter (1976b). It is evident that a band of values is called for, rather than a single line, but there is a discernable trend toward slower oxidation of higher rank coals. It may be noted that two replicate pairs are among the points on this figure and that their agreement is close in comparison with the scatter observed among the different coal types.

Chemical Analysis and Heating Values

Each of the coal samples was analyzed by an independent commercial laboratory to determine heating value, ultimate analysis, and proximate analysis, both before and after oxidation. Representative ultimate analysis results are summarized in Table 5.

It is clear that in general the smaller particle size samples pick up relatively larger quantities of oxygen, in agreement with the observation made by Kam, Hixson, and Perlmutter (1976c) that a coal is more readily rendered noncaking when it is oxidized in a smaller particle form, in particular when the process produces relatively more water and less of the carbonic gases. In the case of lignite (PSOC 87), however, oxygen was lost by the coal during the reaction, and the effect was greatest for the more reactive smaller size particles.

As to heating values of the several coals, the data show a strong correlation with the carbon content of a sample. Regardless of particle size, the heating value of a material changed upon oxidation primarily as the carbon changed. The results are presented in Figure 19, where a correlation coefficient of 0.86 exists for data taken with a wide range of coals of different types. There is also a suggestion in the data that generalizations regarding the fixation of oxygen that occurred for all the various bituminous coals do not apply to the lignite (PSOC 87) and the anthracite (PSOC 80) coals. The results of Table 5 show that for these coals, the most and least reactive among those tested, the result of the oxidative treatment was to increase the percent of carbon in the overall composition.

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NOTATION

k_4 = reaction rate constant in KHP model, hr^{-1}
R = oxygen reaction rate, g/hr/kg coal
R_i = long time asymptotic value of reaction rate
R_0 = zero time intercept of reaction rate curve
t = time, hr

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Criteria for Selective Path Promotion in Electrochemical Reaction Sequences

An analysis of consecutive electrochemical reactions is presented with some emphasis on organic electrocatalytic sequences. The effect of potential and electrode kinetic parameters on reaction selectivity and on current and rate distribution is examined in two model electrochemical reactors with channel flow or with complete mixing. Results and some examples demonstrate that the electrolyte potential is the most significant parameter for selectivity control of complex series reactions in electrochemical processing or energy generation. Criteria developed for selectivity and current or rate variation provide the basis for the design of electrochemical reactors and for optimal operation considerations with multiple electrode reactions. Such criteria and analyses apply to a number of working electrode configurations operating with ionic as well as molecular reactants.

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