

FACTORS AFFECTING REACTIVITY OF COAL CHARs

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It is helpful when attempting to understand reactivity of coal chars to draw on what is known about gas-solid interaction from voluminous studies on both the gasification of more crystalline carbons and heterogeneous catalysis. Rates of gasification of porous carbons are primarily affected by three parameters: active site concentration; accessibility of the reactant gas into the internal area of the char and, hence, to active sites; and presence of catalysts which are active for the dissociation of molecular species into reactive oxygen atoms or hydrogen atoms (1,2). Following a discussion of these parameters, reactivities to air and CO₂ of sixteen chars produced from coals of varying rank will be considered.

THEORETICAL CONSIDERATIONS

It is well to review briefly the structure and thermal behavior of coals insofar as they will determine whether a char is produced from coal and what physical characteristics the char will possess. Extensive x-ray, infrared, and NMR studies have been conducted on coal; and even though there is not today complete agreement on the "building blocks" which make up coal, we will take a position. Our position is based primarily on the detailed x-ray studies of Cartz and Hirsch (3).

Coals are composed of aromatic and hydroaromatic layers, terminated at their edges by various functional groups and crosslinked by various functional groups. The average size of the layers and the number aligned closely parallel increase with increasing rank of coal. More or less poor alignment between packets of layers produces internal porosity and results in coal being a microporous material. Upon heat treatment all coals lose volatile matter, primarily from the periphery of the layers. Further, some coals soften extensively, form an anisotropic mesophase, which coalesces into a coke (4). Other coals, upon heat treatment, do not soften (they behave as thermosetting materials) and are converted to a char. The extent of softening is thought to be primarily determined by the concentration and thermal stability of the crosslinking groups. The micropore structure which was in the precursor coal is essentially preserved in the char if it has not been taken to too high a temperature. Indeed the microporosity can become more accessible to reactant gases because of loss of volatile matter. However, if the processing temperature is taken too high, microporosity in the char is rapidly lost. This is a result of the thermal breakage of crosslinks between planar regions in the char, allowing improved alignment of these regions with loss of porosity between regions. The structure of chars is envisioned as being composed of small trigonally bonded planar regions, terminated by markedly fewer hetero-atom functional groups than in the original coal, and still containing substantial (but somewhat less) crosslinking than the original coal. The exact structure of a char produced from a given precursor coal can be changed by altering such variables as: possible coal pretreatment (to introduce more crosslinks), coal particle size, rate of heating, maximum temperature and time at maximum temperature, atmosphere and total pressure present during heating. It is with this background that the reactivity of coal chars can be considered.

Active sites To understand the kinetics of the gasification of a carbonaceous solid, a correct term for the concentration of sites which can potentially take part in the reaction is needed. Given the ability to measure total surface areas of solids by physical adsorption of gases in 1938, efforts were made to correlate gasification rates

of carbonaceous solids with their total area. These efforts were not successful. Finally, in 1963 Walker and co-workers (5) showed for the C-O₂ reaction that the appropriate concentration term was that given by dissociative oxygen chemisorption onto sites -- this was a measure of active sites. Later Walker and co-workers (6), Hennig (7), and Thomas and Roscoe (8), showed clearly that the active sites involved in the gasification of carbon in a trigonally bonded solid are those located at the periphery of layer planes and at vacancies and non-basal dislocations within layer planes. In this light, it can be said that if one wishes to maximize the reactivity of coal chars, the average crystallite size should be kept to a minimum and the defect concentration in the layer plane kept to a maximum.

Mass transport limitations Thiele (9), Zeldowitsch (10), and Wheeler (11), pioneered the concept that for a gas interacting with a porous solid the active sites within the solid, under some circumstances, may be exposed to the reactant gas at a concentration significantly lower than its concentration at the surface of the solid. This can result in the "utilization efficiency" of the active sites for gasification becoming $\ll 1$. The phenomenon occurs at higher gasification rates when a large concentration gradient of reactant between the surface of the solid and its center is needed to supply the gas within the solid for reaction. The situation has been considered in detail by Walker and co-workers (1) for the gasification of carbon. Figure 1 presents an idealized Arrhenius plot depicting the situation, when one considers a half cylinder of porous carbon. In Zone I, the reactant concentration gradient is negligible within the solid; the utilization efficiency, η , of active sites is ≈ 1 . With increasing temperature and gasification rate, η eventually $\rightarrow 0$. In a char gasification process, it is important to locate the zone in which reaction is occurring in order that the kinetics may be understood.

Mass transport limitations are expected to vary significantly as chars produced from coals of different rank are gasified. That is, coals and coal chars have a trimodal pore distribution, with most of the active sites located within the micropores which are defined as being less than 12A in diameter (12). Walker and co-workers (13) have shown that the rate of gaseous diffusion within the micropore system is slow and, indeed, an activated process for pores (apertures) less than about 5A. Thus it is certain that if the sites located in the micropores are to be well utilized for reaction (that is $\eta \rightarrow 1$), the interior of the solid must have an adequate number of larger, feeder pores off which the micropores connect. Diffusion through the feeder pores to the mouths of the micropores will be reasonably rapid; and, therefore, reactant concentration at the mouths of the micropores can closely approach the value of reactant concentration at the exterior particle surface.

Walker and co-workers (12) show that low rank coals tend to have a greater percentage of their total pore volume in larger pores than do the higher rank coals. Thus, it is expected that chars derived from the lower rank coals will have a larger feeder pore system and be less mass transport limited during their gasification.

Catalysis Almost every metal in a reduced and/or oxidized state is a catalyst for carbon gasification (2). Catalyst activity varies between impurities and with their concentration and extent of dispersion (ratio of atoms in the surface to total atoms). Specific catalyst activity, that is activity per unit catalyst weight, usually decreases as the amount of catalyst present and its particle size increase (2). Therefore, even though most of the inorganic impurity content in most coals is located in the mineral matter, the possible catalytic activity of trace and minor elements (present as organo-metallics) cannot be ignored. That is, many of the trace elements are very highly dispersed within the coal matrix compared to the extent of mineral matter dispersion.

In this regard the situation with lignitic chars is most interesting. Lignites have high concentrations of carboxyl groups at the edges of their layers. Ion exchange has occurred in nature with cations like calcium replacing a significant amount of hydrogen on the carboxyl groups. Upon the thermal conversion of lignites to chars, the

carboxyl groups decompose depositing large amounts of highly dispersed calcium (and other metals) onto the char surface. Probably, as a result, the reactivity of chars to air has been found to correlate reasonably well with the amount of calcium present (14).

EXPERIMENTAL

The coals used were the same as those used in a previous reactivity study (14). Table 1 presents analyses of the coals. Methods of char preparation and procedures for measuring char reactivity have been described previously by Jenkins et al on their studies in air (14). A small quantity of coal (5-10 mg) was placed on a Cahn Model RG Electrobalance of a Fisher TGA apparatus and heated at a rate of 10°C per min to 1000°C in a N₂ atmosphere. Samples were held at 1000°C until no further weight loss was detectable.

Selected coals were treated with warm 10% HCl for 48 hr, followed by their being washed with water, dried, and charred. Demineralized samples were prepared by taking acid washed coals and treating them with warm HF, followed by extensive washing and drying prior to charring.

Samples of PSOC 127, a relatively unreactive low volatile coal char, and PSOC 87, a highly reactive lignite char, were chosen for an investigation of the effect of particle size on reactivity. Both chars derived from the parent coals and demineralized coals were studied. Approximately 40 g of each coal of 40x100 mesh particle size were further ground using a pestle and mortar. The ground coals were then hand sifted for 20 min to obtain four cuts: +100, 100x150, 200x325, and -325 mesh. Chars were prepared and reactivities measured for all cuts.

In this study reactivity of chars to CO₂ has been measured, with the objective of comparing reactivities with those measured previously in air (14). Since the carbon-carbon dioxide reaction is a much slower reaction than the carbon-air reaction (1), it must be carried out at a much higher temperature to obtain the same rate as for the air reaction. A temperature was selected at which the rate of reaction of the more reactive lignites in CO₂ corresponded closely to their reactivities in the air at 500°C. Such a temperature was 900°C for the 40x100 mesh coal-derived chars. The use of less than 5 mg of char ensured that the reactivity per unit weight of char was independent of char weight (or bed depth).

Following preparation of a char at 1000°C, it was cooled in dry N₂ to 900°C prior to reaction. Dry CO₂ was admitted at a flow rate of 300cc (NTP) per minute, and weight of the char was continuously recorded. As with the air reaction, burn-off curves usually go through three regions of reactivity: purge and activation, linear burn-off rate, and decreasing burn-off rate. During the linear region the char loses weight but increases in specific surface area because of activation. This region continues until the specific surface area no longer increases; the gasification rate begins decreasing and the third region is entered. The linear region for each coal varies in duration, but in each case the rate in the linear period is measurable. The linear region represents the maximum rate at which chars gasify.

Reactivities of the chars were calculated as follows:

$$R = \frac{1}{W} \frac{dW}{dt}$$

R = reactivity of the char (mg hr⁻¹ mg⁻¹)

W = weight of initial char on ash free basis (mg)

dW/dt = change in char weight with time (mg hr⁻¹)

RESULTS AND DISCUSSION

Figure 2 plots reactivity of the chars versus carbon content of the parent coals for both the CO_2 and air reactions. As with the air reaction, the lignites are the most reactive chars and have the widest spread of reactivity values. Reactivities in CO_2 and air at 900°C and 500°C , respectively, are closely similar for all chars. The lowest reactivity for both reactions was recorded for a char from LV bituminous coal PSOC 127. For the CO_2 reaction this coal was over 150 times less reactive than was a highly reactive Montaña lignite, PSOC 91. This low reactivity of PSOC 127 char is attributed to a relative absence of large (feeder) pores in coal of this rank and, hence, poor utilization of the surface area in the micropores for reaction. The high reactivity of the lignites is attributed, at least in part, to a large percentage of pore volume in macro and transitional pores and, hence, better utilization of the micropore surface area for reaction.

Ash in the coals was studied by Jenkins et al (14). The ash was analyzed for K plus Na, Ca, Mg, and Fe. A reasonably good linear correlation between increasing Ca content (up to about 7% CaO in the coal) and increasing reactivity of the chars in air or CO_2 was found. A similar correlation for Mg was found up to about 1% MgO. No correlations were found for Fe or for Na plus K.

Reactivity measurements were made in CO_2 on four particle sizes of chars from original and demineralized samples of PSOC 127 and 87. Results are listed in Table 2. For all samples, a decrease in particle size results in an increase in reactivity which is an indication that reactivities are in part controlled by diffusional resistance of CO_2 into the interior of the particles. Whereas reduction in particle size of PSOC 87 from 40x100 to 200x325 mesh results in a reactivity increase of only 2.7 fold, a similar particle size reduction of PSOC 127 results in a reactivity increase of 35 fold. The fact that particle size reduction of PSOC 127 has a very marked effect on increasing reactivity is as expected since this char, produced from a low volatile coal, presents a high resistance to the internal diffusion of reactant gases.

For each particle size studied demineralization of PSOC 87 results in a decrease in reactivity, whereas demineralization of PSOC 127 leads to an increase in reactivity. These results show the important roles and balance which catalysis and mass transport resistance play in affecting reactivity of coal chars. For PSOC 87, mass transport resistance is at a minimum since lignites and their chars possess significant macro and transitional (feeder) porosity. Introduction of additional feeder porosity by mineral matter removal results in decreasing mass transport resistance relatively little compared to the effect of mineral matter removal on decreasing catalytic activity for gasification. By contrast, since PSOC 127 has little macro and transitional porosity, removal of mineral matter results in a dramatic increase in this porosity and, hence, a substantial decrease in mass transport control of gasification. In this case the decrease in mass transport resistance more than offsets the loss of catalytic activity due to mineral matter removal.

Thus reactivity of chars which differ by more than 100 times can be brought increasingly closer together by reduction in their particle size and/or acid treatment of the parent coal. Undoubtedly other approaches are available to modify reactivities of chars. Some of these are being studied at present.

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REFERENCES

1. Walker, P. L., Jr., Austin, L. G. and Rusinko, F., Jr., *Advances in Catalysis*, Vol. 11, Academic Press, New York, 1959, pp. 133-221.
2. Walker, P. L., Jr., Shelef, M., and Anderson, R. A., *Chemistry and Physics of Carbon*, Vol. 4, Marcel Dekker, New York, 1968, pp. 287-383.
3. Cartz, L. and Hirsch, P. G., *Trans. Royal Soc. (London)*, A252, 557 (1960).
4. Brooks, J. D. and Taylor, G. H., *Chemistry and Physics of Carbon*, Vol. 4, Marcel Dekker, New York, 1968, pp. 243-286.
5. Laine, N. R., Vastola, F. J., and Walker, P. L., Jr., *J. Phys. Chem.*, 67, 2030 (1963).
6. Walker, P. L., Jr., Austin, L. G., and Tietjen, J. J., *Chemistry and Physics of Carbon*, Vol. 1, Marcel Dekker, New York, 1966, pp. 327-365.
7. Hennig, G. R., *ibid*, Vol. 2, 1966, pp. 1-49.
8. Thomas, J. M. and Roscoe, C., *ibid*, Vol. 3, 1968, pp. 1-44.
9. Thiele, E. W., *Ind. Eng. Chem.*, 31, 916 (1939).
10. Zeldowitsch, J. B., *Acta Physicochim. USSR*, 10, 583 (1939).
11. Wheeler, Ahlborn, *Advances in Catalysis*, Vol. 3, Academic Press, New York, 1951, pp. 249-327.
12. Gan, H., Nandi, S. P. and Walker, P. L., Jr., *Fuel*, 51, 272 (1972).
13. Walker, P. L., Jr., Austin, L. G., and Nandi, S. P., *Chemistry and Physics of Carbon*, Vol. 2, Marcel Dekker, New York, 1960, pp. 257-371.
14. Jenkins, R. G., Nandi, S. P., and Walker, P. L., Jr., *Fuel*, 52, 288 (1973).

TABLE 1

ANALYSES OF COALS

PSOC Sample No.	ASTM Rank	State	Ash Content (Dry Basis) %	Ultimate Analysis (wt % daf)					Vitrinite Content Volume % (mmf)
				C	H	N	S	O (by diff)	
89	Lignite	N. Dakota	11.4	63.3	4.7	0.47	1.60	29.9	70.3
91	Lignite	Montana	7.9	70.7	4.9	0.81	0.41	23.2	66.4
87	Lignite	N. Dakota	7.0	71.2	5.3	0.56	0.70	22.2	64.7
138	Lignite	Texas	8.5	74.3	5.0	0.37	0.75	19.6	75.1
98	Sbb. A	Wyoming	6.6	74.3	5.8	1.20	1.30	17.4	84.6
101	Sbb.C	Wyoming	6.2	74.8	5.1	0.89	0.50	18.7	70.8
26	HVB	Illinois	9.6	77.3	5.6	1.10	7.50	8.5	89.2
22	HVC	Illinois	14.4	78.8	5.8	1.50	2.90	11.0	88.2
24	HVB	Illinois	11.6	80.1	5.5	1.10	4.50	8.8	88.1
105A	HVC	Indiana	7.5	81.3	5.8	1.10	1.80	10.0	62.5
171	HVA	W. Va.	7.2	82.3	5.7	1.40	3.40	7.2	71.1
4	HVA	Kentucky	1.7	83.8	5.8	1.60	0.88	7.9	67.4
114	LV	Pa.	10.5	88.2	4.8	1.20	0.68	5.1	89.6
127	LV	Pa.	5.0	89.6	5.0	1.00	0.83	3.6	77.7
81	Anthracite	Pa.	9.7	91.9	2.6	0.79	0.54	4.2	96.3
177	Anthracite	Pa.	4.0	93.5	2.7	0.25	0.70	2.9	86.5

TABLE 2

EFFECT OF PARTICLE SIZE ON REACTIVITY IN CARBON DIOXIDE

Mesh Size	Reactivity (mg hr ⁻¹ mg ⁻¹)		
	PSOC 87	PSOC 87 Dem.	PSOC 127 Dem.
40x100	2.7	0.23	0.02
100x150	4.8	0.65	0.29
200x325	7.4	1.1	0.69
-325	*	-	1.2

*Rate too rapid to measure.

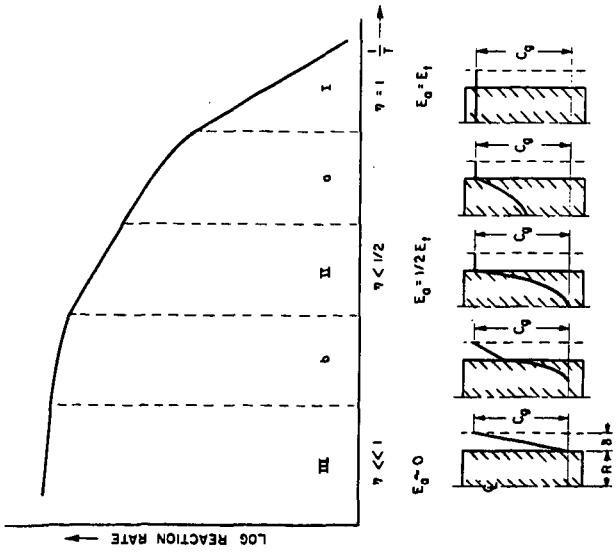


Figure 1 Ideally, the three zones representing the change of reaction rate of a porous carbon with temperature.

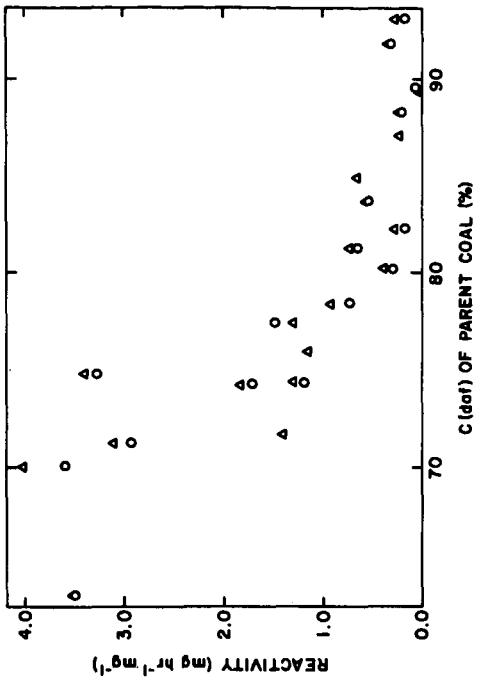


Figure 2 Variation of reactivity of 1000°C chars produced from coals of different rank. (○) CO₂ at 900°C, (△) air at 500°C.