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Reactivity of heat-treated coals in carbon dioxide at 900°C

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Reactivities of sixteen 40 x 100 (U.S.) mesh U.S. coals charred to 1000°C were measured in carbon dioxide at 900°C. Chars derived from coals with less than 80% carbon, on a dry-ash-free basis, were the most reactive. These chars also gave the widest spread in reactivity. Plots of inorganic element content in the chars versus reactivity showed that magnesium and calcium are important to char reactivity. Six coals were acid-washed with hydrochloric acid and four coals were further demineralized with hydrofluoric acid. Most acid-treated coals showed a decrease in reactivity; but two coals of high rank increased in reactivity. This increase in reactivity is attributed to the creation of additional porosity as a result of mineral matter removal and thus a reduction in resistance to carbon dioxide diffusion to reactive sites. Two demineralized and two original coals were divided into four size ranges and chars were produced from each size of each coal. Gasification rates increased monotonically with decreasing particle size reacted.

Increasing interest in coal gasification has brought about a need to understand coal char* reactivity better. Numerous reactivity studies have been conducted on coal, chars, and cokes and are well reviewed in the literature[1-5]. In the past, reactivity measurements have been used as an indication of the oxidation behaviour of carbonaceous solids. The aim of this investigation is to take a simple reactivity test developed by Jenkins et al[1] and to determine the effect of several physical and chemical variables on reactivity in a dry carbon dioxide atmosphere. Among the variables studied are rank of parent coal, mineral matter content, and particle size.

This investigation was made to further extend knowledge

*The word char is used throughout this paper to mean both coke and char

obtained by Jenkins et al[1]. The major difference in experimental operation from the previous study is the change in oxidant gas from air to carbon dioxide and a consequent change in reaction temperature from 500°C to 900°C.

EXPERIMENTAL

Char selection

In order to make a valid comparison with results obtained from the air reactivity study, a number of coals selected for that study were used. All the coals used in this study were rich in vitrinite. Table 1 presents analyses of the parent coals.

Table 1 Analysis of coals

PSOC Sample No.	ASTM Rank	State	Ash content (%, dry basis)	Ultimate analysis (wt %, daf)					Vitrinite content (vol.%, 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 bed weight on reactivity at 900°C for PSOC 91

Starting weight of char (mg)	Reactivity (mg h^{-1} mg^{-1})
.0·4	2·86
8·91	2·93
7·52	3·16
6·50	3·31
5·43	3·51
4·48	3·52
3·88	3·50
2·81	3·54

Char preparation

Most of the chars were available from the previous investigation. Methods of preparation used by Jenkins *et al* have been described previously[1]. For chars not available, a similar preparation method was used. A small quantity of coal (5–10 mg) was placed on the Cahn Model RG Electrobalance of a Fisher TGA apparatus and heated at a rate of 10°C/min to 1000°C. An inert atmosphere of nitrogen was passed over the sample while it was being heated. Samples were held at 1000°C until no further weight loss was detectable.

Selected coals were treated with warm 10% hydrochloric acid for 48 h, then washed with water, dried, and charred. Demineralized samples were prepared by taking acid-washed coals and treating them with warm hydrofluoric acid, followed by extensive washing and drying prior to charring.

Samples of PSOC 127, a relatively unreactive low-volatile ,al 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 40 × 100 U.S. 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, 100 × 150, 200 × 325, and −325 mesh. Chars were prepared and reactivities measured for all cuts.

Chemical analyses of char ash

Chemical analyses were made on samples of ashes by Jenkins *et al*[1]. Major elements were studied using atomic absorption following the procedures of Medlin *et al*[6]. Alkalies were estimated by flame photometry, and some data were taken from studies performed in this laboratory on mineral matter in American coals[7].

Temperature selection

Since the carbon–carbon dioxide reaction is a much slower reaction than the carbon–air reaction[8], 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 ʰich the rate of reaction of the more reactive lignites in .rbon dioxide corresponded closely to their reactivities in air at 500°C. Such a temperature was 900°C for the 40 × 100 mesh coal-derived chars.

Effect of starting bed weight on reactivity

To ensure that the effect of diffusion through the bed was negligible, a small weight of char was used. *Table 2* lists char reactivities of 40 × 100 mesh PSOC 91, a lignite, at various bed weights (or bed heights). For weights between about 2–6 mg, reactivity is constant, within experimental error, at a value of 3·5 mg h^{-1} mg^{-1}. Above 6 mg, reactivity decreases continually with increasing bed weight because of the increasing effect of diffusional resistance of carbon dioxide down through the bed on gasification rates. Thus, for this investigation reactivity measurements were made on char samples of less than 5 mg starting weight.

Reactivity measurements

Following preparation of a char at 1000°C, as previously described, it was cooled in a dry nitrogen atmosphere to 900°C prior to reaction. Chars were held at 900°C for 5–10 min to ensure thermal equilibrium. Then dry carbon dioxide was admitted at a flow rate of 300 cm^3 (NTP) per minute. The weight of the char was continuously recorded. In addition, by using a Cahn derivative computer accessory, the rate of weight loss was simultaneously recorded.

As with the air reaction, burn-off curves go through three regions of reactivity: purge and activation, rectilinear burn-off rate, and decreasing burn-off rate. During the middle region the char loses weight but increases in specific surface area because of activation. This region continues until the surface area no longer increases; gasification rate begins decreasing and the third region is entered. The rectilinear region for each coal varies in duration but in each case the rate in this period is measurable. It represents the maximum rate at which chars gasify, and involves much less than 1% of the carbon dioxide flow.

Reactivities of the chars were calculated following the procedure of Jenkins *et al*[1]. The following equation was used:

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

Table 3 Reactivities of coal chars

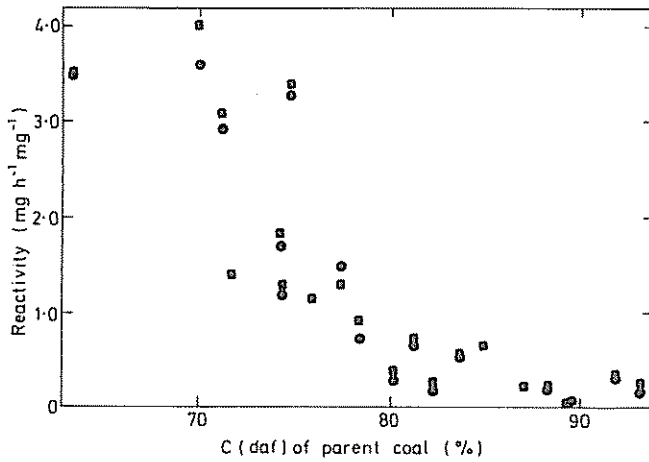| PSOC Sample No.	Maximum rate (mg h^{-1} mg^{-1})	
	Air, 500°C	CO_2, 900°C
89	3·5	3·6
91	4·0	3·5
87	2·9	2·7
138	1·3	1·2
98	1·8	1·7
101	3·4	3·3
26	1·3	1·5
22	0·94	0·66
24	0·38	0·36
105A	0·75	0·62
171	0·24	0·19
4	0·42	0·43
114	0·21	0·22
81	0·30	0·28
177	0·16	0·10

Figure 1 Variation of reactivity of 1000°C chars produced from coals of different rank.
● CO_2 at 900°C, ▣ air at 500°C

where R = reactivity of the char (mg h^{-1} mg^{-1}), W = weight of the initial char on ash-free basis (mg), and dW/dt = change in char weight with time (mg h^{-1}).

RESULTS AND DISCUSSION

Effect of coal rank

Reactivities for all coals charred to 1000°C are listed in *Table 3*. *Table 3* includes all data available for both the air and carbon dioxide reactivity studies for a particle size of 40 × 100 mesh. Generally the values for reactivities in air (500°C) and carbon dioxide (900°C) are similar. In *Figure 1* are plotted reactivity of the chars versus carbon content of the parent coals for both the carbon dioxide and air reactions. As for results for the air reaction, the lignites are the most reactive chars and have the widest spread of reactivity values. The lowest reactivity for both reactions was recorded for a char from LVB coal PSOC 127. For the carbon dioxide reaction this coal was over 150 times less reactive than was a highly reactive Montana 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[9] 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[10] and, hence, better utilization of the micropore surface area for reaction.

Effect of mineral matter on reactivity

Ash in the coals was studied by Jenkins *et al*[1]. The ash was analysed for K plus Na, Ca, Mg, and Fe. *Figure 2* shows plots of % impurity, calculated as weight % metal oxide in the char, versus char reactivity in both carbon dioxide and air. *Figure 2(a)* shows a reasonably good rectilinear correlation between Ca content and reactivity of the chars. *Figure 2(b)* is a plot of Mg content in the char versus char reactivity. Although only limited data exist at MgO contents greater than 1%, it appears that greater Mg contents have negligible effect on further increasing reactivity.

Figure 2(c) shows that there is no correlation between iron content and reactivity, and *Figure 2(d)* between total K and Na content and char reactivity. Separate K and Na content data were not available. Iron, K, and Na are expected to catalyse gasification reactions[11]. Lack of a correlation
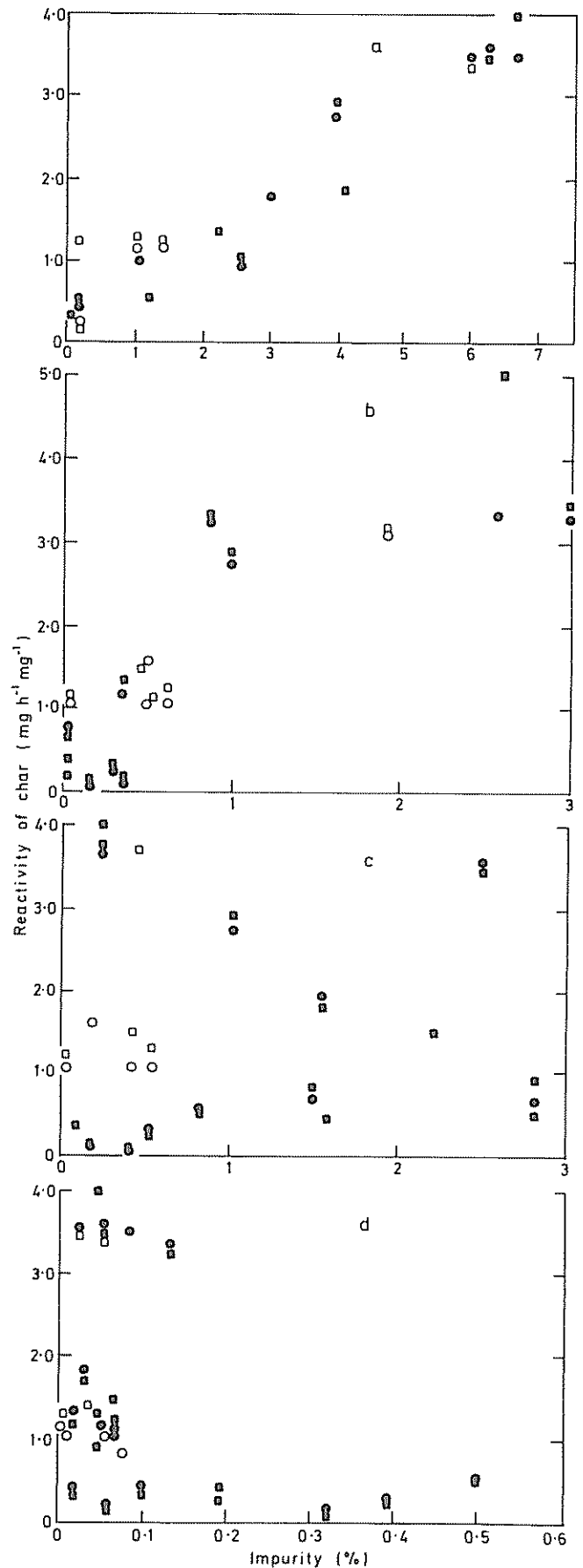

Figure 2 Plots of CO_2 and air reactivities of 1000°C chars versus percentages (by weight) of (a) CaO, (b) MgO, (c) Fe_2O_3, and (d) $K_2O + Na_2O$ present in the chars. Closed and open symbols represent chars from original and acid-washed coals respectively.
●○ CO_2 at 900°C, ▣▢ air at 500°C.

Table 4 Effect of particle size on reactivity in carbon dioxide

	Reactivity (mg h^{-1} mg^{-1})			
esh size	PSOC 87	PSOC 87 demin.	PSOC 127	PSOC 127 demin.
40 × 100	2·7	0·23	0·02	0·23
100 × 150	4·8	0·65	0·29	0·70
200 × 325	7·4	1·1	0·69	0·92
−325	*	−	1·2	−

*Rate too rapid to measure.

between K and Na content and char reactivity is perhaps due to the small amounts of K and Na present compared with Ca. As for the Fe, the state of the element during reaction is not known. This is important since Fe is a good catalyst for carbon gasification but the oxides are not[11]. It is expected that Fe would be oxidized to Fe_3O_4 in the presence of carbon dioxide at 900°C [11].

Effect of particle size on reactivity

Reactivity measurements were made in carbon dioxide on four particle sizes. Chars from original and demineralized samples of PSOC 127 and 87 were used in this study. Results are listed in *Table 4*. 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 to carbon dioxide penetrating into the interior of the particles. Whereas reduction in particle size of 'SOC 87 from 40 × 100 to 200 × 325 mesh results in a re-..ctivity 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 opposing balance of catalysis and mass-transport resistance respectively 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[10]. Introduction of additional feeder porosity by mineral-matter removal decreases mass transport resistance relatively

little compared to the effect of mineral-matter removal in 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 retardation of gasification. In this case the decrease in mass-transport resistance more than offsets the loss of catalytic activity due to mineral-matter removal.

CONCLUSIONS

Conclusions reached by Jenkins *et al*[1] were confirmed by this investigation. Namely: (1) reactivity of chars to carbon dioxide decreases with increase in rank of the parent coal; (2) impurities affect reactivity, magnesium and calcium appearing particularly to increase it; and (3) resistance to diffusion of the reactant gas into the char particles can have a significant effect in retarding char gasification. Diffusional resistance can be reduced by reduction in the particle size of the char to be gasified.

ACKNOWLEDGEMENTS

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