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Published by IPC Science and Technology Press Ltd

Reactivity of heat-treated coals in air at 500°C

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(Received 16 January 1973)

Twenty one US coals, of widely ranging rank, have been carbonized under controlled conditions to 1000°C, and the reactivity in air at 500°C of the resulting chars or cokes has been measured by a gravimetric method. The reactivities lie within a well-defined band when plotted against rank of the parent coal. The lower-rank coal chars are more reactive than those prepared from high-rank coals. In extreme cases, the reactivity found for a Montana lignite char is some 100 times as great as that obtained for a char produced from a Pennsylvania low-volatile coal. Variation of reactivity with heat-treatment temperature (600 to 1000°C) has been studied for three coals. As heat-treatment temperature increases, there is a decrease in reactivity. Some results are reported on the effects which mineral matter and pore structure have on the reactivity parameter. Chars containing high concentrations of magnesium and calcium impurities are most reactive. The amount of macro and transitional porosity in a char has a marked influence on reactivity.

It has become evident that there is a need for a better understanding of coal-char reactivity. In the past there have been numerous reactivity studies on coals, cokes and chars, which are well reviewed in the literature[1–4]. It has been stated that char reactivity measurements have no precise meaning; however, they can be used as an indication of the oxidation behaviour of carbonaceous solids[1,5]. The aims of this investigation were to develop a simple reactivity test, to use this test systematically on a wide range of coal chars*, and to obtain some measure of the variables which affect it. Since reactivity is affected by both chemical and physical properties of chars, the variables chosen for investigation were the rank of the parent coal, heat-treatment temperature, pore structure, and mineral-matter composition.

Dried air was selected as the oxidizing gas. A gravimetric procedure, using an electronic microbalance, was chosen because it can both directly and accurately record small weight changes with time, and because the determination is not subject to errors in gas analysis[6].

Although this investigation is, in part, semi-quantitative, it is suggested that its findings will help in the understanding of some of the factors that affect coal gasification.

EXPERIMENTAL

Char preparation

The coals chosen were selected because of their wide variation in rank, type and location (see *Table 1*). All but one of these coals were rich in vitrinite. The exception was PSOC-6, which has a comparatively high concentration of exinite.

Two methods of char preparation were used. The first method, which utilized a Fisher T.G.A. apparatus, was used to prepare small quantities of all samples and to obtain thermogravimetric data for the coals. The Fisher T.G.A. apparatus enables continuous weight measurements to be made on a sample whilst it undergoes thermal treatment in a flowing controlled atmosphere. A small amount of sample is placed in a weighing pan and suspended from a recording Cahn Model RG Electrobalance. A furnace, which is controlled by a temperature programmer, is placed around the sample pan. Specifically, the preparation technique involved heating about 30 mg (40 × 100 US mesh) of coal in a stream of dry nitrogen in the T.G.A. apparatus to some maximum temperature at a constant heating rate of 10°C min^{-1}. It was then held at that temperature for about 2 h, or until no further weight loss was observed. The other preparative technique was used on some of the coals to produce larger amounts of char (10–20 g) so that porosity and surface-area determinations could be made. A 1¼ in* diameter fluidized-bed system was utilized for the preparation of these bulk samples. As in the micropreparation technique, dry nitrogen was used as the inert atmosphere and the controlled heating rate was similar.

As a part of the investigation into the effect of mineral matter on reactivity, some of the coals were treated with warm 10% hydrochloric acid for 48 h. The 'acid-washed' coals were then washed with water and finally dried. A few samples were further treated with warm hydrofluoric acid in an attempt to demineralize them more completely. These treated coals were subsequently carbonized.

Measurement of reactivity

The Fisher T.G.A. apparatus was also used for measurement of reactivity. About 5–10 mg (40 × 100 mesh US) of char was placed in the T.G.A. pan and heated at 10°C

* Strictly speaking, thermal treatment of the coals led to either a char or a coke. If upon heating the organic precursor goes through a liquid state the resulting solid is termed a coke. If however negligible softening occurs, the resulting solid is termed a char. For convenience, we have used the term char throughout this paper.

* 1 in = 25·4 mm

Table 1 Analyses of coals

Sample No.	ASTM rank	State	Ash (%, dry basis)	Ultimate analysis (wt %, daf)					Vitrinite content (volume %, mmf)
				C	H	N	S	O (by diff)	
PSOC-89	Lignite	N. Dakota	11·4	63·3	4·7	0·47	1·60	29·9	70·3
PSOC-91	Lignite	Montana	7·9	70·7	4·9	0·81	0·41	23·2	66·4
PSOC-87	Lignite	N. Dakota	7·0	71·2	5·3	0·56	0·70	22·2	64·7
PSOC-140	Lignite	Texas	10·2	71·7	5·2	1·30	1·10	20·7	69·8
PSOC-138	Lignite	Texas	8·5	74·3	5·0	0·37	0·75	19·6	75·1
PSOC-98	Sbb. A	Wyoming	6·6	74·3	5·8	1·20	1·30	17·4	84·6
PSOC-101	Sbb. C	Wyoming	6·2	74·8	5·1	0·89	0·50	18·7	70·8
PSOC-189	HVC	Illinois	12·5	76·0	5·7	1·00	5·50	11·8	78·0
PSOC-26	HVB	Illinois	9·6	77·3	5·6	1·10	7·50	8·5	89·2
PSOC-22	HVC	Illinois	14·4	78·8	5·8	1·50	2·90	11·0	88·2
PSOC-24	HVB	Illinois	11·6	80·1	5·5	1·10	4·50	8·8	88·1
PSOC-67	HVB	Utah	4·9	80·4	5·8	1·20	1·50	11·1	82·9
PSOC-105A	HVC	Indiana	7·5	81·3	5·8	1·10	1·80	10·0	62·5
PSOC-171	HVA	W. Va.	7·2	82·3	5·7	1·40	3·40	7·2	71·1
PSOC-4	HVA	Kentucky	1·7	83·8	5·8	1·60	0·88	7·9	67·4
PSOC-6	HVA	Kentucky	4·2	84·9	5·6	1·30	0·69	7·5	27·8*
PSOC-137	MV	Alabama	7·1	87·0	4·8	1·50	3·10	3·6	73·8
PSOC-114	LV	Pa.	10·5	88·2	4·8	1·20	0·68	5·1	89·6
PSOC-127	LV	Pa.	5·0	89·6	5·0	1·00	0·83	3·6	77·7
PSOC-81	Anthracite	Pa.	9·7	91·9	2·6	0·79	0·54	4·2	96·3
PSOC-177	Anthracite	Pa.	4·0	93·5	2·7	0·25	0·70	2·9	86·5

* Coal PSOC-6 contains 37·0% exinite by volume (mmf)

h^{-1} to 500°C in dry nitrogen. After a period of about 30 min (thus ensuring thermal stability) a stream of dry air (500 cm^3 min^{-1}) was admitted to the apparatus. The weight of the sample was then continuously recorded. In addition, by using a Cahn derivative computer accessory, it was possible to record simultaneously the first derivative of weight change with time ($dw/d\theta$). A small initial weight of char was used to ensure that the bed temperature did not rise appreciably and that the bed was very thin (≈1 mm), hence minimizing bulk diffusional effects. *Figure 1* is a typical reactivity plot, where the burn-off is calculated on the basis of the whole char, that is on an ash-containing basis. Under the conditions selected the burn-off plots for every char had a rectilinear portion, which usually extended over a period in which about 40% of the material was gasified. In this rectilinear region maximum reactivity was observed, and it was from this portion of the plots that the reactivity parameter was calculated by the following equation:

$$R_T = -\frac{1}{w}\left(\frac{dw}{d\theta}\right)$$

where R_T is the maximum reactivity at a temperature T°C (mg h^{-1} mg^{-1}), w is the initial mass of char (mg), on an ash-free basis, and $dw/d\theta$ is the maximum rectilinear weight loss rate (mg h^{-1}).

Inspection of *Figure 1* indicates that there are three distinct regions in the burn-off curve. In the first region, ... the reaction rate increases slowly, three processes take place: (1) the system is purged of nitrogen; (2) there is a buildup of oxygen complexes on the char's surface; and

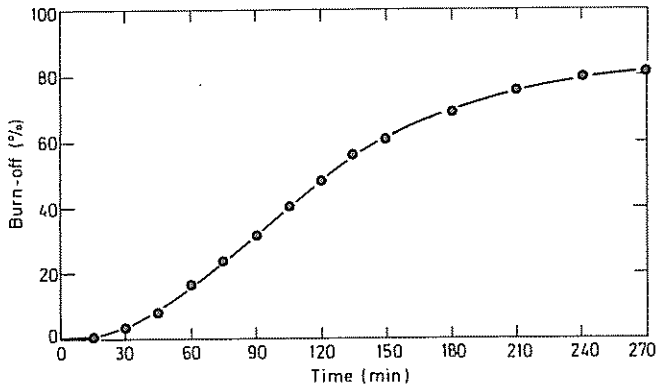

Figure 1 Burn-off curve (on ash-containing basis) in air at 500°C for 1000°C char from PSOC-24

(3) the char undergoes activation, which leads to the increased rate. This region is followed by a period in which increase in the burn-off is directly proportional to the increase in time, indicating a zero-order reaction. As activation proceeds, the surface area per unit weight increases up to some maximum value; but offsetting this there is a corresponding weight decrease. Hence a constant effective active-site concentration is maintained. The third region occurs, in this case after about 130 min, when the surface area per unit weight starts decreasing, thereby leading to a reduced rate.

Porosity and surface-area measurement

Techniques used in this part of the investigation are described in more detail elsewhere[7]. Surface areas were estimated by adsorption of carbon dioxide at 298 K (using the Dubinin–Polanyi approach) and by nitrogen at 77 K (using the BET approach). Densities of the chars were measured by the displacement of both helium and mercury, and from these data total pore volumes were calculated. It is generally accepted that for coals and chars the surface area accessible to nitrogen at 77 K is to some degree a measure of the macro and transitional pores[7]. These pores, in processes which involve mass transport, act as 'feeder' pores for reactant gases. Their distribution determines the ease with which a reactant can enter the microporous substructure of the solid, where reaction predominantly occurs. Carbon-dioxide adsorption at 298 K is used to estimate specific surface area in the micropores[8], which for coals closely approximates the total surface area.

Chemical analyses of char ash

Chemical analyses were made on samples of ash obtained by heating the coals in air to 600°C. Determination of major elements was performed using an atomic absorption technique, following procedures of Medlin *et al*[9]. Alkalies were estimated by flame photometry. Some of the data used in this investigation were taken from studies of mineral matter in US coals performed in this laboratory[10].

RESULTS AND DISCUSSION

Effect of rank on reactivity

Some 21 coals were heat-treated to 1000°C and the reactivities of the resulting chars measured. *Table 2* lists the values obtained for the reactivity parameter for each 1000°C char. Multiple determinations were made on eight of the 1000°C char samples (those from PSOC-89, -91, -140, -138, -101, -24, -171, -81). The results were found to be reproducible within a maximum spread of ±5%. The lower-rank coal chars were found to be the most reactive, confirming Blayden's observation[1]. However, there is quite a spread of values for these low-rank chars; for example, the reactivity of the Montana lignite char (PSOC-91) is three times as great as that found for the Texas lignite char (PSOC-138). In general, coals of over 80% carbon content (w/w) produce chars or cokes which are much less reactive; in the extreme case the char from a low-volatile Pennsylvania bituminous coal (PSOC-127) is some 100 times less reactive to air than the Montana lignite char (PSOC-91). A plot of reactivity versus carbon content (wt% daf) of the parent coal (*Figure 2*) shows that they lie within a fairly well-defined band, the spread being most marked for the lignites.

Table 2 Reactivities in air of 1000°C chars

Parent coal PSOC	Max. rate at 500°C ($mg\,h^{-1}\,mg^{-1}$)
89	3·5
91	4·0
87	2·9
140	1·4
138	1·3
98	1·8
101	3·4
189	1·2
26	1·3
22	0·94
24	0·38
67	0·46
105A	0·75
171	0·24
4	0·42
6	0·59
137	0·23
114	0·21
127	0·04
81	0·30
177	0·16

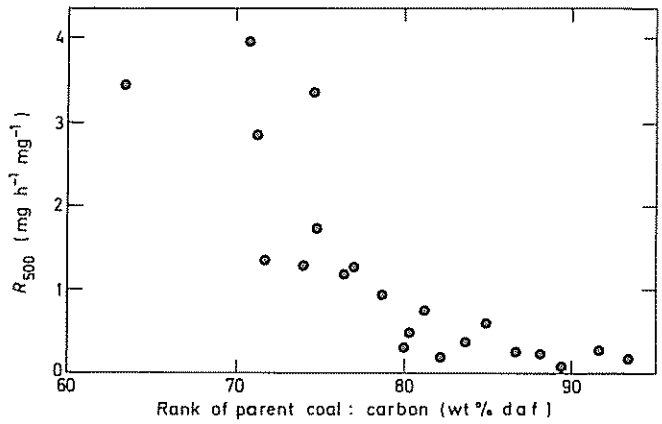

Figure 2 Variation of reactivity in air of 1000°C chars produced from coals of different ranks

Effect of mineral matter on reactivity

The coal ashes were analysed for K, Na, Ca, Fe, and Mg. *Figures 3a* to *3d* are plots of the concentrations of these elements, expressed as weight percent of oxide in the char, versus measured reactivities. From these plots it appears that there are relations between reactivity and the amounts of magnesium and calcium oxides present in the chars. To generalize, the most reactive chars are those which contain the highest amounts of calcium and magnesium. From these results, no such relations are evident for the other three elements (potassium, sodium and iron). However, it is well known that these elements do have high catalytic activities with respect to carbon oxidation[11]. It is suggested that these results reflect the distributions and concentrations of these catalysts throughout the chars. If a catalyst is well distributed, then its apparent activity is enhanced; however, if it is concentrated in large agglomerates, its activity will be restricted. It is not possible to determine, from these data, in what state the elements exist in the chars. For example, if iron is in its elemental state then it will be a very effective catalyst; but if it is present as oxide its activity is much reduced[11]. In addition, it will be noted that for most of the samples under investigation the combined levels of sodium and potassium are low. It is probably for these reasons that there are no apparent relations between reactivity and the concentration of these elements.

Five of the lower-rank coals were acid-washed with hydrochloric acid and three coals were demineralized in hydro-

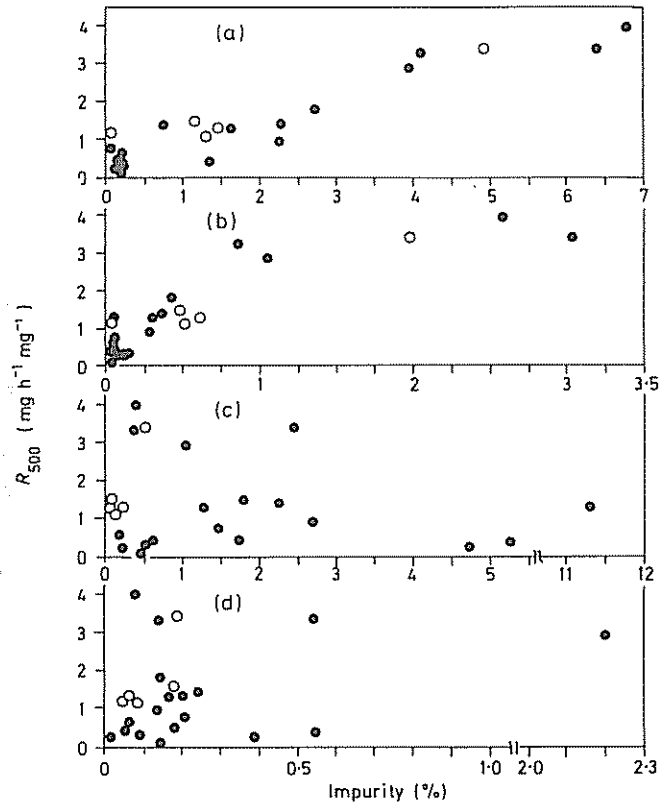

Figure 3 Plots of air reactivity of 1000°C chars *v*. percentages (by weight) of: (a) CaO, (b) MgO, (c) Fe_2O_3, and (d) K_2O + Na_2O present in the chars
● chars from original coals, ○ chars from acid-washed coals

fluoric acid. Chars were prepared at 1000°C from these treated coals. *Table 3* lists the reactivities of these chars. Three of the chars derived from acid-washed coals show a considerable reactivity decrease. This is especially seen for PSOC-91, where a four-fold decrease in reactivity is reported. However, reactivities of PSOC-138 and PSOC-89 chars show little change. It is interesting to note that the values of reactivity for all but one of the acid-washed coal chars are similar, whereas the values for the coal chars are widely different. *Table 3* also lists the concentrations of calcium and magnesium for the acid-washed samples. In all cases the concentrations have been reduced by the treatment. But in the case of 'acid-washed' PSOC-89, there are comparatively large residual amounts of calcium and magnesium; and it is suggested, therefore, that the partial removal by the acid has been insufficient in reducing the catalytic effect of these two elements. For three of the samples (PSOC-91, PSOC-87, and PSOC-101), the reduction would appear to have brought about reduced reactivity. In the case of PSOC-138, lowering of the concentrations of these two impurities has not resulted in a decreased reactivity. It would seem that some limiting value of reactivity has been reached because of the combined effect of all the impurities remaining in the sample. All the values obtained for these acid-washed coal chars are also plotted in *Figure 3*, and it can be seen that for the calcium and magnesium concentrations they fall within the general relations observed with the other coal chars.

Almost complete demineralization of the coals, using hydrofluoric acid, can have an even more drastic effect. It has brought about a ten-fold decrease in the reactivity of the char of the lignite PSOC-87. However, demineralization of the anthracite has had only a marginal effect in decreasing reactivity. Further, the reactivity for treated LV bituminous coal PSOC-127 shows an increase. These results show the complexity involved in understanding reactivity data. For PSOC-127, it is suggested that the additional porosity produced by mineral-matter removal, with the resultant increasing ease of accessibility of oxygen into the pore structure, more than offsets a reduction in catalytic activity. That is, LV bituminous coals have a particularly small percentage of their total accessible pore volume in macropores and transitional pores (the 'feeder' pores)[7] and, hence, are particularly affected by the introduction of 'feeder' pores through mineral-matter removal. A similar effect was noted in a previous study on chlorinated anthracite chars[12]. The chlorinated chars had enhanced reactivity in carbon dioxide and steam.

Effect of heat-treatment temperature on reactivity

Three coals were selected for this study, namely PSOC-138 (lignite), PSOC-24 (HVB), and PSOC-171 (HVA).

Table 3 Reactivities in air of chars prepared at 1000°C from acid-treated coals

Parent coal PSOC	Type	Ash (%)	R_{500} (mg h^{-1} mg^{-1})	CaO in char (Wt %)	MgO in char (Wt %)
89	Lignite	11·4	3·5	6·4	3·0
Acid-washed 89		7·5	3·4	4·9	1·9
91	Lignite	7·9	4·0	6·8	2·6
Acid-washed 91		2·7	1·1	1·3	0·52
87	Lignite	7·0	2·9	3·9	1·0
Acid-washed 87		3·2	1·3	1·4	0·61
Demin. 87		<1	0·27	–	–
138	Lignite	8·5	1·3	1·6	0·31
Acid-washed 138		5·1	1·1	0·05	0·03
101	Sbb. C	6·2	3·4	4·1	0·86
Acid-washed 101		2·5	1·5	1·1	0·47
127	LV	5·0	0·04	–	–
De 127		1·4	0·12	–	–
81	Anthracite	9·7	0·30	–	–
Demin. 81		<1	0·23	–	–

Table 4 Volatile matter remaining in chars from heated coals at different heat-treatment temperatures

Heat-treatment temperature (°C)	% of total VM remaining		
	PSOC-138	PSOC-24	PSOC-171
600	25·0	25·0	15·5
700	14·0	12·2	6·8
800	6·5	5·5	2·5
900	2·7	1·6	1·1

They were heated in nitrogen at temperatures of 600, 700, 800, 900, as well as 1000°C, prior to studying their reactivity in air at 500°C. Assuming that the samples lost all their moisture by 135°C, their total volatile matters were equated to the total weight losses measured when the coals were heated between 135 and 1000°C. VM values for coals PSOC-138, PSOC-24, and PSOC-171 were 46·5%, 35·2%, and 38·9%, respectively. In *Table 4*, percentages of the total volatile matter remaining at each heat treatment are given.

It is known that disordered carbons, in general, become less reactive as heat-treatment temperature is increased[13]. The results of this study, shown in *Figure 4*, confirm this observation. Results for the lignite char show that reactivity is particularly sensitive to the preparation temperature: the 700°C char is about twice as reactive as the 800°C char. It was found impracticable to obtain a reliable result for a 600°C char from this lignite because it was extremely reactive in air at 500°C and did not show a rectilinear reactivity region in the burn-off curve. Inspection of *Figure 4* shows that the other coal chars follow a trend similar to that of the lignite series, the change of reactivity with preparation temperature being marked.

Table 5 summarizes the results obtained for three chars prepared in the fluidized bed. Agreement of reactivities of these chars with reactivities of chars prepared in the T.G.A. apparatus is remarkably good. These bulk samples prepared in the fluidized bed were then used for measurements of porosity and surface area.

Inspection of the results of the pore structure determinations (*Table 6*) shows the great effect that 'feeder' pores (estimated from nitrogen adsorption) have on reactivity. In the highly reactive lignite chars (PSOC-138), the nitrogen surface area is markedly developed to a maximum at 600°C and then declines to a value of 13 $m^2 g^{-1}$ for the 1000°C char. However, for the less reactive HVA coal chars (PSOC-171) there is only a slight development of nitrogen surface area, again showing a maximum at 600°C, followed

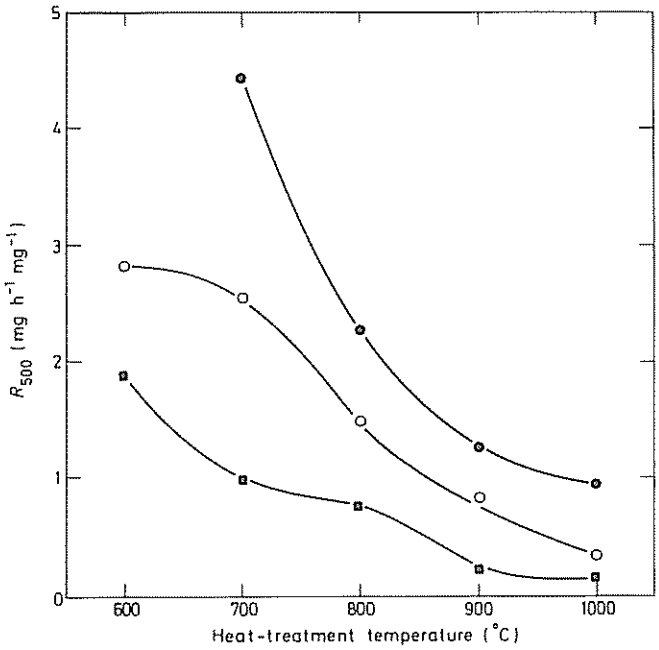

Figure 4 Effect of temperature of heat treatment of selected chars on their air reactivity
● PSOC-138, ○ PSOC-24, ■ PSOC-171

by a decrease to a small value at 900°C. The carbon-dioxide surface areas show that the lignite char contains more micropores in which the gasification reactions can take place. These correlations are further substantiated by the differences in total pore volumes. At any heat-treatment temperature, the total pore volume of a lignite char is considerably higher than that for a corresponding HVA coal char. The values of nitrogen surface area and total pore volume for the chars of PSOC-24, which has an intermediate reactivity, lie between those of the other two coal-char series.

Of course, as seen from the volatile-matter results presented in *Table 4*, the chemical nature of the char surface continuously changes with changing carbonization temperature. That is, with increasing temperature the volatile matter yield continuously decreases, and hence the fraction of the surface which is represented by carbon atoms should increase. Snow and co-workers[14], studying the influence of hydrogen content on oxidation of carbon blacks, noted that the reactivity to oxygen depended on hydrogen content. The higher the hydrogen content, the higher was the reactivity. Further, they noted that the C/H

Table 5 Reactivity in air at 500°C of chars prepared from selected coals at different temperatures

Coal	Char preparation method	R_{500} for chars prepared at T°C (mg h^{-1} mg^{-1})				
		600	700	800	900	1000
PSOC-138	Static bed	—	4·7	2·4	1·4	1·2
PSOC-138	Fluidized bed	—	4·5	2·3	1·4	1·0
PSOC-24	Static bed	3·1	2·5	1·5	0·90	0·38
PSOC-24	Fluidized bed	2·8	2·6	1·6	0·95	0·46
PSOC-171	Static bed	—	1·1	0·80	0·29	0·24
PSOC-171	Fluidized bed	2·0	1·0	0·84	0·31	0·24

Table 6 Physical properties of coals and chars

Temperature of heat treatment (°C)	N_2 surface area, dry basis ($m^2 g^{-1}$)	CO_2 surface area, dry basis ($m^2 g^{-1}$)	Total open pore volume, dry basis ($cm^3 g^{-1}$)
	PSOC-138 (lignite)		
None	2·2	225	–
500	106	438	0·244
600	266	670	0·234
700	107	633	0·300
800	116	606	0·300
900	113	680	0·308
1000	13	528	0·296
	PSOC-24 (HVB)		
None	2·2	228	–
500	5·7	364	0·238
600	29	604	0·219
700	31	615	0·200
800	22	687	0·187
900	8·1	416	0·187
	PSOC-171 (HVA)		
None	<1·0	185	–
600	1·5	400	0·150
700	1·0	400	0·145
800	0·8	196	0·155
900	0·5	38	0·133

ratio of the residue increased sharply with increasing burn-off of the sample, suggesting that the hydrogen was being preferentially oxidized relatively to carbon. We suggest that in our studies a similar phenomenon is occurring and that this can be, at least in part, responsible for the reactivity results. That is, hydrogen removal by oxidation leaves nascent carbon sites behind which are, by definition, more reactive to oxygen. That nascent sites of high reactivity can be produced by the removal of complexes from carbon surfaces has been shown previously in this laboratory. For example, the carbon–carbon dioxide reaction rate is enhanced in the presence of a significant thermal desorption of carbon monoxide from the carbon surface[15].

CONCLUSIONS

The reactivities of chars produced under the same conditions of temperature and heating rate are predominantly determined by mineral-matter composition and rank of the parent coal. In general, coals of under 80 wt% (daf) carbon content produce the most reactive chars. The wide spread of values obtained for the lower-rank coals is thought to be due, in part, to the differences in mineral-matter content. Coals with high magnesium and calcium levels are highly reactive. Partial removal by acid washing can reduce the concentrations of these catalysts, resulting in reduced reactivity.

It has been shown that the level of macro and transitional porosity markedly affects reactivity. Chars which contain a large proportion of these 'feeder' pores are highly reactive since the ability of a reactant gas to diffuse into the internal surface of the micropores is enhanced.

The temperature of preparation is important in determining reactivity for any one series of chars prepared from the same coal. In this case it is suggested that the combination of pore structure and chemical nature of the char are governing factors. As heat-treatment temperature is increased up to about 600°C, there is an increasing development of porosity. Further heating (above 600°C) results in a decrease in concentration of feeder pores and a simultaneous degradation of reactive chemical structures (e.g. involving hydrogen), resulting in a progressive decrease in reactivity.

None of the variables occurs in isolation; the reactivity of a char is determined by a combination of all the effects. For example, the open pore structure of a lignite char makes it relatively easy for a reactant gas to diffuse to the surface which contains a comparatively high concentration of chemically reactive groups. At the surface the reaction is catalysed by the mineral matter. In the chars of higher-rank coals, the concentrations of feeder pores and the more reactive sites on the surface are much lower than in lignite, resulting in a substantially lower reactivity.

ACKNOWLEDGMENTS

This research was supported by the US Office of Coal Research on Contract No. 14-01-0001-390. The chemical analysis of the char ash was performed by N. Suhr of the Mineral Constitution Laboratories, The Pennsylvania State University. Professor W. Spackman, Jr supplied the coals studied.

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