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Low-temperature air oxidation of caking coals.
1. Effect on subsequent reactivity of chars produced

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(Received 1 March 1979)

The effect of preoxidation of two highly caking coals in the temperature range 120–250°C on weight
loss during pyrolysis in a N_2 atmosphere up to 1000°C and reactivity of the resultant chars in 0.1 MPa
air at 470°C has been investigated. Preoxidation markedly enhances char reactivity (by a factor of up
to 40); the effect on char reactivity is more pronounced for lower levels of preoxidation. For a given
level of preoxidation, the oxidation temperature and the presence of water vapour in the air used dur-
ing preoxidation have essentially no effect on weight loss during pyrolysis and char reactivity. An in-
crease in particle size of the caking coals reduces the rate of preoxidation as well as subsequent char
reactivity. Preoxidation of caking coals sharply increases the surface area of the chars produced.
Compared to heat treatment in a N_2 atmosphere, pyrolysis in H_2 of either the as-received or preoxi-
dized coal results in a further increase in weight loss and a decrease in subsequent char reactivity.

It is established that caking coals, that is, coals in the range
between low-volatile bituminous and hvb bituminous, are
usually undesirable precursors for gasification and combus-
tion. Upon heating to 350–450°C, these coals cake and/or
swell to such a degree as to interfere with passage of reac-
tant gas through the reactor, thereby affecting the ease of
gasification and combustion. Caking coals are converted
from thermoplastic to thermosetting precursors by their
preoxidation in air at temperatures below 400°C. Such pre-
oxidation introduces oxygen into the coal and acts to cross-
link the aromatic and hydroaromatic building blocks.

Although the effect of preoxidation of caking coals on
their subsequent fluidity and dilatation upon heating has
been reported[1,2], the possible effect of this preoxidation on
subsequent reactivity of the resultant char appears to have
been ignored. The present communication describes the
results of such a study. The effect of different levels of pre-
oxidation of two highly-caking coals on weight loss during
pyrolysis up to 1000°C and reactivity of the resultant chars
to air at 470°C has been investigated. The other variables
chosen for this study were: particle size of the coal precur-
sor, preoxidation temperature, and presence of water vapour
in the air used for preoxidation. In a few cases, the effect
of preoxidation of the coals on surface area of the chars
produced has also been examined. Prior to hydropyrolysis,
caking coals are frequently preoxidized in air. Thus, the
effect of preoxidation of a caking coal followed by hydro-
pyrolysis on subsequent reactivity of the char to air has also
been examined.

EXPERIMENTAL

Coals studied

Two highly caking coals, PSOC-127 (low-volatile bitu-
minous) and PSOC-337 (hva bituminous), having free swell-

ing indices of nine and eight respectively, were used in the
present study. The proximate and ultimate analyses of the
–60 US mesh fraction of the coals are given in *Table 1*. The
–20 mesh fractions of the two coals (which had been stored
in sealed containers under N_2) were ground and sieved in a
glove bpx in a N_2 atmosphere. The 40 × 70 and 200 × 250 US
mesh fractions, held under N_2 until used, were selected for
this study. These fractions of PSOC-337 coal had ash con-
tents of 7.9 and 9.6 wt % (dry basis), respectively. The
corresponding ash levels of the PSOC-127 coal fractions
were 3.7 and 3.8 wt % respectively.

*Measurement of weight changes during preoxidation, pyro-
lysis and gasification*

Weight changes were measured gravimetrically using a
DuPont 951 TGA system in conjunction with a 990 Ther-

Table 1 Proximate and ultimate analyses of raw coals

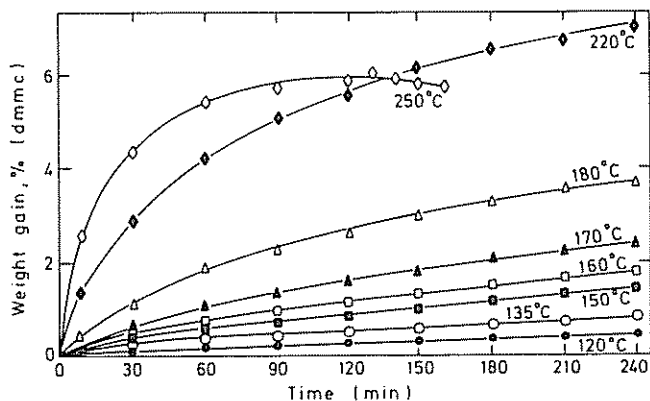| Constituent	Wt %	
Proximate analysis		
	PSOC-337	PSOC-127
Ash (dry basis)	8.5	5.7
Volatile matter (daf)	38.2	20.6
Fixed carbon (daf)	61.8	79.4
Ultimate analysis (daf)		
	PSOC-337	PSOC-127
C	84.9	89.6
H	5.8	5.0
N	1.6	1.0
S (Organic)	0.70	0.52
O (by difference)	7.0	3.9

Figure 1 Weight gain of PSOC-337 coal (220 x 250 mesh) during preoxidation at different temperatures as a function of time. ⊖, 120°C; ○, 135°C; ▣, 150°C; □, 160°C; ▲, 170°C; △, 180°C; ◆, 220°C; ◇, 250°C

mal Analyzer. In a typical run, about 6 mg coal were taken in a platinum pan. The TGA system was flushed with ultra high purity grade N_2 (100 cm^3/min) for 20 min to displace air. The sample was then heated to the desired preoxidation temperature. When the sample attained a constant weight, N_2 was replaced by air at the same flow rate. Progress of the oxidation process (as measured by weight increase) was followed for a desired period of time. After this, air was replaced by N_2 or H_2 and the sample heated up to 1000°C at a heating rate of 10°C/min. Soak time at 1000°C was 1 h. During the heat treatment, the sample weight was monitored continuously. When calculating the per cent weight loss during pyrolysis of the oxidized sample, the weight of the coal following preoxidation was taken as the initial weight. After heat treatment in N_2 or H_2, the sample was cooled in the same atmosphere to 470°C. This temperature was kept constant for 1 h after which the atmosphere was replaced by air at the same flow rate. The extent of gasification was followed as a function of time. Throughout this study, weight changes occurring during preoxidation, pyrolysis and gasification have been expressed on a dry-mineral-matter-containing (dmmc) basis.

We have recently suggested that a suitable parameter to express the reactivity of a char during gasification is $t_{0.5}$, that is the time corresponding to a fractional burn-off of 0.5 [3]. Therefore, in the present study we have used this criterion.

For measurement of surface areas of chars, relatively larger quantities (about 1 g) of samples are needed. Since these amounts cannot be handled in a conventional TGA unit, an alternate experimental approach was used to prepare the chars. About 2 g of coal were spread uniformly in a ceramic boat which in turn was placed in a horizontal tube furnace with a sufficiently long constant temperature zone. Preoxidation, pyrolysis and gasification were carried out under conditions simulating those in the TGA runs.

Surface area

Total surface area of chars was determined from CO_2 adsorption at 25°C using the Polanyi–Dubinin equation[4]. Prior to making an adsorption run, samples were outgassed at 500°C for 16 h at a pressure of 1.3 x 10^{-3} Pa. For each adsorption point on the isotherm, an arbitrary adsorption time of 30 min was allowed. Surface areas of chars have been expressed on a dmmc basis.

RESULTS

Weight change during preoxidation

The extent of weight gain during preoxidation of the 200 x 250 US mesh fraction of PSOC-337 coal at different temperatures when oxidation is carried out for a maximum of 4 h (except at 250°C) is shown graphically in *Figure 1*. At 250°C, weight increase attains a maximum value in about 2 h; thereafter a slow, continual decrease in weight is observed.

Effect of preoxidation on weight loss during pyrolysis

Weight loss during pyrolysis of as-received (i.e. unoxidized) PSOC-337 coal and selected preoxidized samples prepared therefrom are plotted as a function of temperature in *Figure 2*. It is seen that oxidative treatment at different temperatures has little or no effect on weight loss up to about 450°C. Preoxidation to a weight gain of 0.45% has essentially no effect on the devolatilization behaviour of the coal up to 1000°C. However, with further increase in the extent of preoxidation, weight loss above 450°C decreases progressively.

PSOC-127 coal (200 x 250 mesh) was oxidized in air to different levels of weight gain (up to a maximum of 4.5 wt %) in the temperature range 180–250°C (*Table 2*). For reasons to be discussed later, arbitrary oxidation temperatures were used in this case to attain the desired level of preoxidation. The effect of preoxidation on weight loss during pyrolysis of selected PSOC-127 samples is shown graphically in *Figure 3*. In contrast to the results for PSOC-337 samples, oxidation of PSOC-127 coal increases the weight loss during pyrolysis up to about 500°C. At higher temperatures, weight losses for the oxidized samples show a random variation with respect to those for the as-received sample.
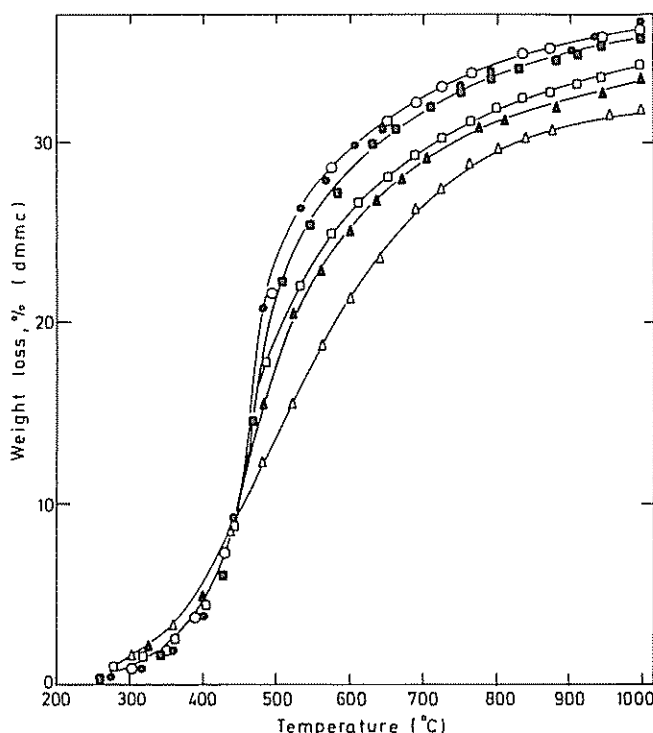

Figure 2 Effect of preoxidation on weight loss during pyrolysis of PSOC-337 coal (200 x 250 mesh). Weight gain during preoxidation (%, dmmc): ⊖, none; ○, 0.45; ▣, 0.75; □, 1.4; ▲, 2.4; △, 7.0

Table 2 Effect of preoxidation of PSOC-127 coal on char reactivity

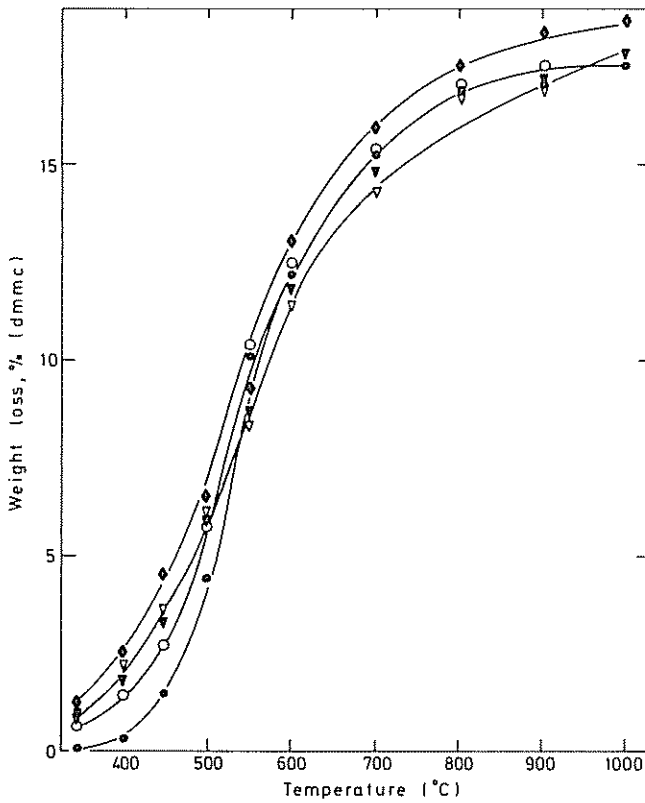| Preoxidation temp. (°C)	Preoxidation time (min)	Weight increase during preoxidation (wt %, dmmc)	$t_{0.5}$ (min)
None	—	0	2040
180	62	0.45	690
180	120	0.66	129
200	118	1.4	65
220	90	1.9	57
250	37	3.0	53
250	65	4.5	52

Figure 3 Effect of preoxidation on weight loss during pyrolysis of PSOC-127 coal (200 x 250 mesh). Weight gain during preoxidation (%, dmmc): ●, none; ○, 0.45; ▼, 1.9; ▽, 3.0; ◆, 4.5

Effect of preoxidation on char reactivity

Burn-off versus time plots for various PSOC-337 and PSOC-127 char samples reacted in 0.1 MPa air at 470°C are plotted in *Figures 4* and *5*, respectively. Burn-off plots for the chars produced from the as-received PSOC-127 coal and the coal preoxidized to a weight gain of 0.45% appear to be of different shape than those of the other samples (*Figure 5*). This is an apparent effect because when the two curves are plotted on an extended time scale, they have the same general shape as that of the other char samples in *Figures 4* and *5*. Values of $t_{0.5}$ for various char samples are given in *Tables 2* and *3*. As seen in *Table 3*, a weight increase of only 0.45 wt % during oxidation of PSOC-337 coal leads to a dramatic decrease in $t_{0.5}$ from 95 min to 54 min. Further decrease in $t_{0.5}$ with additional increase in the level of pre-oxidation is less pronounced; and when weight increase during oxidation exceeds 3.8 wt %, $t_{0.5}$ attains a limiting value.

The char produced from the as-received PSOC-127 coal is much less reactive than the corresponding PSOC-337 char

(*Tables 2* and *3*). The effect of preoxidation on char reactivity is more marked for samples produced from PSOC-127 coal (*Table 2*). In this case, a weight increase of only 0.45% during preoxidation brings about a three-fold decrease in $t_{0.5}$ from 2040 to 690 min. Values of $t_{0.5}$ decrease further, by a factor of over five, when weight gain during preoxidation increases from 0.45 to 0.66%. Higher levels of preoxidation have a relatively smaller additional effect on reducing $t_{0.5}$; and for weight gain above 2%, $t_{0.5}$ attains a constant value. For a weight gain of only 1.4% during preoxidation of PSOC-127 coal, char reactivity increases by a factor of about 30. These results show, perhaps for the first time, the marked effect of preoxidation of highly caking coals on subsequent char reactivity.

Effect of temperature of preoxidation on pyrolysis and gasification behaviour

It is desirable to examine if for a given level of preoxidation the preoxidation temperature has any effect on subsequent char pyrolysis or reactivity. In order to examine this aspect, a 200 x 250 mesh fraction of PSOC-337 coal was preoxidized to a weight gain of 1.4% at each of the following temperatures: 120, 150, 180, 220 and 250°C. To attain this level of weight gain, preoxidation was carried out for
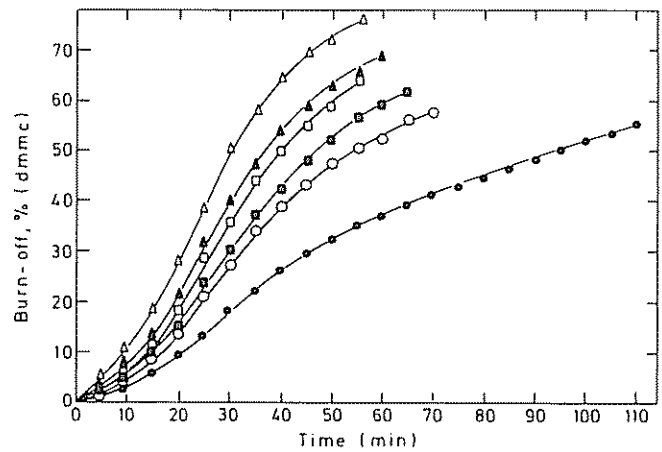

Figure 4 Effect of different levels of preoxidation on burn-off curves in air at 470°C for chars produced from PSOC-337 coal (200 x 250 mesh). Weight gain during preoxidation (%, dmmc): ●, none; ○, 0.45; ■, 0.75; ▫, 1.4; ▲, 2.4; △, 7.0
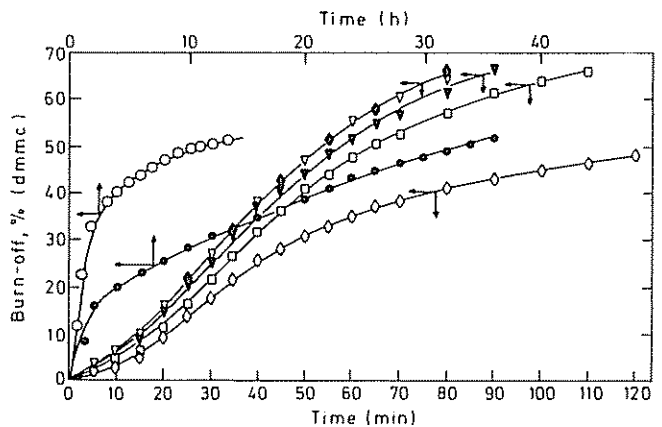

Figure 5 Effect of different levels of preoxidation on burn-off curves in air at 470°C for chars produced from PSOC-127 coal (200 x 250 mesh). Weight gain during preoxidation (%, dmmc): ●, none; ○, 0.45; ◇, 0.67; ▫, 1.4; ▼, 1.9; ▽, 3.0; ◆, 4.5

Table 3 Effect of preoxidation of PSOC-337 coal on char reactivity

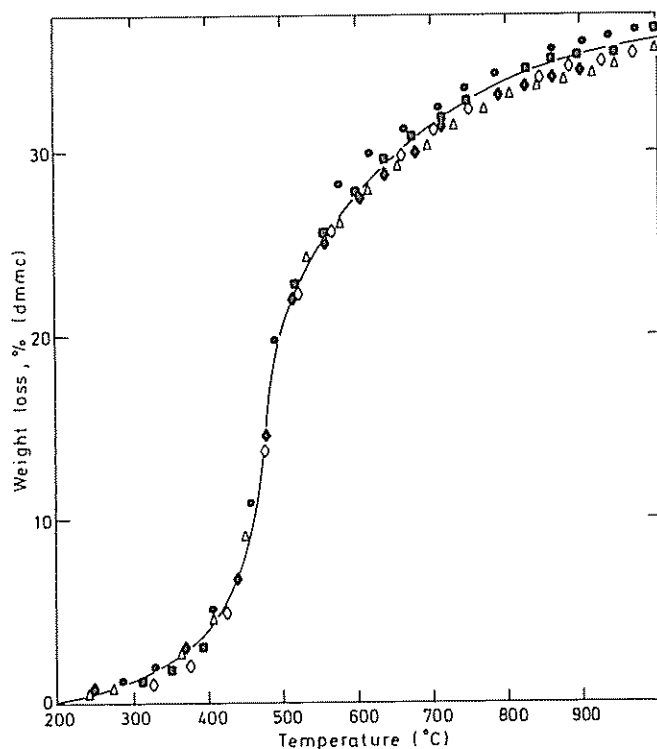| Preoxidation temp (°C)	Wt increase during preoxidation (wt %, dmmc)	$t_{0.5}$ (min)
None	0	95
120	0.45	54
135	0.75	47
150	1.4	40
160	1.8	38
170	2.4	36
180	3.8	32
220	7.0	30
250	5.9	30

Figure 6 Effect of preoxidation to 1.4% weight gain at different temperatures on weight loss during pyrolysis of PSOC-337 coal (200 x 250 mesh). Temperature, °C: ●, 120; ■, 150; △, 180; ◆, 220; ◇, 250

1320, 240, 43, 11 and 3 min, respectively. It is seen that the preoxidation temperature used has essentially no effect on weight loss during pyrolysis (*Figure 6*) and $t_{0.5}$ values (*Figure 7*). Similar results were also obtained when PSOC-337 coal was preoxidized at 180, 220 and 250°C to a weight gain of 3.8%.

For a given level of preoxidation, the effect of oxidation temperature on coal and char properties was also studied for the 200 x 250 mesh fraction of PSOC-127 coal. The coal was oxidized to a weight gain of 1.4% at 200, 220 and 250°C. At these temperatures the desired level of oxidation was attained by carrying out the reaction for 116, 57 and 14 min, respectively. It was found that neither the weight loss during pyrolysis nor $t_{0.5}$ values for char reactivity were significantly affected by preoxidation temperature. These results show that it is only the level of preoxidation and not the temperature of preoxidation which determines the reactivity of the char produced from a caking coal.

Effect of water vapour in air on coal preoxidation and subsequent coal pyrolysis and char reactivity

So far only preoxidation of the coals carried out in dry air has been considered. However, in commercial gasification and combustion units, preoxidation of caking coals is carried out in air which is always associated with some water vapour. Therefore, it is desirable to understand the role which water vapour contained in air during preoxidation may have on subsequent char reactivity. To study this effect, preoxidation was carried out in 0.1 MPa of an air–H_2O mixture containing water vapour at a partial pressure of 1.68 kPa. This water vapour pressure was generated by bubbling air through deaerated distilled water thermostated at 15°C. The 200 x 250 mesh fraction of PSOC-337 coal was oxidized at 150 and 180°C to a weight gain of 1.4% in both dry air and an air–H_2O mixture. Oxidation is slower in wet air, as seen in *Figure 8*. For example, to achieve a weight gain of 1.4% during oxidation at 150°C, it takes 240 min in dry air and 342 min in wet air. The corresponding times for oxidation at 180°C are 43 and 66 min, respectively. It was found that for samples oxidized at 150 and 180°C to a weight gain of 1.4%, the presence (or absence) of moisture in air used during preoxidation had no noticeable effect on weight loss during pyrolysis or subsequent char reactivity.

Effect of particle size

Effect of particle size on rate of preoxidation, weight loss during pyrolysis and char reactivity was studied by using 40 x 70 and 200 x 250 mesh fractions of PSOC-337 and 127 coals. Although the two size fractions of PSOC-337 coal differ somewhat in their ash levels (as discussed in the Experimental section), the results described here were not corrected for this difference because the corrected weight changes would approximate, within the experimental errors, the uncorrected values.

To study the effect of coal particle size on the rate of preoxidation, the 40 x 70 mesh fractions of the two coals were oxidized to the same level of weight increase at the same oxidation temperature as for the corresponding 200 x 250 mesh fractions. Results, given in *Table 4*, show that for both the coals studied the time required for attaining the same level of oxidation at a given temperature increases sharply (in some cases by more than an order of magnitude) with increase in the particle size. However,
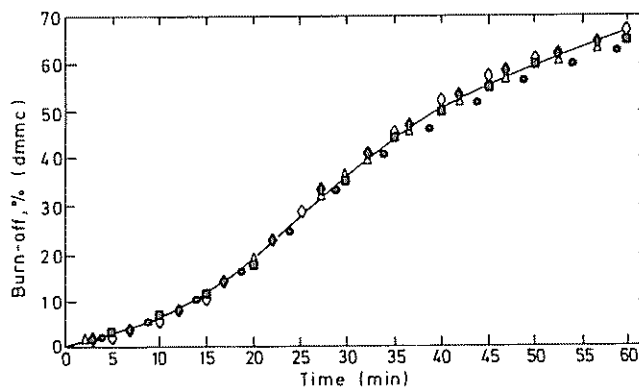

Figure 7 Effect of preoxidation to 1.4% weight gain at different temperatures on subsequent reactivity of chars produced from PSOC-337 coal (200 x 250 mesh) to air at 470°C. Temperature, °C: ●, 120; ■, 150; △, 180; ◆, 220; ◇, 250

while it was possible to attain a 7.0 wt % increase during the preoxidation of the 200 × 250 mesh fraction of PSOC-337 coal at 220°C (*cf. Table 3*), it was not possible to exceed 3.5 wt % increase for the 40 × 70 mesh fraction for oxidation temperatures up to 250°C; at higher temperatures the sample started losing weight due to gasification.

Weight losses at different temperatures during pyrolysis, of 40 × 70 mesh fractions of the two coals preoxidized to different levels, are given in *Table 5*. Considering first the results for PSOC-337 coal, it is seen that for both size fractions weight loss above 450°C decreases with increase in the level of preoxidation. Further, for the same level of

preoxidation, weight loss above 450°C is generally larger for the smaller size fraction.

For the 40 × 70 mesh fraction of PSOC-127 coal, preoxidation to a weight gain of 1.4% results in a significant increase in weight loss upon pyrolysis up to 450°C; at higher temperatures, weight loss is essentially independent of preoxidation. However, further increase in the level of oxidation results in a monotonic increase in weight loss. Although for both the as-received coals weight loss during pyrolysis is larger for the smaller size fraction, pyrolysis behaviour of the oxidized samples is different in the two cases. Results in *Table 5* show that, unlike the behaviour for the PSOC-337 coal, weight loss during pyrolysis of the two size fractions of PSOC-127 coal preoxidized to the same level of weight gain shows little dependence on particle size.

Values of $t_{0.5}$ for char samples produced from the two size fractions of the two coals preoxidized to the same level of weight gain are given in *Table 6*. For the chars produced from the as-received PSOC-337 and 127 coals, an increase in particle size from 200 × 250 to 40 × 70 mesh decreases the reactivity of the two chars by factors of about 6 and 2, respectively. For both the particle size fractions, an increase in the extent of preoxidation increases the subsequent char reactivity. However, for the same level of preoxidation, the char produced from the larger size fraction is less reactive during gasification. It is noteworthy that $t_{0.5}$ for the chars produced from the 200 × 250 mesh fractions of the two
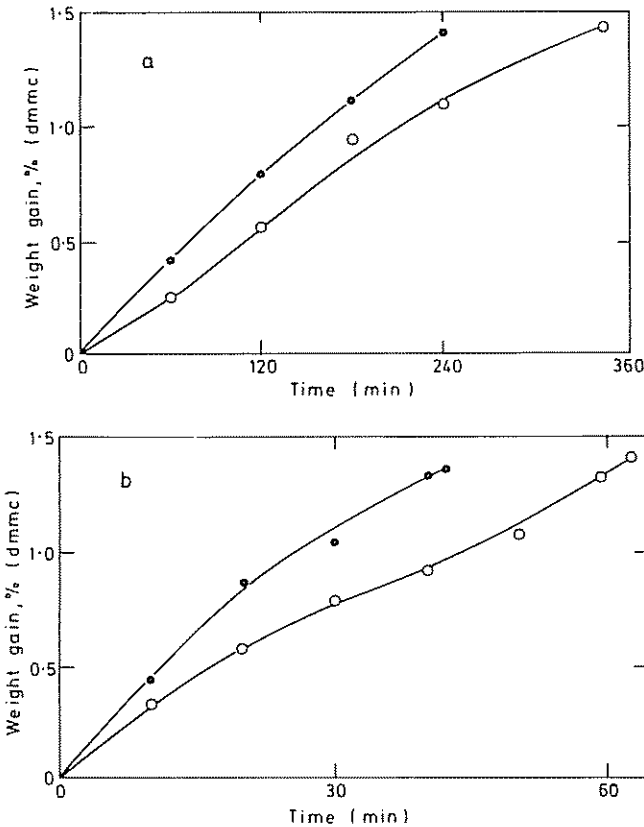

Figure 8   Rate of preoxidation of PSOC-337 coal (200 × 250 mesh) in dry air (●) and air—H₂O mixture (○) at (a) 150°C and (b) 180°C

Table 4 Effect of particle size on rate of preoxidation of caking coals

Preoxidation temp (°C)	Wt increase during preoxidation (wt %, dmmc)	Oxidation time (min)	
		200 × 250 mesh	40 × 70 mesh
	PSOC-337		
135	0.75	47	745
180	1.4	43	305
	PSOC-127		
180	0.66	120	202
220	1.9	90	384
250	3.0	37	394
250	4.5	65	945

Table 5 Effect of coal particle size on weight loss during pyrolysis

Wt increase during preoxidation (%, dmmc)	40 × 70 mesh					200 × 250 mesh				
	Wt loss during pyrolysis (wt %, dmmc) at: (°C)					Wt loss during pyrolysis (wt %, dmmc) at: (°C)				
	450	500	600	700	1000	450	500	600	700	1000
					PSOC-337					
0	11.9	22.8	28.2	29.5	32.2	10.0	22.3	29.0	32.0	36.4
0.75	10.3	21.2	26.4	29.6	31.6	10.0	20.0	28.0	31.2	35.8
1.4	10.3	19.0	23.5	26.0	28.7	8.7	18.4	26.0	29.5	34.1
2.4	9.2	16.4	21.4	25.4	27.9	8.6	16.4	24.9	28.4	33.2
3.8	9.9	14.6	19.7	23.5	27.2	7.9	15.4	23.0	27.2	31.9
					PSOC-127					
0	0.88	3.7	11.2	13.4	15.1	1.4	4.3	12.2	15.2	17.5
1.4	2.5	3.5	12.4	13.8	14.9	3.2	6.0	12.0	15.0	17.5
3.0	3.2	5.9	11.8	15.2	18.2	3.5	6.0	11.3	14.4	17.7
4.5	4.8	7.8	14.2	18.8	22.3	4.5	9.3	13.0	16.0	18.8

Table 6 Effect of preoxidation of coals of different particle sizes on subsequent char reactivity

PSOC-337			PSOC-127		
Wt increase during preoxidation (wt %, dmmc)	$t_{0.5}$ (min)		Wt increase during preoxidation (wt %, dmmc)	$t_{0.5}$ (min)	
	200 x 250 mesh	40 x 70 mesh		200 x 250 mesh	40 x 70 mesh
0	95	610	0	2040	3720
0.75	47	250	0.66	129	2100
1.4	40	232	1.4	65	366
2.4	36	195	1.9	57	306
3.8	32	140	3.0	53	246
			4.5	52	156

coals decrease to essentially constant values after about 2.0 wt % gain during preoxidation. In contrast, $t_{0.5}$ values for chars produced from the 40 x 70 mesh coals decrease monotonically with further increase in the extent of pre-oxidation. The marked effect of particle size on reactivity is further shown by the fact that for the char produced from the 40 x 70 mesh fraction of PSOC-337 coal oxidized to a weight gain of 3.8%, $t_{0.5}$ is still higher than that for the char produced from the as-received 200 x 250 mesh coal.

Effect of pyrolysing preoxidized coal in H_2 on coal and char properties

Prior to hydropyrolysis of caking coals, they are given a preoxidative treatment with air to decrease or eliminate their caking characteristics. The reaction of coals with H_2 at high temperatures and pressures proceeds in two stages: (1) a very rapid first-stage reaction which is transient and exists for a period of a few seconds[5-7], and (2) a slow second stage reaction[5]. In order to make hydropyrolysis economically feasible, it will be necessary to make the best possible use of the chars produced during the first stage of reaction. These chars can potentially be converted into low and medium BTU gases by gasification with air and steam. Since treatment of oxidized coal with H_2 (during hydro-pyrolysis) is expected to restore, at least partly, the fluidity of the coal[8], it is desirable to understand the effect which hydropyrolysis will have on subsequent reactivity of the char produced. This aspect was examined by using a 200 x 250 mesh fraction of PSOC-127 coal.

For this portion of the study, the following set of experiments was performed: (a) Pyrolysis of the 'as-received' coal was carried out in N_2 up to 1000°C using a heating rate of 10°C/min; soak time at 1000°C was 1 h. Following heat treatment, the sample was cooled in N_2 and reacted with 0.1 MPa air at 470°C. (b) The as-received coal was heated in H_2 (0.1 MPa) up to 1000°C using the same heating cycle as in (a). The sample was then cooled in H_2 to 470°C after which H_2 was replaced by N_2 (to displace H_2) and N_2 in turn was replaced by air and char reactivity measured in the usual manner. (c) The as-received coal was preoxidized at 220°C to a weight gain of 1.4%. Following preoxidation, weight loss during pyrolysis in a N_2 atmosphere and reactivity to air were measured as in (a). (d) For the sample preoxidized to a weight gain of 1.4%, pyrolysis in H_2 and subsequent measurement of reactivity of the char to air were carried out as described in (b) above.

Weight loss during pyrolysis of the as-received coal in H_2 exceeded that found during pyrolysis in N_2 over the entire temperature range. Burn-off versus time plots for reactivity in air of the chars produced in N_2 and H_2 atmospheres showed major differences.

Table 7 Effect of preoxidation of coals on surface areas of chars produced

Wt increase during preoxidation (wt %, dmmc)	Surface area (m^2/g, dmmc)
PSOC-337	
0	12
1.9	33
3.8	138
PSOC-127	
0	6
1.7	12
4.2	45

For the as-received coal pyrolysed in a N_2 atmosphere, reactivity was greatest at low burn-offs and decreased monotonically as burn-off increased above 10%. For the as-received coal pyrolysed in a H_2 atmosphere, reactivity up to about 40% burn-off increased monotically and then began to decrease.

Differences in weight loss during pyrolyses in the two atmospheres, below 650°C, were relatively smaller for the preoxidized sample than for the as-received sample. However, at higher temperatures the preoxidized coal showed a relatively higher weight loss in H_2 than in N_2. Reactivity of the char produced by pyrolysis of the preoxidized coal in N_2 ($t_{0.5}$ = 1.4 h) was much greater than the reactivity of the char produced by pyrolysis of the preoxidized coal in H_2 ($t_{0.5}$ = 7.0 h). The chars produced from the preoxidized coals and then pyrolysed in N_2 and H_2 atmospheres were about 23 and 4 times more reactive than the corresponding chars produced from the unoxidized coal.

Effect of preoxidation of caking coals on surface areas of chars produced

Results given in *Table 7* show that for the 40 x 70 mesh fractions of the two coals, the surface area of the char produced following pyrolysis in N_2 increases sharply with increase in the extent of preoxidation given to the coal precursor. Surface areas of chars produced from the PSOC-337 and 127 coals oxidized to a weight gain of about 4% are about 12 and 8 times larger than those of the chars produced from the as-received coals.

DISCUSSION

Caking coals have a liquid-like structure as shown by the X-ray studies of Hirsch[9], and upon heat treatment exhibit fluidity. This fluidity enables the planar regions in the cak-

ing coals to better align, with a consequent loss of surface area and porosity. Thermoplastic caking coals can be converted to thermosetting materials by their preoxidation in air at temperatures below 400°C. It is generally agreed that ether-type crosslinks between the coal lamellae structure formed either during the oxidative treatment itself[1] or during subsequent heat treatment of the preoxidized coal[2] are responsible for the decrease or elimination of caking properties.

The major aim of the present investigation is to study the effect which preoxidation of the caking coals has on gasification rates of the resultant chars. In order to understand this phenomenon, it is important to understand the three major factors which control gasification rates of microporous carbons. They are: (1) concentration of active sites, that is carbon atoms located at the edges of crystallites or building blocks, (2) diffusional limitations on how rapidly the reactant gas molecules can diffuse to the active sites located in the micropores, and (3) catalytic effect of inorganic impurities[10,11]. Any increase in reactivity of chars produced from caking coals following their preoxidative treatment can most likely be attributed to changes in one or more of the three aforementioned factors.

With the above brief background, the more significant results of the present study can now be considered.

Preoxidation of coals

When coals are exposed to air there are broadly two processes which can take place: (1) addition of oxygen to the coal leading to a weight gain and (2) removal of carbon and heteroatoms from coal as volatile oxides, leading to a weight loss. At sufficiently low temperatures, process (1) is dominant; and at sufficiently elevated temperatures, process (2) is dominant. In the present studies process (1) was dominant at preoxidation temperatures up to 250°C, as seen in *Figure 1*.

As with subsequent gasification of the coal chars, preoxidation rate will depend upon available active site concentration, accessibility of O_2 to the active sites, and possible catalysis of the reaction by inorganic impurities present. Therefore, as expected, the rate of preoxidation is dependent not only on temperature, but also on the particular coal being oxidized, its particle size, and the presence of moisture in the air. Enhanced resistance to O_2 diffusion to the active sites with increase in particle size will decrease oxidation rate, as was found experimentally. The presence of water in the air can retard oxidation rates by partial coverage of active sites and/or blockage of some of the micropores.

An increase in particle size of the coal preoxidized also resulted in a decrease in maximum weight gain during preoxidation. It is suggested that the extent of grinding of coal affects the concentration of macrocracks introduced into the particle and, therefore, the extent to which the closed pore volume in coal is opened and made accessible to gases[4].

Effect of preoxidation of coals on their weight loss during pyrolysis

The effect of preoxidation of coal on its weight loss during subsequent pyrolysis is complex. All of the oxygen introduced into the coal during preoxidation is expected to be removed, primarily as water and the oxides of carbon, upon pyrolysis up to 1000°C. This would result in an increase in weight loss. However, to the extent that hydrogen

is removed during pyrolysis as water, it cannot be utilized to remove carbon as volatile hydrocarbons. This would result in a decrease in weight loss. Another factor of importance is the rate at which the volatile hydrocarbons, once formed, can diffuse out of the pore network of the coal; the more rapid the rate, the less the opportunity for secondary cracking reactions to occur resulting in carbon deposition within the particle. Preoxidation clearly leads to the production of a carbonaceous solid having a more open pore structure and, hence, a solid in which diffusion rates of volatiles should be enhanced. The above factors combine in complex ways to produce either enhanced or reduced weight losses upon pyrolysis of coals of different particle sizes and different levels of preoxidation, as seen in *Figures 2* and *3* and *Table 5*.

Effect of preoxidation on char reactivity

Preoxidation of caking coals reduces their subsequent fluidity upon heat treatment and leads to the production of chars of higher surface areas. The greater the extent of preoxidation, the greater is the surface area in the char produced. Therefore, the enhancement of char reactivity as a result of preoxidation of the precursor caking coal is attributed primarily to this increase in surface area. It is of significance, however, that it is the level of oxygen addition during preoxidation which is the important factor determining subsequent char reactivity and not the rate of oxygen addition as affected by oxidation temperature or moisture in the air. This suggests that preoxidation could be conducted at still higher temperatures than those used in this study in order to substantially decrease preoxidation time and still achieve its beneficial effects. For example, extrapolation of the rate data given in *Figure 1* and *Tables 2* and *3* suggests that preoxidation times of about 5 s at 400°C would be adequate to produce significant effects. Studies in this laboratory are now in progress to examine this possibility.

It is of interest that the effect of preoxidation of the two coals studied on the extent of enhancement in reactivity of the chars produced is substantially different. That is, as seen in *Table 6*, a weight gain of 3.8% during preoxidation produces a subsequent four-fold decrease in $t_{0.5}$ for the char produced from the 40 x 70 mesh fraction of PSOC 337 and about an eighteen-fold decrease in $t_{0.5}$ for the char produced from PSOC-127. However, the extent of these changes in reactivity cannot be correlated quantitatively with changes in surface areas of the chars produced as a result of preoxidation. That is, preoxidation of PSOC-337 to a weight gain of 3.8% resulted in a twelve-fold increase in surface area of the char produced (*Table 7*); whereas for PSOC-127, a comparable weight gain during preoxidation resulted in less than an eight-fold increase in char surface area. It is obvious that surface area as measured by the physical adsorption of CO_2 at 25°C is not necessarily a good predictor of char reactivity since it does not necessarily reflect differences in active site concentration and/or accessibility of reactant gas (at gasification temperatures) to the active sites.

Previously we have studied the reactivities of coal chars in air[12], CO_2[13], and steam[14] produced from coals of rank varying from lignite to anthracite. In each reactant medium, the char produced from PSOC-127 had the lowest reactivity. In the extreme case, its char was about 150-fold less reactive than the most reactive char produced from a lignite. It is now clear that one way to close the gap in the large reac-

tivity differences found in American coal chars produced from coals of varying rank is to preoxidize the caking bituminous coals prior to their conversion to chars. That is, preoxidation of thermosetting low-rank coals is expected to have little effect on the structure and reactivity of chars which are produced. Therefore, the 150-fold difference in char reactivity resulting in the use of a lignite versus PSOC-127 can be reduced to less than about a four-fold difference in reactivity by the preoxidation of PSOC-127. The fact that some difference in reactivity still exists is expected because of the more highly dispersed state of the inorganic (catalytic) impurities which are thought to be present in the lignite chars[15].

It is important to note that some of the beneficial effects of preoxidation of caking coals on the subsequent reactivity of their chars can be removed if pyrolysis of the coal is conducted in a H_2 atmosphere. Clearly, during pyrolysis H_2 is removing some of the oxygen added to the coal during preoxidation as water and, thereby, reducing the extent of crosslinking which would normally be produced. Also the char subsequently produced is expected to have a fraction of its active sites covered by hydrogen. Both these factors are expected to reduce subsequent char reactivity in air. It means that if a certain level of reactivity in the char produced from a caking coal is desired, it will be necessary to add more oxygen to the coal originally if that coal is pyrolyzed in H_2.

The effect of pyrolysis of the untreated PSOC-127 coal in H_2 as compared to pyrolysis in N_2 on subsequent char reactivity is also of interest. The initial reactivity of the char produced by pyrolysis in N_2 is substantially higher than the reactivity of the char produced by pyrolysis in H_2. However, the shapes of the burn-off plots are very different, with total weight loss of the latter char being the greater after about 20 h reaction time. This finding points out the complexity of burn-off curves of coal chars, as they are affected by the concentration of available active sites and the chemical and physical nature of inorganic constituents present. Obviously, a reducing versus an inert atmosphere

during pyrolysis can produce important differences in these factors.

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