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Low-temperature air oxidation of caking coals.
2. Effect on swelling and softening properties

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Three highly swelling bituminous coals (<75 um >63 um size) were pre-oxidized to various levels of weight gain and then their plastic properties monitored during carbonization. Additions of relatively small amounts of oxygen (<1–2% by wt) cause marked changes in swelling and softening properties. In general, oxidation causes: substantial reductions in volume changes, increases in softening and dilation temperatures, and a slight reduction in resolidification temperatures. For coals which exhibit high fluidities, slight oxidation results in an increase in expansion prior to destruction of swelling properties. For a given level of weight gain, reduction in plastic behaviour of a coal becomes more severe as the temperature of pre-oxidation is increased. Weathering studies indicate that exposure of an hvA bituminous coal to moist air at ambient temperature has more effect on subsequent swelling and softening properties than exposure to dry air. Fine coal particles stored for extended periods of time in atmospheres with even slight oxygen concentrations show definite signs of weathering. The plastic properties of an oxidized coal may be partially resotred by grinding to expose new surface.

(Keywords: bituminous coal; oxidation; caking; swelling; softening)

It is well known that caking coals, when heated in the absence of air, soften (i.e. become plastic). agglomerate, and, as gases and vapours are evolved, swell to form cokes. These properties make the direct use of some coals in gasifiers and combustion units impractical because agglomerates impede gas flow.

The most common method of removing this caking behaviour is mild oxidation of the coal in air prior to heating it to elevated temperatures. Although this method has been shown to be very effective in removing softening properties,[1-3] efforts have been made to eliminate this procedure in industrial applications because: (1) pre-oxidation involves an extra processing step which is costly; and (2) oxidation reduces the overall thermal efficiency of the process by lowering the carbon and hydrogen contents of the coal and, thus, its calorific value.[3]

Recently, Mahajan *et al.*[4] have published results which indicate that mild oxidation of caking coals prior to carbonization leads to the production of chars having a higher reactivity towards air; as gasification of char represents the slow step in any combustion or gasification scheme, these results may be significant. It is possible that the advantages gained through higher char reactivity outweigh the disadvantages inherent in the pre-oxidation process.

In the present study the effects of mild oxidation on the caking properties of three highly swelling coals are presented. Swelling and softening behaviour of these coals was monitored with a highly sensitive microdilatometer system; this method was selected because dilatometers

provide several characteristic parameters for study, and they supply detailed information on the plastic transitions occurring in coal during heat treatment.[1,2] High sensitivity allows work with small coal samples over a wide range of heating rates (0.5–50 $^\circ$C min^{-1}). The versatility of this system is important because the caking behaviour of a coal is enhanced as the heating rate is increased.[1,5]

In the past, many studies, mostly qualitative, have been conducted to assess the effects of oxidation on the swelling and softening behaviour of coals.[3,6] More recently, Montgomery and coworkers[7-10] and Perlmutter *et al.*[11] have tried to quantify these effects. The work presented here adds to present understanding of oxidation effects on coal carbonization.

EXPERIMENTAL

Coals studied

Three highly caking coals, PSOC-1099 (a hvA coal from the Pittsburgh seam in Pennsylvania), PSOC-1103 (a hvA coal from the Elkhorn No. 3 seam in Kentucky), and PSOC-1133 (a low-volatile coal from the Lower Kittaning seam in Pennsylvania) were selected for examination. To minimize the extent of oxidation of these coals prior to use, samples were collected fresh and immediately stored (size, <25 mm) in sealed containers under N$_2$. Size fractions of these coals (<425 μm >250 μm and <75 μm >63 μm) were prepared for use by grinding and sieving in a N$_2$ atmosphere. The proximate and ultimate analyses of these coals are given in *Table 1*. Ash

Table 1 Proximate and ultimate analyses of raw coals

	PSOC-1099	PSOC-1103	PSOC-1133
	Proximate analysis (wt %, as received)		
Moisture	1.8	2.0	0.9
Ash	11.2	4.6	19.0
Volatile matter	33.6	40.1	19.0
Fixed carbon	53.4	53.3	61.1
	Ultimate analysis (wt %, daf)		
C	83.9	83.1	87.6
H	5.7	5.6	5.2
N	1.5	1.5	1.4
Cl	0.2	0.1	0.1
S (organic)	1.5	2.0	2.0
O (by difference)	7.2	7.7	3.8

yields and moisture contents of particular sieve fractions studied varied little from values given for the whole coal.

Pre-oxidation procedure

Pre-oxidized samples were prepared in a Fisher Thermo Gravimetric Analyzer (TGA) System, Series 300. In a typical run, ≈ 150 mg of coal were placed in a quartz sample bucket. The TGA system was flushed with N_2 (300 cm^3 min^{-1}) for 20 min to displace air from the system; the N_2 was purified by passing through heated copper turnings maintained at 500°C to remove O_2 and then anhydrous calcium sulphate to remove moisture. The sample was then heated in a flow of N_2 from ambient to 200°C to remove moisture from the coal. Temperature was maintained at 200°C until constant weight was attained and then adjusted to the desired oxidation temperature. The gas flow was changed to air (300 cm^3 min^{-1}) and the sample was allowed to oxidize until the desired weight gain was achieved. The air flow was then stopped, N_2 flow was resumed, and the sample was cooled rapidly to ambient temperature.

In this study, samples were oxidized at temperatures >70°C. Above this temperature the initial coal–oxygen complexes formed (thought to be peroxidic in nature) are unstable and decompose to yield other, more stable, coal–oxygen complexes concurrent with the evolution of CO, CO_2 and H_2O.[6,12–15] Because carbon and hydrogen are lost from the coal in this process, weight gain on exposure to air will not give a quantitative measure of oxygen uptake, but provides a lower limit for the amount of oxygen added. Thus, the values for weight gain for a given sample should be compared on a relative, and not an absolute, basis.

Dilatometer procedure

Swelling and softening properties of raw and pre-oxidized coals were analysed using a DuPont 942-Thermomechanical Analyzer (TMA) dilatometer system (*Figure 1*). The heart of the 942-TMA unit is a movable-core, linear variable differential transformer (LVDT). It provides a d.c. voltage proportional to the linear displacement of the dilatometer probe. The derivative of this voltage is determined by an electronic derivative circuit and can be used to define more clearly transitions occurring during heat treatment. The sample is surrounded by a cylindrical heater, which is controlled by a DuPont 990-Temperature Programmer Controller capable of maintaining linear heating rates in the range 0.5–50°C min^{-1}.

In a typical run, ≈ 20 mg of coal were placed in a quartz sample vial, levelled by gently tapping the vial and then packed with a tamping rod. The vial was then placed in position in the sample holder and the dilatometer probe was lowered until it made contact with the sample (see *Figure 1*). A 1 g weight was placed on the probe for increased stability. The starting volume of the coal was calculated from the height of the sample as determined by the displacement of the dilatometer probe from the bottom of the empty vial. The heater was then placed around the sample and the sample holder cell was flushed for 20 min with a stream of purified N_2 (300 cm^3 min^{-1} at 25°C). The heating programme (results at 50°C min^{-1} are described in this paper) was then started, and the softening and swelling behaviour of the coal was followed over the temperature range from ambient to 650°C.

Complete details of the operating procedures, together with an assessment of the capabilities of the dilatometer unit, are reported elsewhere.[12] This paper includes a sensitivity study to determine the effects of carbonization conditions on dilation behaviour and results of dilatometer studies on several unoxidized caking coals.

Surface areas of chars

Total surface areas of chars were determined from CO_2 adsorption at 25°C using the Polanyi–Dubinin equation. Samples were first outgassed at 110°C for 16 h at a pressure of 1.3 mPa. For each point on the isotherm, an arbitrary adsorption time of 30 min was allowed. Surface areas of chars have been expressed on a dry. mineral matter-containing (dmmc) basis.

For measurement of surface areas, relatively large samples (1 g) of chars were needed. Because such amounts could not be prepared in the dilatometer unit, the necessary samples were prepared by heating ≈ 5 g of coal, spread uniformly in a ceramic boat, in a horizontal tube furnace. The coal was heated as rapidly as possible (≈ 40–50°C min^{-1}) in N_2 to simulate conditions in the
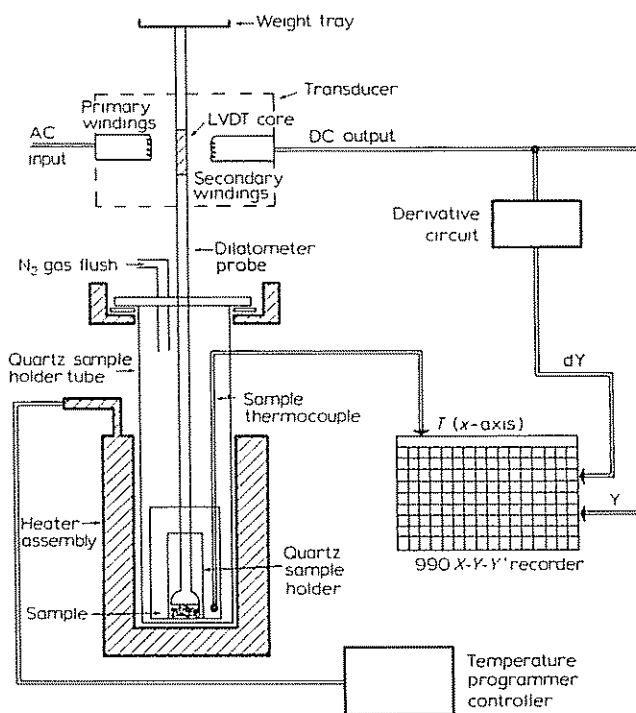

Figure 1 Schematic diagram of microdilatometer system

dilatometer runs. When a sample reached the desired carbonization temperature, it was quenched rapidly by removing it from the furnace.

RESULTS

Analysis of dilatometer data

Figure 2 is an example of a dilatometer experimental run using hvA coal (size, <75 μm >63 μm). Careful examination of this Figure shows that much information about the softening and swelling behaviour of the coal can be obtained. Parameters defined by the dilatometer trace and selected for study in this work are:

(1) onset of softening temperature (T_s), point (A)
(2) initial dilation or fusion temperature (T_d), point (B)
(3) resolidification temperature (T_r), point (C)
(4) initial contraction, length (D)
(5) maximum expansion, length (E)
(6) total dilation, length (E + D)
(7) final contraction, length (F)

Values of transition temperatures and volume changes reported in this study are given as 95% confidence values obtained from five or six experimental runs. Volume transitions such as contraction and expansion are reported as per cent volume changes calculated on the

basis of the starting volume of the coal. Complete details of the procedures followed here and the methods used to determine transition temperatures and volume changes can be found elsewhere.[12]

Effect of pre-oxidation temperature on plastic properties

Samples of PSOC-1099 (size, <75 μm >63 μm) were oxidized to a fixed weight gain (0.5%) at a number of temperatures ranging from 75 to 200°C. The results (*Table 2*) show that the oxidation rate increases sharply with increasing temperature; an increase from 75 to 200°C decreased the time required to reach a weight gain of 0.5% by 500-fold. In addition, as the temperature of oxidation increased, reduction in plastic behaviour of the coal became greater. An increase in oxidation temperature caused reduction in contraction, expansion, and total dilation and in the resolidification temperature. At the same time, softening and dilation temperatures increased.

Effect of pre-oxidation level on plastic properties

All subsequent pre-oxidations reported were conducted at 125°C. PSOC-1099 was oxidized to a number of levels of weight gain prior to studying its plastic properties, and *Figure 3* illustrates the marked effects that pre-oxidation had on its swelling and softening behaviour. The dilatometer traces presented here have been modified slightly for the sake of clarity, large oscillations, e.g. as in *Figure 2*, having been removed to prevent overlap of curves. In general, additions of small amounts of oxygen caused 'substantial reductions in volume expansion and contraction values, increases in softening and dilation temperatures, and a slight decrease in the resolidification temperature. Results are summarized in *Table 3*. Note that the extent of final contraction was not very reproducible.

The effect of the level of pre-oxidation of PSOC-1099 on subsequent volume expansion upon carbonization is evident from *Figure 4*. Low levels of pre-oxidation (≤0.1% increase in weight) resulted in an increase in expansion. Similar behaviour was observed for the other hvA coal studied (*Table 4*), but further pre-oxidation caused a sharp decrease in expansion until a weight gain of ≈1.5% was reached. Above this oxidation level, relatively little volume change occurred during carbonization.

Results for the effects of pre-oxidation of the low-volatile coal (PSOC-1133) on its subsequent plastic properties are summarized in *Table 5*. The initial increase in expansion at an oxidation level of 0.1% weight gain found for the two hvA coals was not observed for this coal. Further, this low-volatile coal was more sensitive to pre-oxidation than was PSOC-1099; swelling during carbonization disappeared following pre-oxidation to a
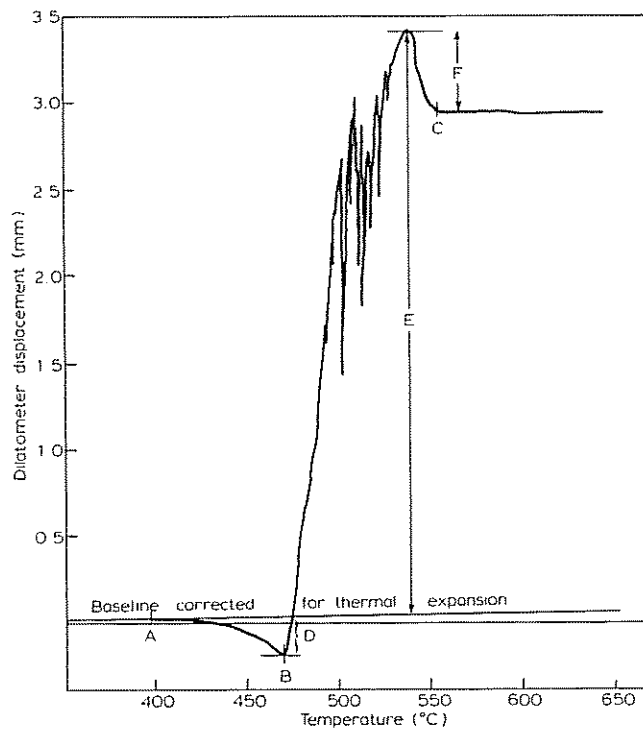

Figure 2 Dilatometer output of an hvA coal (PSOC-1099)

Table 2 Effects of pre-oxidation temperature on plastic properties of PSOC-1099 upon carbonization

Weight gain (%)	Oxidation temp. (°C)	Oxidation time (min)	Contraction (%)	Expansion (%)	Total dilation (%)	T_s (°C)	T_d (°C)	T_r (°C)
Fresh coal	—	—	41 ± 11	703 ± 17	744 ± 18	393 ± 3	475 ± 2	559 ± 3
0.49	75	530.0	42 ± 4	440 ± 25	482 ± 26	394 ± 4	488 ± 1	560 ± 4
0.50	100	74.0	40 ± 4	402 ± 7	443 ± 4	398 ± 6	491 ± 1	557 ± 8
0.50	125	15.6	39 ± 3	382 ± 15	420 ± 14	397 ± 7	487 ± 8	557 ± 5
0.50	150	3.87	35 ± 3	309 ± 22	344 ± 23	402 ± 6	489 ± 4	553 ± 1
0.53	175	1.57	28 ± 3	247 ± 11	275 ± 12	415 ± 6	499 ± 1	551 ± 3
0.51	200	1.27	23 ± 1	130 ± 35	153 ± 35	429 ± 5	507 ± 2	547 ± 5

weight gain of only ≈0.5%. Dilation temperatures increased sharply with increased oxidation, whereas softening and resolidification temperatures changed only slightly.

Effect of room temperature oxidation on plastic properties

Samples of PSOC-1099 coal were allowed to weather in both dry and moist (88% humidity) air for various periods
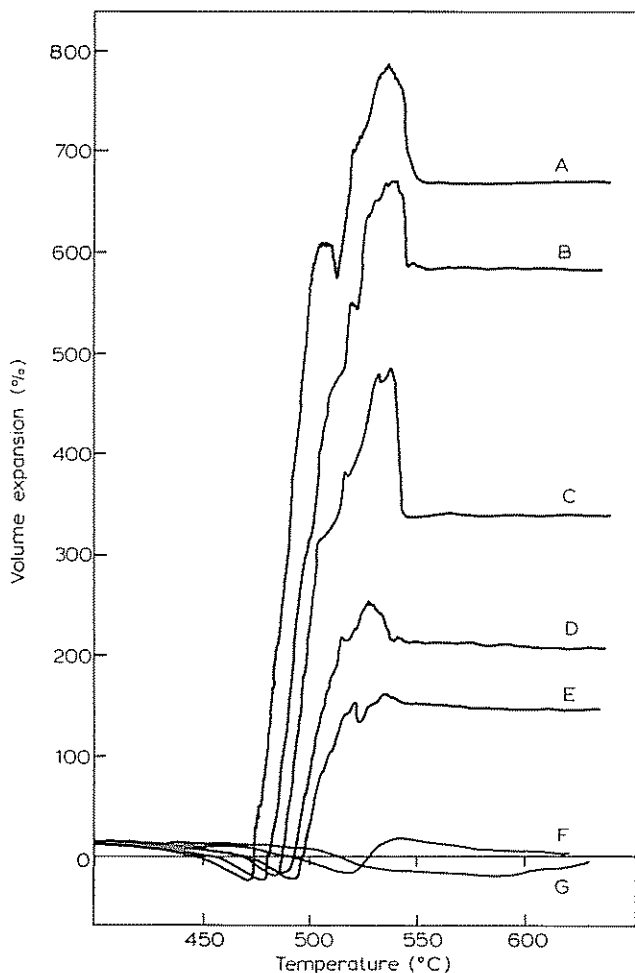
of time, prior to carbonization. As seen in *Table 6*, on weathering, the dilation values of PSOC-1099 first increased to a maximum value and then began to decrease. After storage of the coal for 80 days in N_2, the dilation values increased significantly. However, although the samples were stored under N_2, this gas was not scrubbed completely free of O_2, and samples stored in this atmosphere for approximately 3 months showed definite signs of oxidation. The data in *Table 6* show that exposure of coal to dry air had less effect on subsequent volume expansion of PSOC-1099 than did exposure to wet air.

Effect of grinding of oxidized coals on plastic properties

Kinetic studies have shown that oxidation is a surface phenomenon[6,16,17] and suggest that the rates of low-temperature oxidation are controlled by diffusion of
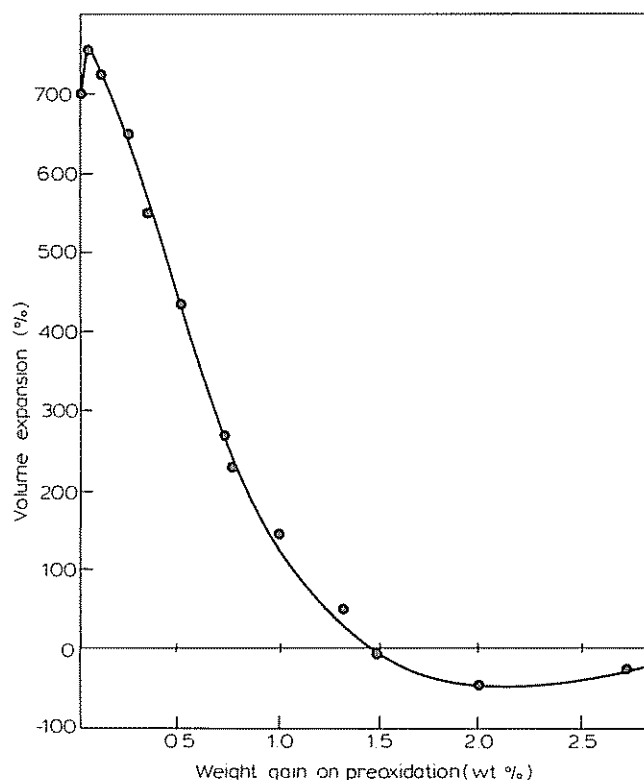
Figure 3 Dilatometer data for PSOC-1099 coal (size, <75 μm >63 μm) pre-oxidized to different levels. Plots are simplified for clarity. A, Unoxidized; B, 0.24 wt % gain; C, 0.49 wt % gain; D, 0.75 wt % gain; E, 0.99 wt % gain; F, 1.48 wt % gain; G, 1.99 wt % gain

Figure 4 Effect of level of pre-oxidation on volume expansion upon carbonization of PSOC-1099

Table 3 Effect of oxidation level at 125°C on plastic properties of PSOC-1099 upon carbonization

Weight gain (%)	Contraction (%)	Expansion (%)	Total dilation (%)	Final contraction (%)	T_s (°C)	T_d (°C)	T_r (°C)
Fresh coal	41 ± 11	703 ± 17	744 ± 18	53 ± 64	393 ± 3	475 ± 2	559 ± 3
a	50 ± 3	755 ± 22	805 ± 24	88 ± 48	395 ± 7	475 ± 2	559 ± 3
0.10	50 ± 2	728 ± 26	777 ± 28	107 ± 51	385 ± 5	473 ± 2	555 ± 2
0.24	45 ± 5	650 ± 8	695 ± 8	85 ± 30	389 ± 2	479 ± 2	555 ± 4
0.33	43 ± 6	552 ± 29	595 ± 27	122 ± 48	390 ± 1	483 ± 3	554 ± 4
0.50	45 ± 3	435 ± 17	479 ± 16	118 ± 67	397 ± 7	487 ± 8	557 ± 5
0.72	44 ± 6	269 ± 15	313 ± 14	55 ± 50	398 ± 3	484 ± 4	550 ± 3
0.75	39 ± 3	229 ± 29	268 ± 29	43 ± 40	397 ± 4	494 ± 1	546 ± 4
0.99	40 ± 4	144 ± 12	183 ± 12	17 ± 10	396 ± 11	491 ± 3	543 ± 4
1.31	37 ± 6	49 ± 8	86 ± 10	ND	411 ± 7	492 ± 3	ND
1.48	38 ± 5	−8 ± 10	30 ± 8	ND	412 ± 7	516 ± 2	ND
1.99	48 ± 4	−48 ± 4	ND	ND	417 ± 5	ND	ND
2.74	30 ± 2	−30 ± 2	ND	ND	418 ± 9	ND	ND

a Coal stored 80 days under N_2
ND — Not Detectable

oxygen through the micropores of the coal particles. van Krevelen[5] showed an example of 'oxidation edges' on coal particles, and Sevenster[18] discussed the diffusion limitations of low-temperature oxidation. A higher concentration of oxygen groups may be expected, therefore, at the outer edges of coal particles. To test this hypothesis, several samples of PSOC-1099 (size, <425 μm >250 μm) were oxidized to various levels. These samples were split and one half of each sample was ground in N₂ to <75 μm. The plastic properties of the oxidized samples, of both size fractions, were then measured. *Figure 5* plots the expansion values for the oxidized coal samples relative to those of the raw unoxidized coals of the same particle size. These results show the partial restoration of dilation upon grinding to expose fresh coal surface.

DISCUSSION

It has been shown previously that mild oxidation of caking coals prior to carbonization leads to the production of more highly reactive coal chars.[4] This

increase in char reactivity is attributed primarily to an increase in surface area as a result of pre-oxidation. It is thought that increases in surface area are a direct result of a loss in fluid properties of the coal. In *Figure 2* it is seen that over the temperature region from softening to resolidification (A–C) hvA coal (PSOC-1099) exhibits a high degree of fluidity. In the initial stages (A–B), the coal particles soften and fuse together; the coal becomes sufficiently plastic to be compressed under a slight load. This fluidity enables planar regions in the coal to align better, with a consequent loss of surface area. Evidence of this can be seen in the formation of anisotropic mesophase
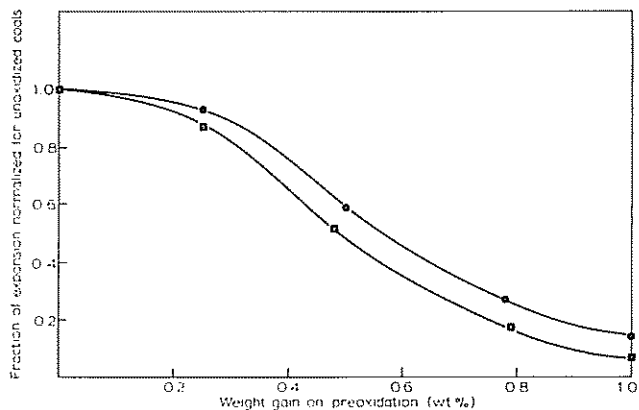
Table 4 Effect of pre-oxidation level at 125°C on volume expansion of PSOC-1103 upon carbonization

Weight gain (%)	Expansion (%)
Fresh coal	577 ± 50
a	616 ± 39
0.05	650 ± 51
0.10	587 ± 75

a Coal stored 119 days under N₂

Figure 5 Effect of grinding pre-oxidized samples on restoring plastic properties of PSOC-1099. ▣, Size <425 μm >250 μm; ●, oxidized at size <425 μm >250 μm then ground to <75 μm under N₂

Table 5 Effect of pre-oxidation level at 125°C on plastic properties of PSOC-1133 upon carbonization

eight gain (%)	Contraction (%)	Expansion (%)	Total dilation (%)	Final contraction (%)	T_s (°C)	T_d (°C)	T_r (°C)
Fresh coal	41 ± 3	473 ± 29	514 ± 29	75 ± 38	463 ± 2	523 ± 1	586 ± 7
0.10	40 ± 3	343 ± 15	381 ± 17	20 ± 12	455 ± 3	525 ± 2	583 ± 4
0.25	35 ± 4	256 ± 17	292 ± 16	9 ± 7	463 ± 4	531 ± 2	585 ± 3
0.43	36 ± 4	99 ± 31	134 ± 34	ND	462 ± 3	541 ± 3	ND
0.56	32 ± 4	14 ± 8	47 ± 11	ND	466 ± 6	548 ± 2	ND
0.75	35 ± 6	−35 ± 6	ND	ND	463 ± 2	ND	ND
1.00	27 ± 2	−27 ± 2	ND	ND	466 ± 4	ND	ND

Table 6 Effect of weathering on plastic properties of PSOC-1099 upon carbonization

Weathering time (days)	Contraction (%)	Expansion (%)	Total dilation (%)	T_s (°C)	T_d (°C)	T_r (°C)
Fresh coal	41 ± 11	703 ± 17	744 ± 18	393 ± 3	475 ± 2	559 ± 3
a	50 ± 3	755 ± 22	805 ± 24	395 ± 7	475 ± 2	559 ± 3
			Weathering in dry air			
13	47 ± 4	769 ± 15	817 ± 13	387 ± 3	472 ± 1	559 ± 2
25	50 ± 5	754 ± 19	804 ± 24	390 ± 2	477 ± 1	557 ± 2
44	48 ± 4	748 ± 15	796 ± 16	390 ± 4	477 ± 2	556 ± 2
65	50 ± 3	746 ± 41	796 ± 43	396 ± 5	482 ± 4	561 ± 2
94	48 ± 6	709 ± 56	758 ± 60	390 ± 8	479 ± 3	558 ± 1
			Weathering in moist air			
13	49 ± 3	759 ± 33	808 ± 33	389 ± 4	477 ± 1	557 ± 4
25	48 ± 5	695 ± 38	743 ± 38	392 ± 4	479 ± 4	555 ± 1
44	48 ± 3	673 ± 41	721 ± 40	395 ± 7	480 ± 3	556 ± 2
	47 ± 4	651 ± 47	697 ± 49	395 ± 7	483 ± 5	560 ± 3
4	47 ± 5	577 ± 26	624 ± 26	397 ± 5	483 ± 2	556 ± 5

a Coal stored 80 days under N₂

Table 7 Effect of temperature of carbonization of PSOC-1099 on surface area of cokes produced

Temperature (°C)	Surface area (m² g⁻¹)
Raw coal	135
350	133
400	138
450	107
500	124
600	188

structures in cokes prepared from caking coals.[19] In the temperature region over which dilation occurs (B–C) the coal has fused together to such a degree that individual coal particles no longer exist as such. At this stage the plastic coal mass offers some resistance to the escape of volatile pyrolysis products, leading to development of internal gas pressure in the plastic mass and resulting dilation of the coal. For the hvA coal shown in *Figure 2*, the total dilation is approximately 750%. Such a large increase in volume may be expected to cause a corresponding increase in surface area; however, most of this volume increase on dilation results from pores formed by large gas bubbles. As most of this porosity is in the form of large pores, increases in surface area are relatively small. To illustrate this point, the surface areas of several carbonized samples were measured as described previously. As expected, these areas (*Table 7*) pass through a minimum in the plastic temperature region where contraction of the coal occurs.

For a given level of weight gain, the temperature of pre-oxidation has a marked effect on the plastic behaviour of a coal. This result provides further evidence that the coal–oxygen complexes formed initially during pre-oxidation are increasingly unstable as the oxidation temperature is increased.[6,12–14] At all pre-oxidation temperatures, two processes occur concurrently, that is, gain of oxygen by the coal, and removal of hydrogen, carbon and oxygen from the coal as CO, CO_2, and water. The latter process becomes of increasing importance as temperature is increased. Therefore, the weight gains which are shown to be constant with increasing temperature (*Table 2*) in fact mean that the amount of oxygen added to the coal increases monotonically with increasing oxidation temperature. It was reported previously that, for a given level of oxygen uptake, the temperature of pre-oxidation had no effect on resultant char reactivity.[4] This may appear to contradict the present results but when re-examined the results of both studies can be reconciled. In the former study samples were oxidized to 1.4% weight gain, a level at which almost all of the plastic properties exhibited by the hvA coal used in the present work had been destroyed. As increases in char reactivity are directly related to the loss in fluidity of the coal, it is not surprising that, at oxidation levels as high as 1.4%, char reactivity is relatively independent of oxidation temperature.

The dilatometer studies conducted on oxidized coal samples show that additions of oxygen bring about marked changes in plastic behaviour of the coals. The hvA coals tested show an initial increase in expansion upon carbonization following very low levels of oxidation, whereas the low-volatile coal exhibits no such behaviour. This difference is believed to be due to large differences in fluidity between these coals. Maximum Gieseler fluidities

measured for each of the fresh coals were 14 681 DDPM, 29 944 DDPM, and 58 DDPM for PSOC-1099, PSOC-1103 and PSOC-1133, respectively.

Weathering studies show that the maximum Gieseler fluidity for PSOC-1099 is reduced by more than 60% during the first 14 days of exposure to air at room temperature. It is estimated that the amount of oxygen chemisorbed in this time is less than 0.1%. This large decrease in fluidity of the coal may be the cause of the observed increase in dilation. Lower fluidity increases the resistance of the plastic coal mass to escape of volatile gases and so these gases will require a longer time to escape from the less fluid material. Increased residence time of gases in the plastic mass leads to an increase in internal gas pressure and a subsequent increase in swelling. An increase in swelling was not observed for the low-volatile coal because the initial fluidity of the raw coal was very low, and oxidation could not cause the same large decrease in fluidity observed for PSOC-1099 without totally destroying all fluid behaviour.

The fact that swelling of PSOC-1099 and PSOC-1103 passed through a maximum with increasing extent of oxidation indicates that factors other than coal fluidity are involved in determining the behaviour of coals during carbonization. *Table 3* shows that as a coal is oxidized and fluidity decreases, the dilation temperature increases steadily. An increase in T_d should result in a decrease in the amount of volatile gases available to produce swelling; i.e., as T_d increases a larger percentage of the total pyrolysis gases escape from the coal particles before the particles are fused together sufficiently for swelling to begin. A smaller percentage of total volatile release while the coal particles are in the plastic state results in a decrease in dilation.

The strong dependence of dilation temperature upon the amount of oxygen added to a coal suggests that the role of oxygen in reducing plastic properties is to inhibit the fusion of coal particles. Schmidt and coworkers[20,21] have shown that oxidation leads to a reduction in the yield of tars produced on carbonization. It is likely that some of these tars make up the plasticizing fraction which is thought to be responsible for fusion of the coal particles. The fusion temperature reflects this loss in plasticizing medium and so represents a sensitive measure of the degree of oxidation of a coal.

The results of weathering studies emphasize the great difficulty involved in trying to obtain truly 'fresh unoxidized' coal samples. Special precautions were taken to minimize oxidation of the samples prior to use, but even so the samples still showed signs of oxidation. The amount of oxygen required to alter plastic properties of caking coals is indeed small.[9,10] The accelerating effect of moisture on the weathering process, seen in this study, suggests that water is interacting with oxygen groups on the coal surface. It is known that oxidation of carbon in the presence of moisture leads to the formation of surface peroxide groups.[22] Thus, this result supports the theories of Jones and Townend[13] and Chakravarty[14,15] that formation of peroxygen groups is an important step in the low-temperature oxidation of coal.

Recently Painter *et al.*[23] reported, from FTIR studies, that in the early stages of oxidation of a bituminous coal, one of the main functional groups formed is carboxyl. Further they outlined how carboxyl groups can enter in cross-linking reactions with other entities in the coal upon carbonization. It has been shown that oxidation of carbon surfaces in the presence of moist air results in the

formation of more carboxyl groups on the surface than does oxidation in dry air.[24,25]

Finally, it has been shown that plastic properties of oxidized coals can be partially restored by grinding of the coal in N_2. This result suggests that one of the roles of oxygen in the reduction of plastic properties is to prevent plasticizing fluids from wetting and softening the coal particle surfaces, thereby preventing fusion of the coal particles. These ideas have been expressed previously by Mott and coworkers.[26-29] It is thought that fresh surface is exposed on grinding and that the plasticizing fluids have better access to these surfaces; fusion, therefore, occurs at lower temperatures and the resulting dilation is higher.

ACKNOWLEDGEMENT

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Selective separation and identification of olefins in petroleum and synthetic fuel naphtha

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An analytical procedure, based on the specific and quantitative conversion of olefins to alcohols by the hydroboration–oxidation reaction, is described. The alcohols are subsequently separated from the hydrocarbon mixture by chromatography on alumina. The conversion was monitored by proton magnetic resonance (p.m.r.). A gas chromatograph interfaced with a quadrupole mass spectrometer (g.c.–m.s.) was used to identify the individual alcohols, using retention indices of pure compounds as well as library search data. The assignment of structures to the parent olefins is based on the stereochemistry of the hydroboration reaction. The procedure was applied to two synthetic fuel naphthas produced by thermal and catalytic processing of the Lloydminster heavy oil. The results indicate that the olefins are produced during processing. The olefins of the catalytic naphtha have predominantly higher average molecular weights (C_7–C_{10}) than those of the thermal naphtha (C_5–C_8). Chemical configurations have been assigned for 24 different olefins in both products. The hydroboration–oxidation procedure permits highly selective isolation of olefins in the form of alcohols and provides a pure alcohol mixture for identification by g.c.-m.s.

The application of heat to bitumens and light and heavy crude oils during refining and processing frequently produces olefins. Chemical characterization of the olefinic components in the naphtha product produced by hydrocracking[1] is necessary to understand the mechanism and effect of the catalyst and changing reactor conditions on olefin formation.

A method for the determination of the olefinic content based on hydroboration–oxidation of the olefins, resulting in quantitative conversion to alcohols, has been developed in this laboratory.[2] In this method, the alcohol mixture was recovered from the hydrocarbon fraction by elution on an alumina column. This reaction procedure, coupled with g.c.-m.s., has been used in the present work to establish a highly selective analytical approach for identifying olefins in petroleum and synthetic fuel naphthas.

Several workers have used g.c.-m.s. techniques for separating and characterizing hydrocarbons in the gasoline range.[3–5] However, without selective separation of olefins in the form of alcohols, characterization by g.c.-m.s. would be difficult because of the overlap of olefins with paraffins in the gas chromatographic separation, and the similarity of the parent ions of linear olefins to those of cycloalkanes having the same carbon numbers. Hydrocarbon-type separation of olefins, saturates and aromatic compounds by high-performance liquid chromatography (h.p.l.c.) has been investigated by some workers.[6,7] No structural elucidation of the olefins was made to show the selectivity of the methods.

Two synthetic fuel naphthas, produced from hydrocracking the Lloydminster heavy oil, were analysed. Alcohols were identified by correlations with retention indices and boiling points of pure alcohols and mass spectral library search data. The assignment of structures to the parent olefins is based on the stereochemistry of the hydroboration reaction, which proceeds by an anti-Markovnikov addition of diborane to the olefinic double bond.[8] Twenty-four different olefinic components have been identified in two naphthas resulting from both thermal and catalytic processing of the heavy oil.

EXPERIMENTAL

Samples

(1) Naphtha (30–200°C) obtained by distillation of virgin Lloydminster oil.
(2) Naphtha (30–200°C) obtained by distillation of thermally hydrocracked Lloydminster oil.
(3) Naphtha (30–200°C) obtained by distillation of catalytically hydrocracked Lloydminster oil.
(4) Synthetic alcohol mixture prepared by dissolving 0.1 ml of each individual alcohol in 2 ml pentane (*Table 1*).

Hydroboration procedure

Approximately 2.2 g of petroleum distillate naphtha was introduced into a 250 ml, three-neck, round-bottom flask equipped with a magnetic stirring bar, a condenser and a dropping funnel and containing 25 ml of dry ethyl ether. The system was purged with nitrogen and, using a syringe, a large excess (1 ml) of borane–methyl sulphide complex (10M in BH_3) was added slowly, via a septum, into the flask which was maintained at 0°C.[2] The solution was stirred at room temperature for 1.5 h; the reaction mixture was then cooled to 0°C and 15 ml of 3N sodium hydroxide was added slowly, followed by 15 ml of 30%