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Swelling and plastic properties of coal devolatilized at elevated pressures of H₂ and He

Influences of added iron oxides

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The influences of Fe₂O₃ and Fe₃O₄ additives on the swelling and plastic properties of a low volatile bituminous coal devolatilized at elevated pressures of H₂ and He were characterized using a high-pressure microdilatometer. The results indicate that added Fe₂O₃ or Fe₃O₄ destroyed the thermoplastic properties of coal at low pressures (<1.0 MPa H₂ or He). In general, Fe₂O₃ appeared to serve as a stronger decaking additive than Fe₃O₄. The presence of either additive increased solid yield during coal pyrolysis. The reduction in the thermoplastic properties by the additives is explained by suggesting that Fe₂O₃ and Fe₃O₄ had a catalytic effect that facilitated char-forming reactions during coal pyrolysis. In addition, a chemical role in the case of Fe₂O₃ (conversion of Fe₂O₃ and Fe₃O₄ and consumption of coal-derived H₂ in the process) was suggested. When coal was devolatilized at elevated pressures of H₂, especially at a slow heating rate ($\approx 5 \text{ K min}^{-1}$), the plastic and fluid behaviour of the coal markedly increased. This behaviour is explained by suggesting that the effects of H₂ were to decrease the extent of char-forming reactions and to reduce iron oxides to elemental iron which serves as an excellent hydrogenation catalyst (especially at the longer residence time resulting from a very slow heating rate).

(Keywords: coal; swelling; iron)

The overall objective of this study is to examine the influences of various low-cost (compared with potassium compounds) inorganic additives on the thermoplastic properties of a Lower Kittanning Seam coal (PSOC 1197, lvb). The effects of adding various low-cost inorganics to coals have been reported elsewhere¹⁻⁸. In this paper, the effects of Fe₂O₃ and Fe₃O₄ additives are presented. Several studies⁹⁻¹³ have addressed the influences of iron oxides on coal pyrolysis. Iron oxides were considered as additives in coal conversion processes as decaking agents or sulphur scavengers¹³. Several studies in the literature¹³ suggest that the addition of iron oxides may influence the swelling and plastic properties of coals. However, the exact nature of the interactions between coal and iron oxide additives is not well understood, as many of these studies were inconclusive. In addition, the effects of gas atmospheres (e.g., H₂ or He) or elevated pressures on the thermoplastic properties of coal in the presence of these additives are not known. The present study addresses these issues by means of systematic experiments utilizing a high-pressure microdilatometer as the primary research tool.

EXPERIMENTAL

A high-pressure microdilatometer (HPMD) system used in previous studies¹⁻⁸ was used in this investigation also. Detailed evaluation and description of this system is provided elsewhere¹⁻³. Samples used in this study were of a Lower Kittanning Seam, lvb coal (PSOC 1197): proximate analysis (as received): H₂O, 0.7; ash, 10.3;

VM, 16.4; and FC, 72.6 wt%; ultimate analysis (daf basis): C, 89.6; H, 4.6; N, 1.8; and S, 1.0 wt%; FSI = 5. The coal was ground and sieved in a nitrogen atmosphere to minimize oxidation during preparation. The raw, untreated coal was dried in ultra-high purity (UHP) N₂ for 1 h at 383 K. The following additives were used in this study: SiO₂ (Baker Chemical, 99.5%); Fe₂O₃, Fe₃O₄ (Baker, 99.9%). All additives were ground and sieved to less than 400 mesh ($-38 \mu\text{m}$). Subsequently, the additives were dried at reduced pressure (10^{-4} MPa) at 383 K. The non-porous silica (SiO₂) used was heated to 773 K (1 h) to remove any silanol groups present on the surface¹⁴. In cases where a mixture of coal and the additive was needed, the mixture was prepared by stirring the components for 30 min, followed by overnight slow shaking. The concentrations of the additives used (in wt % and mmol/g coal) are provided in Table 1. A detailed description of the measured parameters in the HPMD is

Table 1 Concentrations of additives used

Additive	Wt % added	mmol Fe/g coal
Fe ₂ O ₃	5.8	0.72
	23.2	2.9
Fe ₃ O ₄	5.6	0.72
	22.3	2.9
SiO ₂	5	-
	20	-

provided elsewhere¹⁻³. These parameters are:

1. the maximum volume swelling parameter (V_s %);
2. the volume contraction parameter (V_c %);
3. the volume change upon resolidification parameter (V_r %); and
4. the characteristic temperature (softening, T_s ; contraction, T_c ; maximum swelling, T_c ; and resolidification, T_r).

The volumetric parameters are expressed on a percentage basis, based on the initial volume of the coal used. For example, the maximum swelling parameter (V_s %) is defined by the following equation in all cases:

$$V_s \% = \frac{\text{Volume of expanded coal sample} - \text{Initial volume}}{\text{Initial volume of coal sample}} \times 100$$

In cases where experiments are conducted in the presence of various additives, the volume occupied by the additives does not enter into the equation above. Therefore, the reported data are normalized to a coal-alone basis. The volumetric changes observed for iron oxides alone during heat treatment were insignificant compared with that noted for the coal. As stated previously^{1,2}, the V_s parameter can be reproduced to within $\pm 6\%$, whereas V_c can be resolved to within $\pm 3\%$. The characteristic temperatures can be reproduced ± 6 K. All experiments were conducted at controlled heating rates to various maximum temperatures. Coal weight loss during pyrolysis was determined by weighing the samples before and after the runs. Heat treatment of these additives alone showed no weight loss when heated to 923 K. The experimental conditions under which the dilatometric runs were conducted were: pressure range, 0.1–3.6 MPa He or H₂; heating rate, 5–60 K min⁻¹; coal particle size, $-74 \mu\text{m}$; and applied mechanical load, 9.8 kPa.

RESULTS AND DISCUSSION

Diluent versus potential catalytic/chemical roles of the additives

As described in more detail elsewhere^{2,4}, additives can have diluent or catalytic roles in pyrolysis. Non-porous SiO₂ (dry mixed) was used in the study to separate 'diluent' effects of various additives from their potential chemical/catalytic effects. The observed effects of addition of 20 wt% SiO₂ on the resulting thermoplastic parameters of the coal (PSOC 1197, lvb) are relatively small^{2,4,8}. Our studies^{2,8} and other data in the literature have suggested that SiO₂ serves primarily as a diluent. The diluent effect of SiO₂ on the thermoplastic properties of coal can be explained by postulating that the presence of SiO₂ particles in the plastic mass increases the permeability of gas flow. Thus, the internal 'swelling pressure' is reduced. In addition, the presence of a silica particle between two softened coal particles inhibits their fusion (since SiO₂ does not soften at the conditions of measurement) and, therefore, there is a slight reduction in the overall agglomeration of the coal bed.

Effects of iron additives on thermoplastic parameters

Figure 1 shows the effects of addition of various concentrations of haematite (Fe₂O₃) or magnetite

(Fe₃O₄) on V_s in H₂ and He (heating rate 60 K min⁻¹). Addition of haematite or magnetite (at concentrations of 0.72 and 2.9 mmol Fe/g coal, i.e., 5.8 and 23.2 wt% Fe₂O₃, 5.6 and 22.3 wt% Fe₃O₄) destroys the V_s parameter at 0.1 MPa (H₂ or He). However, V_s is significantly restored at elevated pressures of H₂, depending on the quantity of the additive used. The higher the loading of the additives, the lower the V_s parameter. Although V_s appears to be slightly larger at all pressures in the presence of magnetite compared with that in haematite, the observed variations are within the experimental errors of measurement. The effect of these additives in a helium atmosphere is to destroy V_s totally by producing a thermosetting (non-softening or swelling) solid material.

The effects of these oxides on the V_s parameter at a slower heating rate (5 K min⁻¹) are plotted in Figure 2. As was noted at 60 K min⁻¹, pyrolysis of coal in the presence of iron oxides destroys V_s at all pressures of He: the coal behaved as a thermosetting material, and visual examination of the resulting coke showed no evidence of softening or agglomeration. In contrast, in H₂ at 5 K min⁻¹, the resulting coke (pyrolysed in the presence

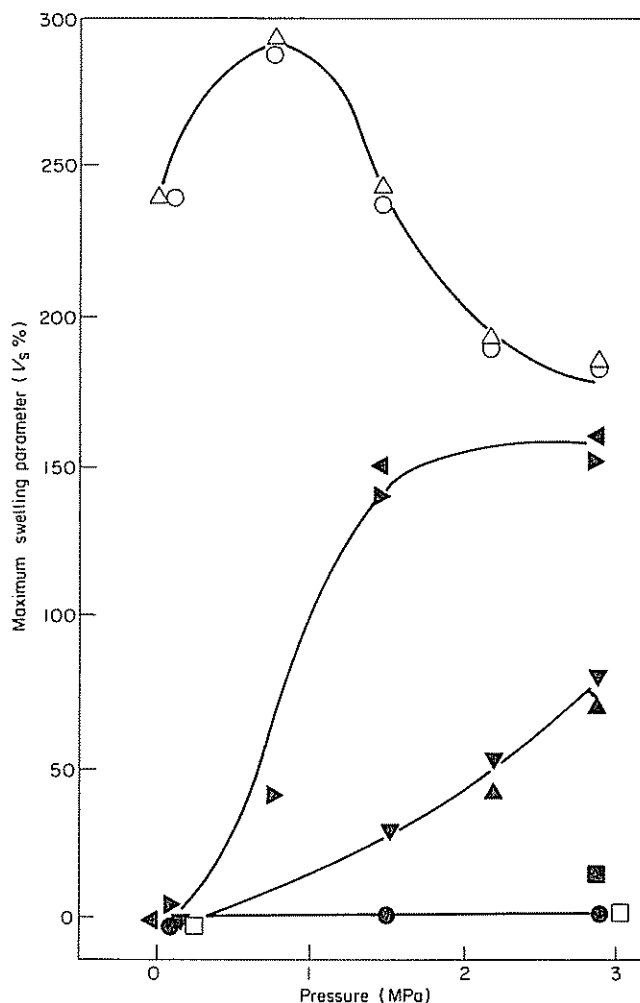


Figure 1 Effect of iron oxide additives (dry mixed) on the maximum swelling parameter (V_s %) for bituminous coal PSOC 1197 (lvb, Lower Kittanning Seam, PA); coal particle size, $-74 \mu\text{m}$; heating rate, 60 k min⁻¹; coal Δ H₂, \circ He; coal + 23.16 wt% Fe₂O₃ \blacktriangle H₂, \bullet He; coal + 22.3 wt% Fe₃O₄ ∇ H₂, \square He; coal + 5.79 wt% Fe₂O₃ \blacktriangledown , \blacksquare He

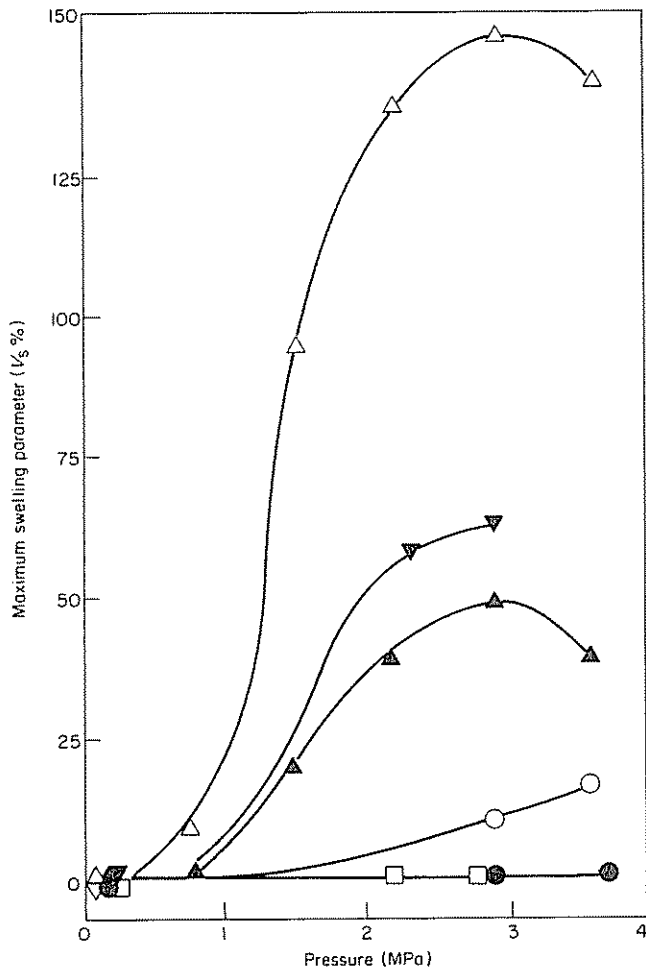


Figure 2 Effect of iron oxide additives (dry mixed) on the maximum swelling parameter ($V_s\%$) for coal PSOC 1197; coal particle size, $-74\ \mu\text{m}$; heating rate, $5\ \text{K}\ \text{min}^{-1}$; see Figure 1 for legend

of Fe additives) appears to be more fused and agglomerated compared with the untreated coal. This observation suggests that the coal passed through a highly fluid intermediate phase during pyrolysis (in H₂). It can be seen (Figure 2) that V_s in H₂ for the coal loaded with iron oxide is significantly lower than that for the untreated coal. This decrease in V_s in H₂ is attributable to the increased fluidity of the coal melt during pyrolysis. A highly fluid melt is unable to 'trap' volatiles, which is a necessity for a high degree of swelling. As will be evident later, at $5\ \text{K}\ \text{min}^{-1}$ in H₂, the iron oxides are partly reduced to elemental iron, which facilitates hydrogenation and ultimately leads to a highly fluid melt.

Figure 3 demonstrates the effect of haematite or magnetite addition on the volume contraction parameter as a function of loading of additives in H₂ and He (heating rate $60\ \text{K}\ \text{min}^{-1}$). Additions of iron oxides have dramatic effects on the V_c parameter, which at $0.1\ \text{MPa}$ (H₂ or He) is reduced from $\approx 30\%$ to $<5\%$. However, V_c is significantly restored to varying degrees (depending on gas atmosphere and the quantity and quality of the additives) at elevated pressures ($2.9\ \text{MPa}$). In general, the greater the loading of the iron oxides, the lower the V_c parameter. In addition, the V_c parameter is smaller in a helium atmosphere, and for identical loading of the additives, the V_c parameter is slightly lower in Fe₂O₃ compared with that in Fe₃O₄. The influence of the iron

oxide compounds on V_c at $5\ \text{K}\ \text{min}^{-1}$ is similar to that noted at $60\ \text{K}\ \text{min}^{-1}$. The addition of iron oxides significantly reduces the V_c parameter at low pressures ($<1.5\ \text{MPa}$ H₂). However, at elevated pressures ($>1.5\ \text{MPa}$) of H₂, the V_c parameter is almost identical to that of the untreated coal. In He, V_c does not increase to the same extent with increase in pressure. The presence of the iron compounds (in He atmospheres) reduces the plastic range significantly. In addition, it is noted that the greater the loading of the iron additives, the narrower the plastic range. At the slow heating rate ($5\ \text{K}\ \text{min}^{-1}$), the plastic range ($T_r - T_s$) at elevated pressures of H₂ in the presence of iron oxides is wider than that of the untreated coal.

Weight loss and gaseous product yield

Figure 4 shows the effect of Fe₂O₃ addition on weight loss during pyrolysis in H₂ and He at $60\ \text{K}\ \text{min}^{-1}$ (to a

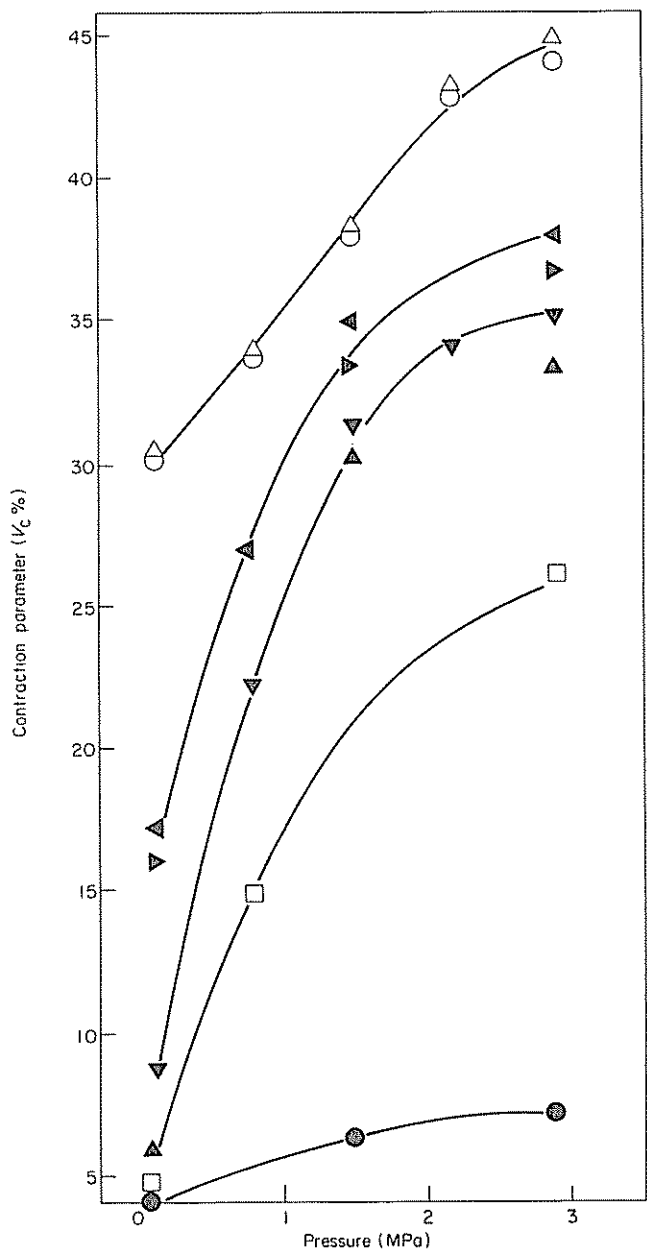


Figure 3 Effect of iron oxide additives (dry mixed) on the contraction parameter ($V_c\%$) for coal PSOC 1197; coal particle size, $-74\ \mu\text{m}$; heating rate, $60\ \text{K}\ \text{min}^{-1}$; see Figure 1 for legend

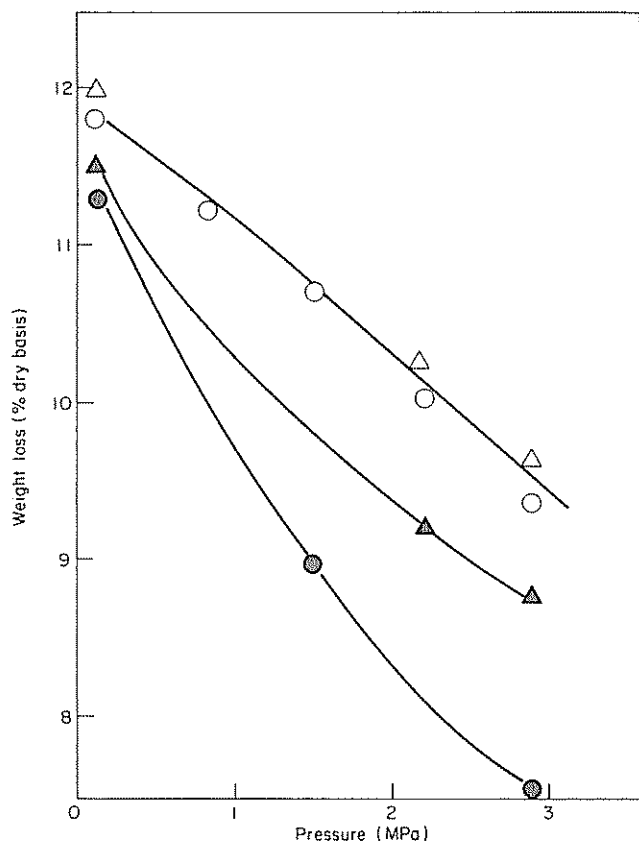


Figure 4 Effect of iron oxide additives (dry mixed) on weight loss during pyrolysis of coal PSOC 1197; coal particle size, $-74 \mu\text{m}$; heating rate, 60 K min^{-1} ; see Figure 1 for legend

maximum temperature of $\approx 900 \text{ K}$). Addition of 23.2 wt % Fe_2O_3 significantly reduces the extent of weight loss at all pressures. However, this effect is more pronounced at elevated pressures. In addition, the weight loss is lower in He compared with that in H_2 . The influence of Fe_2O_3 addition at 5 K min^{-1} (to a maximum temperature of $\approx 913 \text{ K}$) in He and H_2 is shown in Figure 5. The qualitative effects of Fe_2O_3 addition at this slow heating rate (in He) are similar to those at 60 K min^{-1} . The weight loss is slightly reduced in the presence of Fe_2O_3 (in He). However, at 5 K min^{-1} in H_2 , weight loss is significantly greater in the presence of Fe additives compared with that of the untreated coal. It also appears that the extent of weight loss is not a function of H_2 pressure, as is noted in the case of the untreated coal (Figure 4).

The total gas yield (in mmol/g coal at STP) during pyrolysis of the coal in the presence of Fe_2O_3 is listed in Table 2. The presence of Fe_2O_3 reduces the yield of H_2 , hydrocarbon gases ($\text{C}_1\text{--C}_4$), CO and H_2S . Although the yield of CO decreases, the yield of CO_2 increases slightly in the presence of Fe_2O_3 . This effect of haematite addition on the pyrolysis yield is consistent with those reported previously^{1,3}.

X-Ray diffraction (XRD) studies and thermodynamic consideration

A series of XRD patterns was generated to examine the fate of the added iron oxides pyrolysed with the coal in various atmospheres. The compositions of the resulting iron species identified by XRD are summarized in Table 3 (He atmosphere) and Table 4 (H_2) as a function of

pyrolysis conditions when Fe_2O_3 was added. One can see in Table 3 that, regardless of the heating rate (5 or 60 K min^{-1}) or pressure ($0.1\text{--}3.6 \text{ MPa}$), co-pyrolysis of coal in He with haematite at 803 K results in the formation of magnetite. Such transformation of haematite into magnetite is also evident by visible examination of the reactants and products. Haematite is a bright red material which turns black when transformed into magnetite. In addition, the data (Table 3) indicate that this transformation ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$) occurs in the temperature region $763\text{--}803 \text{ K}$ in the presence of this coal.

In H_2 , the composition of the products of pyrolysis of coal with Fe_2O_3 depend both on heating rate (residence

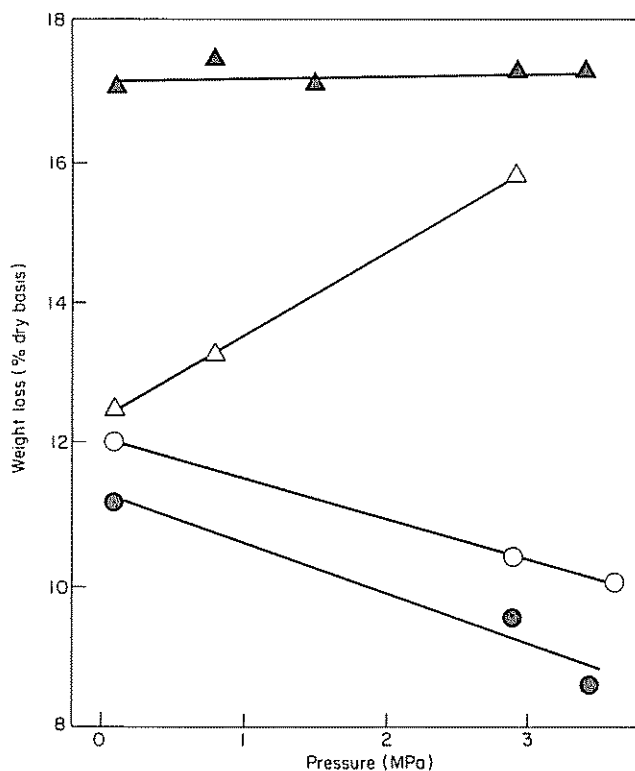


Figure 5 Effect of iron oxide additives (dry mixed) on weight loss during pyrolysis of coal PSOC 1197; coal particle size, $-74 \mu\text{m}$; heating rate, 5 K min^{-1} ; see Figure 1 for legend

Table 2 Effect of Fe_2O_3 on yield of gaseous products^a

Species	Yield (mmol/g coal; STP)		
	Coal [A]	Coal + 23.2 wt % Fe_2O_3 [B]	Ratio B/A
H_2	0.124	0.047	0.377
C_2H_6	0.059	0.02	0.347
CH_4	0.134	0.101	0.827
C_3/C_4	0.212	0.043	0.202
C_2H_4	<0.001	<0.001	-
H_2S	0.003	0.001	0.3
CO_2	0.004	0.005	1.2
CO	0.018	0.008	0.4
Total	0.55	0.224	0.4

^aSample pyrolysed by heating rapidly to 823 K under 2.9 MPa N_2 ; soak time 30 min

Table 3 Summary of results of XRD studies on the products of co-pyrolysis of coal and haematite in He

Experimental conditions				
Heating rate (K min ⁻¹)	Maximum temperature (K)	Pressure range (MPa)	Initial reactant(s)	Final product(s)
5 or 60	803, 823 or 923	0.1-3.6	Fe ₂ O ₃	Fe ₂ O ₃
5 or 60	803	0.1-3.6	Coal + Fe ₂ O ₃	Fe ₃ O ₄
5 or 60	763	0.1-3.6	Coal + Fe ₂ O ₃	Fe ₂ O ₃

Table 4 Summary of results of XRD studies on the products of co-pyrolysis of coal and haematite in H₂

Experimental conditions				
Heating rate (K min ⁻¹)	Maximum temperature (K)	Pressure range (MPa)	Initial reactant(s)	Final product(s)
60	903	0.1-2.9	Fe ₂ O ₃	Fe ₃ O ₄
60	903	0.1-2.9	Coal + Fe ₂ O ₃	Fe ₃ O ₄
5	623	1.5	Fe ₂ O ₃	α-Fe, Fe ₃ O ₄
5	903	0.1-3.6	Coal + Fe ₂ O ₃	α-Fe, FeO
5	623	1.5	Coal + Fe ₂ O ₃	α-Fe, Fe ₃ O ₄

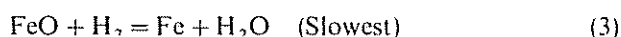
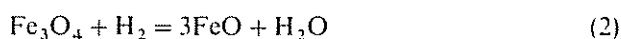
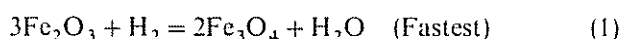
Table 5 Summary of results of XRD studies on the products of co-pyrolysis of coal and magnetite in He

Experimental conditions				
Heating rate (K min ⁻¹)	Maximum temperature (K)	Pressure range (MPa)	Initial reactant(s)	Final product(s)
5 or 60	903	0.1-2.9	Fe ₃ O ₄	Fe ₃ O ₄
5 or 60	903	0.1-2.9	Coal + Fe ₃ O ₄	Fe ₃ O ₄

Table 6 Summary of results of XRD studies on the products of co-pyrolysis of coal and magnetite in H₂

Experimental conditions				
Heating rate (K min ⁻¹)	Maximum temperature (K)	Pressure range (MPa)	Initial reactant(s)	Final product(s)
60	903	0.1-2.9	Fe ₃ O ₄	Fe ₃ O ₄
60	903	0.1-2.9	Coal + Fe ₃ O ₄	Fe ₃ O ₄
5	623	0.1-2.9	Fe ₃ O ₄	Fe ₃ O ₄
5	623	0.1-2.9	Coal + Fe ₃ O ₄	α-Fe and Fe ₃ O ₄
5	823	0.1-2.9	Coal + Fe ₃ O ₄	α-Fe and Fe ₃ O ₄
5	903	2.9	Coal + Fe ₃ O ₄	α-Fe and FeO

time) and on the maximum temperature (*Table 4*). Thermodynamically, the reduction of Fe₂O₃ to Fe₃O₄ in H₂ is feasible even at room temperature. Because this reduction is noted to be a function of heating rate and pressure¹⁵⁻¹⁸, it is suggested that the kinetics of the reduction determined the product composition. At 60 K min⁻¹ in H₂, Fe₂O₃ is reduced to Fe₃O₄ whether or not coal is present. At 5 K min⁻¹ at all H₂ pressures, Fe₂O₃ is reduced to magnetite and α-iron (at 623 K) or to FeO and α-iron (at 903 K). From the literature¹⁵⁻¹⁸ the reduction of Fe₂O₃ to Fe can occur by the following sequence of reactions:



In addition to the above reactions, CO can also reduce iron oxides. It should also be stressed that the relative rate of Reaction (1) is fast, with the reduction in the subsequent steps (2) and (3) being much slower.

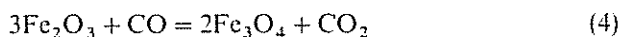
When Fe₃O₄ is pyrolysed at 60 K min⁻¹ in He (*Table 5*) or H₂ (*Table 6*), no change in its composition can be identified by XRD, even at the highest pressure of H₂ (3.6 MPa). At 5 K min⁻¹ in H₂, the reduction of Fe₃O₄ depends on: (a) the maximum temperature; and (b) the presence or absence of coal (*Table 6*). For example, when Fe₃O₄ alone is heated to 623 K (in 3.6 MPa H₂), no significant reduction is noted. However, at identical experimental conditions (0.1-3.6 MPa H₂), magnetite is partly reduced to α-Fe in the presence of coal, suggesting that coal promotes the reduction process better than 2.9 MPa H₂. This finding suggests that, in this case, the hydrogen evolving from carbonizing coal is more reactive

than the gaseous H₂. The products of co-pyrolysis at 823 or 623 K are identified as α-Fe and Fe₃O₄, whereas those at 903 K are identified as α-Fe and FeO (with no detectable Fe₃O₄ peaks present). Devolatilization of coal in the presence of Fe₂O₃ reduces the yield of H₂S (Table 2), which is as expected⁹⁻¹³. This lowering of H₂S concentration is paralleled by the formation of FeS (troilite, identified by XRD). FeS peaks can be identified whenever coal is co-pyrolysed with haematite or magnetite, regardless of heating rate or gas atmosphere (not shown separately on each table, Tables 3-6).

Possible mechanisms of decaking reactions by iron oxides

The added iron oxides can influence the thermoplastic properties of coal by the following possible mechanisms. Iron oxides can exert a physical influence on the coal melt by serving as a 'diluent' (the presence of diluent may facilitate evolution of the devolatilized products). As discussed previously^{2,8}, the diluent effect of an additive (such as SiO₂) on the thermoplastic properties of coal is relatively small. The observed influence of these iron oxides on the measured parameters may be attributed primarily to a chemical and/or catalytic effect. Haematite or magnetite can have catalytic roles during the pyrolysis of coal by promoting solid formation at the expense of tar and hydrocarbon yields. This catalytic effect of iron oxides on coal pyrolysis has also been reported by Cypres *et al.*⁹⁻¹¹, who suggested that iron oxides catalyse polymerization reactions of the intermediate products of pyrolysis (i.e., coal melt) to produce char at the expense of the hydrocarbon gases and tars.

As discussed previously¹⁻⁸, a minimum degree of fluidity is essential for the coal to swell. Depletion of the liquid materials can explain why the thermoplastic properties are markedly reduced when coal is pyrolysed in the presence of these oxides. Haematite can influence the thermoplastic properties of coal by chemical interaction with the pyrolysis products. The results demonstrate that haematite reduces the plastic properties of coal and in the process is transformed into magnetite in the temperature range 763-803 K, a region where softening of coal occurs. It is suggested that transformation of haematite into magnetite by Reaction (1) requires H₂, which is supplied by the available hydrogen in coal. This transfer of hydrogen not only facilitates reduction of Fe₂O₃ to Fe₃O₄, but also dramatically affects the nature of the thermoplastic properties of coal. In the absence of donor hydrogen to stabilize the generated free radicals, retrogressive reactions may occur to produce relatively higher molecular weight materials. The reaction



can also reduce haematite to magnetite if enough CO is present. However, the reduction of haematite by the reaction



has been reported not to occur below 1000 K².

The small restoration of the thermoplastic properties of the coal at elevated pressures of H₂ can be explained by suggesting that the extent of retrogressive/polymerization reactions would be lowered in the presence of gas-phase H₂. Thus, the fluidity of the coal melt is further

enhanced when pyrolysed at elevated pressures of H₂ (60 K min⁻¹), resulting in restored values of V_s. At 5 K min⁻¹ in H₂, the iron oxides are partly reduced to elemental iron (determined by XRD), which serves as sites for H₂ dissociation¹⁵⁻¹⁸. The resulting hydrogenation reactions lead to the formation of a highly fluid system. This highly fluid coal-additive system is unable to 'trap' volatiles or swell (at 5 K min⁻¹, 2.9 MPa H₂).

SUMMARY AND CONCLUSIONS

The addition of Fe₂O₃ or Fe₃O₄ (at ≥ 5 wt %, dry mixed) to a bituminous (lvb) coal destroyed the maximum swelling parameter (V_s) of the coal at 0.1 MPa in H₂ or He. As also observed in the case of added potassium or calcium compounds^{2,4,7,8}, the effectiveness of iron oxides as decaking additives appears to increase with their increasing concentration. However, at elevated pressures of H₂, V_s of the coal was significantly restored. At all pressures of He, the V_s parameter was reduced to zero (or to a very small value). The presence of Fe₂O₃ or Fe₃O₄ additives resulted in increased solid yield (i.e., reduced weight loss of coal during pyrolysis). This increase in solid formation was accompanied by a slight decrease in the total light hydrocarbon gases monitored (primarily C₃/C₄, C₂H₆). It is suggested that char-forming reactions that can be promoted by iron oxides facilitate increased (thermosetting) solid yield at the expense of formation of tars and light gases. In the case of Fe₂O₃, a chemical role (i.e., conversion of Fe₂O₃ to Fe₃O₄ and consumption of H₂ in the process) of the additive may also influence the nature of the thermoplastic properties of coal. It is noted that at elevated pressures of H₂, depending on the composition of the additive (Fe₂O₃ or Fe₃O₄) used, the maximum swelling parameter (V_s %) was restored. The effect of pressure is to increase the fluidity of the coal melt. Therefore, at elevated pressure, the thermoplastic properties of the coal in the presence of the additives are determined by the balance between the decrease in fluidity caused by char-forming reactions promoted by the additives and the increased fluidity of the coal system induced by elevated pressure of H₂. At elevated pressures, the maximum swelling parameter is greater in H₂ than in He. This behaviour is explained by suggesting that the effects of H₂ are: (a) to decrease the extent of char-forming reactions; and (b) to reduce iron oxides to elemental iron, which serves as a hydrogenation catalyst, especially at the longer residence time resulting from a very slow heating rate (i.e., 5 K min⁻¹).

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Study of the pore structure and reactivity of Canadian coal-derived chars

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The pore volume, surface area, compressibility and reactivity of 12 chars derived from Canadian coals ranking from lignite to anthracite, have been determined by mercury porosimetry, gas adsorption-desorption with N_2 and CO_2 adsorbates, helium and mercury densities and thermogravimetric technique. A comparison of the pore structure between the chars and their parent coals was made based on the results obtained from these techniques. The reactivity of chars was correlated with their physical and chemical properties. It has been found that a single relationship exists between the helium density and the carbon content of the coals and their chars. The chars are more porous but less compressible when compared with their parent coals.

(Keywords: char; pore structure; reactivity)

The depletion of oil reserves is a future worldwide problem and alternative energy sources are being sought. One potential alternative receiving increased interest is the direct or indirect conversion of coal or biomass into liquid fuels and the commercial production of gasoline from coal in South Africa proves that this is technologically practical. Recently, the integrated gasification combined cycle process has emerged as one of the most promising new technologies for coal-based electric power generation. The efficiency of any of these coal conversion processes depends largely on coal reactivity, which is greatly influenced by its chemical and physical properties.

In a previous publication¹, it was shown that the reactivity of a range of Canadian coals varied with their pore structure and coal rank. Chars derived from eight Canadian coals have also been studied with respect to the gasification kinetics and the impact on char reactivity by the parent coal rank, and by the CaO and MgO contents of the chars². However, the pore system of these chars was not examined and so the object of this study was to determine the surface area and pore structure of a series of chars and examine the effect of these parameters on the char reactivity.

EXPERIMENTAL

Materials

The chars used consisted of the eight chars used previously² and four additional chars prepared from Canadian coals; Onakawana (lignite) from Ontario, Bienfait (lignite) from Saskatchewan, Tulameen (subbituminous) from Alberta and Mt. Klappan (anthracite) from British Columbia. The devolatilization procedure was similar to that used to prepare the first batch of 8 chars² but in this instance the coal samples (particle size 3–6 mm) were heated at a rate of $5^\circ C \text{ min}^{-1}$

under a flow of N_2 at $2 \text{ dm}^3 \text{ min}^{-1}$ until a temperature of $900^\circ C$ was reached. Tables 1 and 2 show the chemical analyses of the four coals and their derived chars. The analyses of the other eight coals and their chars were reported previously². For physical measurements, the particle size of the char samples was controlled at 425–212 μm (4–70 US standard mesh).

Reactivity measurements

The reactivity of char samples was determined thermogravimetrically using an electrobalance at $500^\circ C$ with air as the gasification medium. A detailed procedure and the apparatus used have been described in an earlier publication².

Apparatus

The mercury densities and pore volumes in the macropore (2.98– $0.06 \mu m$) and mesopore (0.06– $0.0036 \mu m$) ranges were determined using a commercial mercury porosimeter. The surface tension of mercury and contact angle were assumed to be 0.485 Nm^{-1} and 130° . The helium density measurement was obtained using a helium pycnometer. The N_2 and CO_2 sorption studies were conducted using a Carlo Erba Sorptomatic 1822. For N_2 sorption (77 K), the equilibration time was automatically controlled such that negligible change in pressure was observed over a 4 min period for each pressure point. For CO_2 adsorption (195 K) the equilibration time was constantly set for 1 h. Equilibrium pressure (P) was gradually increased until it reached 30% or more of the saturation pressure (P_0).

The N_2 surface area and pore size distribution were determined using the BET equation and a procedure developed by Barrett, Joyner and Halenda³ in which the apparent pore radius was calculated by the Kelvin equation⁴. An effective cross-sectional area of 0.162 nm^2 was assumed for the N_2 molecule.