

## STABLE SURFACE OXIDES FORMED DURING OXIDATION OF LIGNITE CHARS

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### ABSTRACT

Temperature Programmed Desorption (TPD) experiments were conducted to investigate the properties of stable surface oxides formed during low temperature oxidation of lignite chars. For both Loy Yang and Bowmans char, TPD spectra demonstrate a transition at low conversion. A linear increase is found in the fraction of remaining carbon associated with stable surface oxides as conversion increases for both chars. Compared to Loy Yang char, Bowmans char has a significantly greater number of stable surface oxides yielding CO<sub>2</sub> during TPD. It is proposed that the abundant inorganic material in Bowmans char catalyses the formation of CO<sub>2</sub>-yielding stable surface oxides.

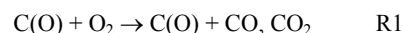
### INTRODUCTION

Recent literature has demonstrated the importance of stable surface oxides during carbon oxidation. These oxides influence the overall reaction rate and are involved in the formation of primary CO<sub>2</sub>. Our interest in stable surface oxides arises from an investigation into the primary CO/CO<sub>2</sub> ratio for lignite chars. In this paper we investigate by Temperature Programmed Desorption (TPD) the properties of stable surface oxides formed during oxidation of two Australian lignite chars.

### LITERATURE REVIEW

During oxidation of solid carbons, stable surface oxides are created in large numbers. These oxides remain on the reacting surface under an inert gas or vacuum at the reaction temperature. However, upon increasing the temperature under such conditions, stable surface oxides will desorb as CO and CO<sub>2</sub>. This procedure constitutes the common technique for investigating stable surface oxides known as Temperature Programmed Desorption (TPD). Numerous TPD studies of the carbon-oxygen reaction exist in the literature, from whence most of our knowledge of stable surface oxide properties is derived. It is generally agreed amongst these works that stable surface oxides are formed with a wide range of thermal stabilities and that CO is the major desorption product. Distributions of activation energies for desorption of CO during TPD have been determined by Ma and Haynes (1996) for Spherocarb; Du et al. (1990) for soot (both pure and calcium-impregnated); and, Calo and Hall (1991) for various coal chars and phenolic resin char. Zhuang et al. (1994) identified particular chemical structures of oxides that yield CO (carbonyl and ether groups) or CO<sub>2</sub> (lactone and/or acid anhydride groups).

Early research into the kinetics of carbon oxidation assumed that stable surface oxides inhibited the reaction by occupying active sites. However, recent studies (Haynes and Newbury, 2000; Zhuang et al., 1995; Zhuang et al., 1996) using isotopic labelling techniques have shown that all stable surface oxides may be "turned over" during oxidation, regardless of their stability under inert conditions, via the reaction



where C(O) represents a CO-yielding oxide. The precise stoichiometry of R1 is unknown, however it may be described as the interaction of a stable surface oxide with gaseous oxygen producing new oxides and either CO or CO<sub>2</sub>. Reaction R1 therefore emerges as a possible major route for primary CO<sub>2</sub> formation during oxidation of pure carbons.

Values of the CO<sub>2</sub> mole fraction obtained from TPD vary in the literature. For the pure carbons, ie. those containing negligible amounts of inorganic material, CO<sub>2</sub> mole fractions are generally less than 0.2 (Lear et al., 1990; Ma and Haynes, 1996; Du et al, 1990). However, for Montana lignite chars - containing substantial amounts of calcium, magnesium and iron - Senneca et al. (1998) indicate values between 0.38 and 0.65. Radovic et al. (1991) indicate values of 0.07-0.26 for pure carbons (graphon and saran char) and 0.26-0.50 for various coal chars including calcium-impregnated lignite. Clearly, the possibility is raised that the presence of inorganic material in solid carbons may affect the balance of products evolved during TPD.

### EXPERIMENTAL METHOD

#### Char preparation

Large particles of Bowmans and Loy Yang coal (5-10 mm) were inserted into the hot zone of a tube furnace under a nitrogen flow. Pyrolysis took place at 1000 C for a duration of 5 minutes before cooling under nitrogen for a further 5 minutes. The particles were then crushed to various pulverised size grades and stored in airtight containers. Typical compositions of the coals and chars are given in Table 1.

#### Oxidation/TPD

The apparatus consists of an externally heated, 10 mm ID horizontal alumina tube to which reactant or inert gas is

supplied at atmospheric pressure. Small (<20 mg) char samples are spread thinly on an alumina combustion boat, which is centrally situated in the tube. A quartz probe is inserted in the tube and withdraws a gas sample for continuous analysis by mass spectrometer (Hewlett-Packard HP5973). Gas mixtures are made by blending single-component gases, of Ultra-High Purity grade, using mass flow controllers. Pure helium or helium/argon mixtures are used as inert gases and a helium/oxygen/argon mixture is used as the reactant gas. Argon acts as a tracer species for accurate determination of product concentrations from the mass spectrometer output. A molecular-sieve trap has been used to remove traces of oxygen from the inert gases and care has been taken to prevent oxygen ingress to the alumina tube through the use of an argon-purged seal.

	Proximate analysis (% dry basis)	
	Loy Yang coal	Bowmans coal
Ash content	1.4	12
Volatile matter	47	40
Fixed carbon	51	48
Expected level of major inorganic species in char based on typical ash analysis and fixed carbon content of coal (g/g carbon)		
	Loy Yang char	Bowmans char
Na	0.0042	0.033
Ca	0.0012	0.012
Mg	0.0021	0.023
Fe	0.0012	0.0034

**Table 1:** Typical compositions of coals and chars.

Oxidation of samples was conducted at 400 C and 0.21 atm oxygen immediately prior to TPD. Char samples of particle size <32  $\mu\text{m}$  were placed in a cool zone of the alumina tube for several minutes under an inert gas flow in order for air to diffuse from the char pores. The sample was then moved to the hot zone of the tube. Once the gas sample probe was in position, oxidation was initiated by switching the gas flow from inert to reactant. The time allowed for oxidation was varied between experiments to achieve a range of carbon conversion values. Oxidation was ceased by switching the gas flow back to inert. At this point the sample was allowed to cool by typically 200 C over several minutes.

The TPD stage of the experiment was conducted by increasing the temperature of the sample at 50 K/min to a final temperature of 1200 C. The sample was then cooled to 600 C, and the gas flow was switched to reactant in order to oxidise all remaining carbon. Data was also obtained for char samples that were not subjected to oxidation, in which case TPD commenced at room temperature.

## RESULTS AND DISCUSSION

It was verified that the oxidation of char samples took place under ‘Zone 1’ conditions – i.e. that mass transfer did not influence the reaction rates. In previous work (Battye and Ashman, 2003) we measured oxidation rates for the same chars at identical temperature and oxygen partial pressure using a fixed-bed reactor. It was confirmed that the rates determined in the fixed bed

reactor were independent of particle size up to at least 75  $\mu\text{m}$ , indicating the absence of mass transfer effects. The rate data obtained using the apparatus described in this paper does not deviate significantly in magnitude, or trend with respect to conversion, from that obtained previously using the fixed-bed reactor.

During ‘blank’ TPD experiments, conducted with no char sample present, it was found that the mass spectrometer background signals for ions of mass 28 and 32 increased once the temperature exceeded 900-1000 C. The cause of this anomaly could not be determined and hence, for quantitative purposes, we only consider data taken up to 900 C. The literature suggests that for coal chars and other solid carbons, no stable surface oxides survive at greater than 1200 C and that only a small fraction of the whole are stable at 900-1200 C.

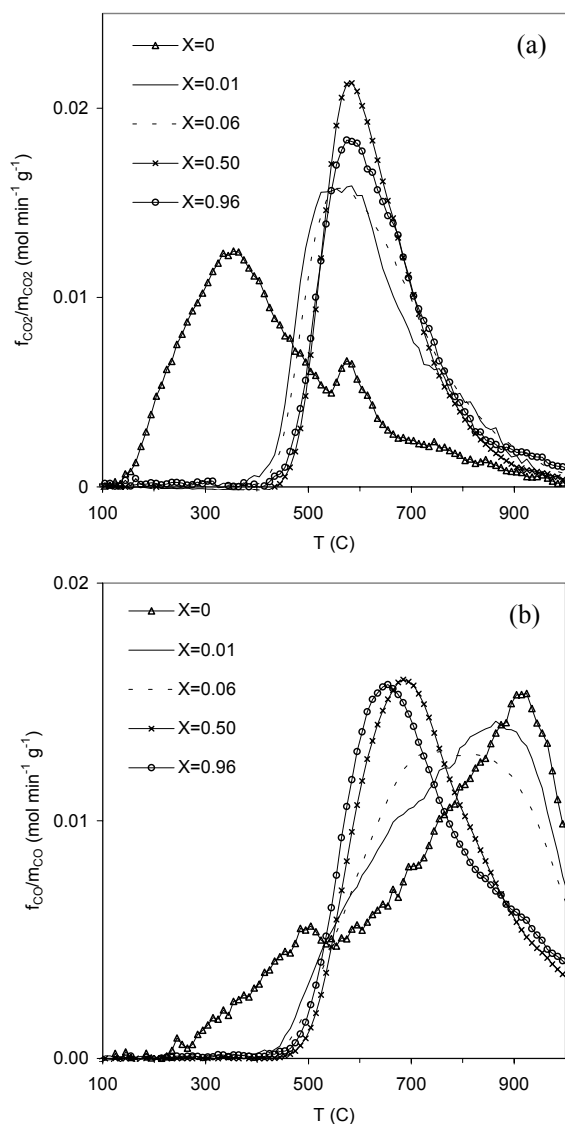
### Characteristics of TPD spectra

TPD spectra for Loy Yang and Bowmans chars at selected fractional conversions,  $X$ , are shown in Figures 1 and 2 respectively. Temperature is plotted on the horizontal axes and the quantity  $f_i/m_i$  is plotted on the vertical axes, where  $f_i$  is the flow-rate of species  $i$  ( $\text{mol min}^{-1}$ ) and  $m_i$  is the mass of carbon desorbed as species  $i$  up to 900 C (g). Hence, the areas under each curve are equal up to 900 C. In this way we may observe the ‘temperature distribution’ of CO- and CO<sub>2</sub>-yielding stable surface oxides. This has been demonstrated by Ma et al. (1993) to have a close correspondence in shape to the activation energy distribution.

From Figures 1 and 2 we observe that the spectra for the non-oxidised chars ( $X=0$ ) are quite different from those at higher  $X$ . The stable surface oxides at  $X=0$  were formed upon exposure of the freshly-pyrolysed chars to air at room temperature. As expected, there are a significant number of oxides that are stable below the reaction temperature (400 C) since the non-oxidised chars were subjected to TPD beginning at room temperature.

For Loy Yang chars, as  $X$  increases there is minimal change in the shape of CO<sub>2</sub> spectra. However, from  $X=0$  to 0.06 the CO spectra exhibit a transition from a high temperature peak near 900 C, to a low temperature peak near 650 C which is maintained from  $X=0.50$  to 0.96. We note that for  $X>0$  there is only one peak for each of CO and CO<sub>2</sub>. The location and shape of these peaks are comparable to those observed in the literature for pure carbons.

Compared to the spectra for Loy Yang chars, those shown in Figure 2 for Bowmans chars are quite different. The CO<sub>2</sub> spectra for  $X>0$  in Figure 2a all exhibit either two peaks, or one peak and a prominent shoulder. Dual peaks are a common feature of TPD spectra in the literature for non-pure carbons. Du et al. (1990) have shown that adding calcium to soot introduces an additional peak at higher temperature in the CO spectra. Zhang and Calo (2001) find that both CO and CO<sub>2</sub> spectra are dual-peaked for Pittsburgh #8 and Wyodak coal chars, with higher-temperature peaks becoming more prominent as conversion increases. Radovic et al. (1991) list the temperatures at which peaks occur in their spectra, from which we find that dual-peaks are in

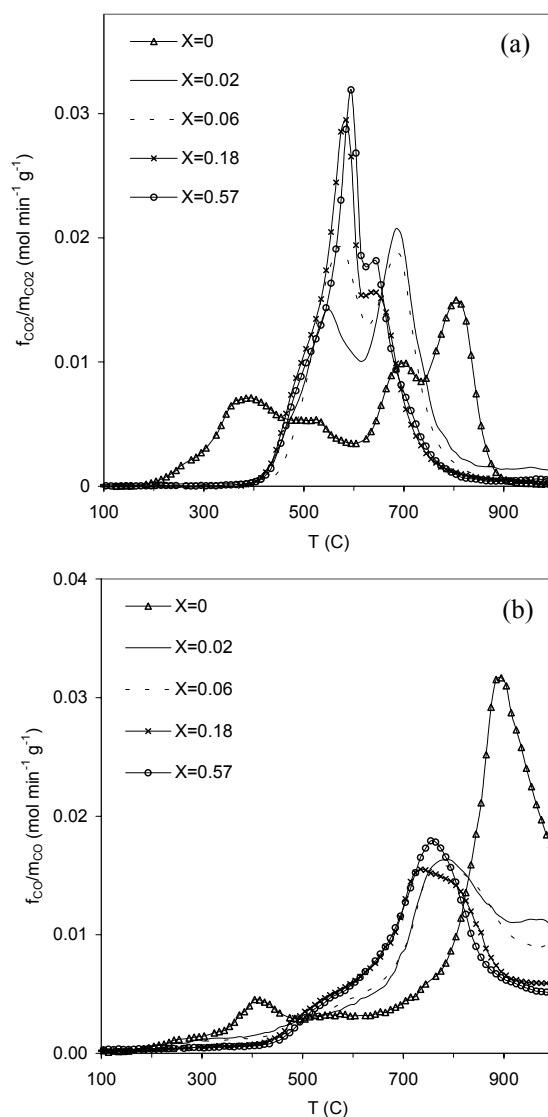


**Figure 1:** (a) CO<sub>2</sub>, and (b) CO TPD spectra for Loy Yang char.

general associated with the non-pure carbons.

Similar to the Loy Yang CO spectra, the Bowmans CO<sub>2</sub> spectra from  $X=0$  to 0.06 demonstrate a transition where the lower-temperature peaks increasingly dominate. From  $X=0.18$  to 0.57 there is little change in shape. The CO spectra are relatively uniform, excepting the  $X=0$  spectrum which peaks near 900 C, similar to its Loy Yang counterpart.

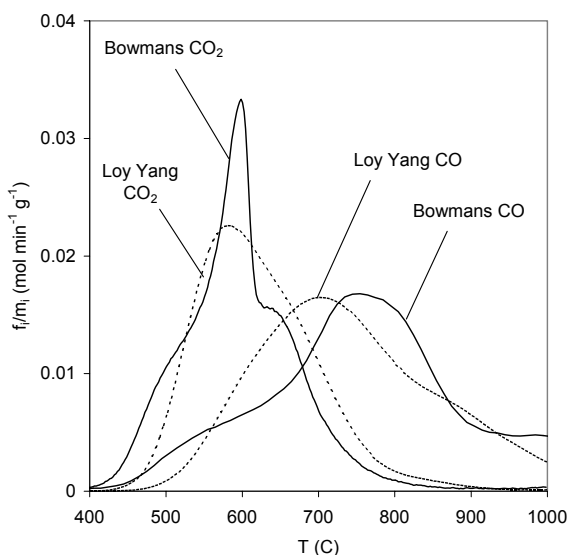
We have observed in the case of both chars that the shapes of TPD spectra - and hence the activation energy distributions of surface oxides - are in transition at low conversion, but subsequently remain steady over a broad range of conversion. “Steady” TPD spectra for Loy Yang and Bowmans chars, are shown in Figure 3. Spectra obtained for Loy Yang char from  $X=0.50$  to 0.96, and Bowmans char from  $X=0.18$  to 0.57 show minimal deviation from those in Figure 3. We are therefore able to compare the characteristics of conversion-independent spectra that are representative of each char.



**Figure 2:** (a) CO<sub>2</sub>, and (b) CO TPD spectra for Bowmans char.

It is evident in Figure 3 that, for each of the desorption products, the spectra are distributed over similar temperature ranges and that peaks occur at similar locations. There are, however, significant differences in spectra shape between the two chars. The Bowmans CO<sub>2</sub> spectrum displays a sharp peak at 600 C and a shoulder at 650 C, whereas the Loy Yang equivalent is a single broad peak centred on 600 C. The Bowmans CO spectrum appears shifted towards higher temperatures in comparison to the Loy Yang equivalent. Another obvious feature of Figure 3 is that CO spectra peak at higher temperatures than the CO<sub>2</sub> spectra. This result is commonly found in the TPD literature, and implies that the average stability of CO-yielding stable surface oxides is higher than that of CO<sub>2</sub>-yielding stable surface oxides.

Ma and Haynes (1996) have provided evidence that the broad distribution of activation energies for desorption of stable surface oxides formed on an amorphous pure carbon is due to the morphological diversity of carbon



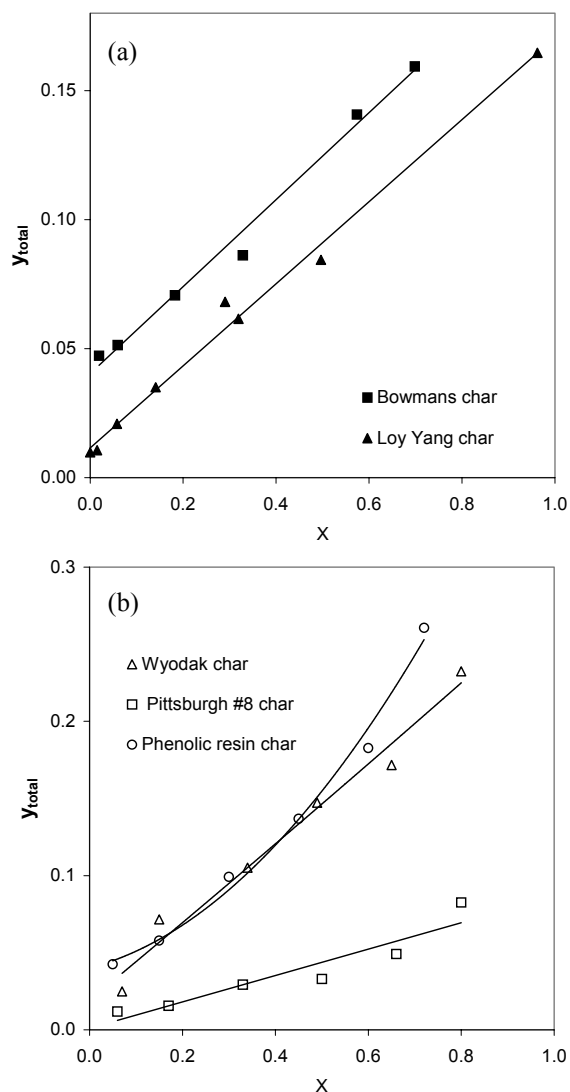
**Figure 3:** Comparison of TPD spectra for Loy Yang char ( $X=0.29$ ) and Bowmans char ( $X=0.34$ ).

bonding interactions and variety of possible oxide structures. A key observation leading to their conclusion is that activation energy distributions are insensitive to the surface density of oxides. Hence, the concept that the desorption kinetics of oxides are influenced by lateral interactions between them has been shown to be invalid in their study. Therefore, it follows that differences in shape between TPD spectra are caused by differences in the proportions of oxides with specific stabilities. For example, the sharp peak at 600 C in the Bowmans  $\text{CO}_2$  spectrum of Figure 3 may represent an increased proportion of  $\text{CO}_2$ -yielding oxides of a particular functional group or environment within the carbon structure in comparison to that for Loy Yang char.

The above understanding of the shapes of TPD spectra can be applied to explain aspects of our results. As previously discussed, dual-peaks are generally found only for non-pure carbons in literature results. Thus, the higher level of inorganic material in Bowmans char is likely to be responsible for the distinct peaks seen in Figure 2a. We may therefore postulate that each peak corresponds to a high fraction of a particular type of  $\text{CO}_2$ -yielding stable surface oxide, promoted by the abundant inorganic material. In Figure 2a, five different peaks or shoulders may be identified at temperatures greater than 400 C. From  $X=0-0.06$  we observe the relative heights of these peaks change, until at  $X>0.06$  only the 600 C peak and 650 C shoulder remain. Thus, it would appear that at low conversion, some oxide types are becoming depleted as others are increasing in number. Eventually, an equilibrium is established, leading to no further significant change in the TPD spectra. The transition of Loy Yang CO spectra in Figure 1b may be explained by the same principle.

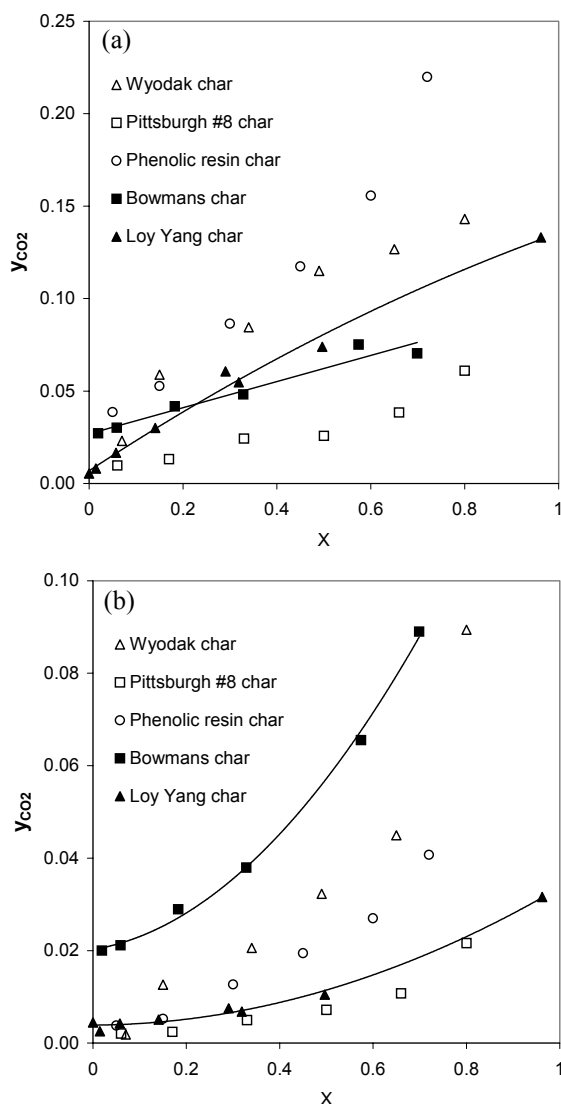
#### **Quantifying stable surface oxides**

The amount of carbon gasified as CO or  $\text{CO}_2$  at each stage in the experiment is determined by integration of  $f_i$  vs time data (in the case of carbon gasified during TPD,  $f_i$  is integrated to 900 C). Thus we are able to quantify the stable surface oxide content of the chars at varying  $X$ .



**Figure 4:** Fraction of remaining carbon associated with stable surface oxides,  $y_{total}$ , versus  $X$  for (a) Loy Yang and Bowmans chars; and (b) Wyodak, Pittsburgh # 8 and phenolic resin chars – calculated from the data of Zhang and Calo (2001).

Figure 4a plots the total carbon associated with stable surface oxides as a fraction of remaining carbon,  $y_{total}$ , against  $X$  for Loy Yang and Bowmans chars. Linear trends are apparent in both cases, with approximately equal slopes. Figure 4b plots  $y_{total}$  vs  $X$ , determined from the data of Zhang and Calo (2001), for stable surface oxides formed at 420-470 C and 1 atm oxygen partial pressure. In calculating  $y_{total}$  from the coal char data of Zhang and Calo (2001), we assume char ash contents based on the proximate analyses given by Vorres (1993). For Wyodak and Pittsburgh # 8 chars in Figure 4b the trends are again linear, however a quadratic curve provides a better fit for the phenolic resin char. The combined results in Figure 4 clearly indicate that with increasing  $X$ , there is a linear or near-linear increase in the concentration of stable surface oxide sites in solid carbons derived from a wide variety of parent materials. Further evidence from the literature is provided by Su and Perlmutter (1985), and Radovic et al. (1991). Both

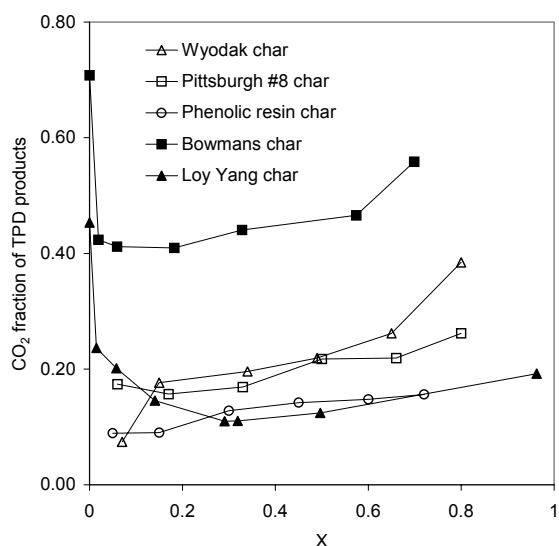


**Figure 5:** Fraction of remaining carbon associated with (a) CO-yielding; and (b) CO<sub>2</sub>-yielding stable surface oxides versus  $X$ . Open data symbols represent points calculated from the data of Zhang and Calo (2001).

studies report a monotonic increase with  $X$  in the mass fraction of oxygen associated with stable surface oxides.

In Figure 5 the fractions of remaining carbon associated with CO- and CO<sub>2</sub>-yielding stable surface oxides,  $y_{CO}$  and  $y_{CO_2}$  respectively, are plotted against  $X$ . The data of Zhang and Calo (2001) is included for comparison. The figures show a marked difference in  $y_{CO_2}$  between Loy Yang and Bowmans chars that is not observed for  $y_{CO}$ . In quantitative terms, from  $X=0.10$  to  $0.70$ ,  $y_{CO}$  for Bowmans char is within 50% of the value for Loy Yang chars. Over the same range of  $X$ ,  $y_{CO_2}$  for Bowmans chars is greater than the value for Loy Yang chars by an approximate factor of 5. We also note that  $y_{CO}$  for the both lignite chars, and  $y_{CO_2}$  for Loy Yang char are generally intermediate between the values for Pittsburgh #8 and phenolic resin chars. However,  $y_{CO_2}$  for Bowmans char is greater than for any other.

A simple explanation for the above discrepancies, as alluded to in the previous section, may be that the



**Figure 6:** CO<sub>2</sub> mole fraction of TPD products vs  $X$ . Open symbols represent the data of Zhang and Calo (2001).

abundant inorganic material in Bowmans char promotes the formation of CO<sub>2</sub>-yielding stable surface oxides. Such a hypothesis is consistent with:

- the trend found in the literature that CO<sub>2</sub> mole fractions of TPD products are higher for non-pure carbons, as discussed in the literature review;
- the finding of Du et al. (1991) that calcium catalyses carbon oxidation by creating additional active sites forming CO<sub>2</sub>; and,
- our own study of the overall rate and CO/CO<sub>2</sub> ratio during oxidation of lignite chars (Battye and Ashman, 2003) which suggests that most variation in these quantities between chars is caused by catalysis of CO<sub>2</sub> formation by inorganic material.

The previous analysis of the shapes of TPD spectra would suggest that CO<sub>2</sub>-yielding oxides supposedly formed by catalysis lead to the appearance of distinct peaks or shoulders.

A final observation relates to the change in CO<sub>2</sub> mole fraction of TPD products with  $X$ , represented in Figure 6. For each char there is a gradual increase in CO<sub>2</sub> mole fraction with increasing  $X$ , although in the case of Bowmans and Loy Yang chars this occurs after a local minimum. Zhang and Calo (2001) demonstrated that non-microporous surface area (from mesopores and external surface area) and the total CO<sub>2</sub> evolved upon TPD are correlated. They conclude that CO-yielding oxides form on microporous and non-microporous surface area, but that CO<sub>2</sub>-yielding oxides form primarily on non-microporous surface areas. According to this theory, the trend in CO<sub>2</sub> fraction of TPD products with respect to  $X$  is indicative of the changing fraction of non-microporous surface area. Given the similarity of the trends shown in Figure 6 for our chars as compared to those of Zhang and Calo, we would not disagree with their conclusion.

## CONCLUSION

The Temperature Programmed Desorption (TPD) technique has been applied to the investigation of stable surface oxides formed during low temperature oxidation of lignite chars. TPD spectra for Loy Yang and Bowmans char reveal a transition in the activation energy distribution of oxides occurring at low conversion ( $X=0-0.06$ ). For  $X>0.06$  the activation energy distribution remains generally constant. With increasing conversion, a linear increase is found in the fraction of remaining carbon associated with stable surface oxides. This trend is found in literature results also. Compared to Loy Yang char, Bowmans char has a significantly greater number of stable surface oxides yielding  $\text{CO}_2$  during TPD. It is suggested that the high level of inorganic material in Bowmans char promotes the formation of  $\text{CO}_2$ -yielding stable surface oxides. These catalytically-formed oxides are responsible for the differences observed in TPD spectra between Bowmans and Loy Yang chars.

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## NOMENCLATURE

$X$	Fractional carbon conversion
$f_i$	Flow-rate of product $i$ during TPD ( $\text{mol min}^{-1}$ )
$m_i$	Mass of carbon desorbed as product $i$ (g)
$y_{total}$	Fraction of remaining carbon associated with all stable surface oxides
$y_{CO}$	Fraction of remaining carbon associated with $\text{CO}$ -yielding stable surface oxides
$y_{CO_2}$	Fraction of remaining carbon associated with $\text{CO}_2$ -yielding stable surface oxides

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