

REACTIVITY OF CHARs FROM PYROLYSIS AND GASIFICATION OF VICTORIAN BROWN COAL

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ABSTRACT

This study investigated the reactivity of char prepared from a raw coal and a set of ion (H⁺, Na⁺, Ca⁺⁺)-exchanged Loy Yang coal samples. A series of pyrolysis/gasification experiments were carried out in helium and CO₂ atmospheres using a wire-mesh reactor at a wide range of temperatures from 500°C to 900°C. The reactivity of resulting char was measured in air at 400 °C in a thermogravimetric analyser (TGA). For both raw and ion-exchanged coal samples, the experimental results revealed that the char reactivity decreased with increasing temperature and holding times. The char reactivity was not only dependent on the catalytic activity of alkali and alkaline earth metallic (AAEM) species but also on the char structure. The volatilisation of AAEM species was found to be mainly a function of temperature. The monovalent species (Na) was always volatilised to a much larger extent than the divalent species (Mg and Ca).

Keywords: Reactivity; Pyrolysis/gasification; Victorian brown coal.

1. INTRODUCTION

The successful development of advanced gasification-based power generation technologies using Victorian brown coal greatly relies on understanding the reactivity of char during pyrolysis and gasification. This is because reactivity of char is the foundation for successful design and operation of a highly efficient gasifier. The dependence of char reactivity on various parameters such as heat treatment temperature, holding time, the form and concentration of catalyst species etc. has been observed [1-4]. These factors are interdependent and contribute to the char reactivity by changing the concentration of active carbon sites, the accessibility of these sites and/or the dispersion and concentration of catalysts present in the char [5].

Victorian brown coal features the presence of alkali and alkaline earth metallic (AAEM) species that are dispersed in coal at atomic scales and can be easily volatilised during pyrolysis/gasification [6]. Na is one of the AAEM species in the brown coal at relatively high concentration and of high volatility. The behaviour of these AAEM species during gasification is an important consideration for power generation based on the gasification of Victorian brown coal. The susceptibility of the AAEM species and the carbonaceous structure in the char from Victorian brown coal requires the measurement of char reactivity. The purpose of the present study is to experimentally investigate the relative importance of the pyrolysis/gasification conditions and

the concentration of AAEM species in the coal to the reactivity of the resulting char.

2. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

A Victorian brown coal from the Latrobe Valley, Victoria, Australia was used in this study. The ash-mined coal was air-dried below 35 °C and sieved to obtain the 106-150 µm fraction that was then sealed in bottles. The bottles were kept in a freezer until required. Prior to an experiment, the coal sample was allowed to reach equilibrium with the moisture in the air. The moisture content of the coal sample was taken into account in the calculation of the pyrolysis yields. This sample, hereafter referred to as raw coal, had an elemental composition of C, 68.5; H, 4.8; N, 0.6; S, 0.3; O, 25.7 (by difference) wt% on a daf basis (wt% - daf) and Na, 0.13; Ca, 0.03; Mg, 0.06 wt% on a dry basis (wt% - db). The raw coal sample was then washed with an aqueous solution of sulphuric acid to prepare an acid-washed (H-form) coal. A Na-form coal sample and a Ca-form coal sample were prepared by ion-exchanging methods [6, 7]. The Na-form coal contained 2.8 wt% Na and the Ca-form coal contained 3.3 wt% Ca.

2.2 Pyrolysis/gasification experiments

Pyrolysis/gasification experiments were carried out in a wire-mesh reactor [6, 7, 8] using atmospheric flow of helium or CO₂ as a carrier/reacting gas. Briefly, less than

10 mg of coal sample was sandwiched between two layers of stainless steel wire-mesh. The wire-mesh also served as the resistance heater which was stretched between two electrodes and heated with an alternating current with a computer-based temperature control system. 4 thermocouple wires (2 alumel and 2 chromel) of 41 μm in diameter were threaded through the mesh to make two thermocouples. An average of two thermocouple readings was taken as the temperature of the mesh during heating. In both helium and CO_2 experiments, a gas flow rate of 3.4 L min^{-1} (measured at 25°C and 1 bar) was used. After the pyrolysis/gasification experiments, all of the char particles were removed from the mesh and the mass of the particles was measured.

2.3 Char analysis

Char was analysed for its contents of Na, Ca and Mg by firstly ashing the char [6]. Following the acid digestion of the ash, the resulting solution was analysed using ion chromatography. A Dionex DX-500 instrument was used with a CS12A column and a cation suppressor.

2.4 Char reactivity measurement

Char reactivity was measured using a Perkin Elmer Pyris-1 TGA following the procedure outlined previously [9]. Approximately 2 mg of a char sample was placed in a platinum crucible and heated in argon for 120 min in the TGA to 105°C to remove the moisture from the char. The temperature was then increased at a rate of 50°C s^{-1} to 400°C and held for 5 min. Reactivity measurement commenced when the purging argon gas into the TGA was switched to air. Once the weight of the char sample reached a plateau value, the sample was heated further to 600°C at 50°C s^{-1} and held for an additional 120 min to complete the combustion of the char material. The final heating at 600°C gave the ash yield of the char directly.

The specific reactivity of char is defined as the rate of weight loss per unit weight of the char at a certain conversion level. The specific reactivity (R_x) of char was calculated according to the formula

$$R_x = -\frac{1}{W} \frac{dW}{dt}$$

where W is the weight (daf basis) of the char at any given time t .

3. RESULTS AND DISCUSSION

3.1 Effects of temperature and holding times on the reactivity of char from the pyrolysis/gasification of H-form coal

Fig. 1 shows the specific reactivities of chars from the pyrolysis of H-form coal under fast heating at different temperatures. The data in Fig. 1 indicate that the specific reactivity decreases with increasing temperature. The H-form coal has very low cation (AAEM) content. Therefore its char reactivity depends mainly on the char (carbon) structure. With increasing temperature, due to

the intensified condensation reactions of char aromatic ring system, the active sites in the char were demolished, resulting in a reactivity loss.

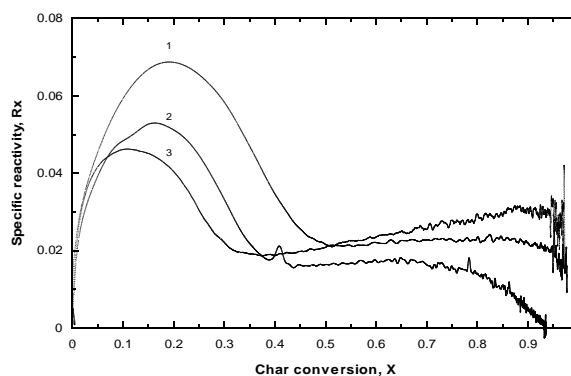


Fig 1. Specific reactivity in air at 400°C as a function of char conversion. The chars were prepared from the pyrolysis of H-form coal in helium at $1000^\circ\text{C s}^{-1}$ (holding time: 0 s). The different temperatures were 700°C , 800°C and 900°C for curves 1-3, respectively.

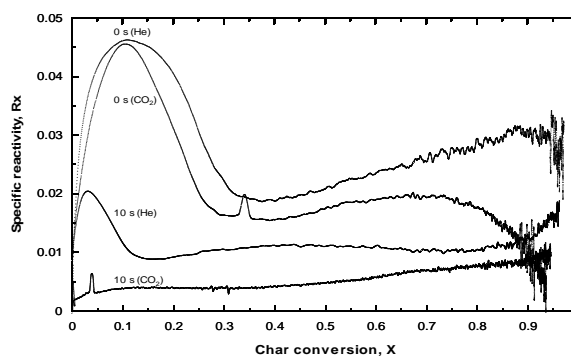


Fig 2. Specific reactivity in air at 400°C as a function of char conversion. The chars were prepared from the pyrolysis/gasification of H-form coal at different holding times with a heating rate of $1000^\circ\text{C s}^{-1}$ (peak temperature: 900°C).

Fig. 2 shows the specific reactivities of chars from the H-form coal decreases with increasing holding times. Decreasing reactivity should demonstrate the char structural changes with holding times. The data in Fig. 2 indicate that the reactivity at '0' s holding time is almost similar in both helium and CO_2 atmosphere at a low conversion level (10%). Similar reactivities between helium and CO_2 may be due to the fact that CO_2 is not able to further decrease the active site concentrations within the '0' s holding time. Rapid decrease in the char reactivity when the holding time was '10' s implies that the destruction of active sites due to the condensation reaction of aromatic ring system was severe not only in helium atmosphere but also in CO_2 atmosphere.

3.2 Effects of temperature and holding times on the reactivity of char from the pyrolysis/gasification of raw Loy Yang coal

Fig. 3 shows the reactivities of chars from the

pyrolysis of raw coal at $1000\text{ }^{\circ}\text{C s}^{-1}$. The data in Fig. 3 indicate that the reactivity decreases with increasing temperature. Fig. 4 shows the retention of AAEM (Na, Mg and Ca) species in char as a function of temperature. It can be seen that there is a decrease in the retention of Na in chars, coinciding with the decrease in char reactivities. The data in Fig. 3 also indicate that at $900\text{ }^{\circ}\text{C}$ reactivity is very low compared to reactivities of other temperatures. It may be due to the fact that increasing volatilisation of Na at $900\text{ }^{\circ}\text{C}$ (Fig. 4) made the char less reactive. The volatilisation of significant amounts of Na would involve not only the Na on the char (pore) surface, but also the Na from inside the char matrix. Therefore, the volatilisation of Na would imply changes in the char structure. Finally, at $900\text{ }^{\circ}\text{C}$, ring condensation reactions within the char particles became significant compared to other temperatures, leading to a more condensed/ordered char, the net effect is the observed decrease in char reactivity.

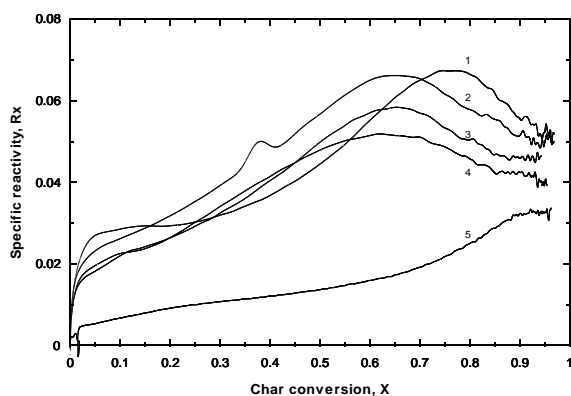


Fig 3. Specific reactivity in air at $400\text{ }^{\circ}\text{C}$ as a function of char conversion. The chars were prepared from the pyrolysis of raw coal in helium at $1000\text{ }^{\circ}\text{C s}^{-1}$ (holding time: 0 s). The different temperatures were 500, 600, 700, 800 and $900\text{ }^{\circ}\text{C}$ for curves 1-5, respectively.

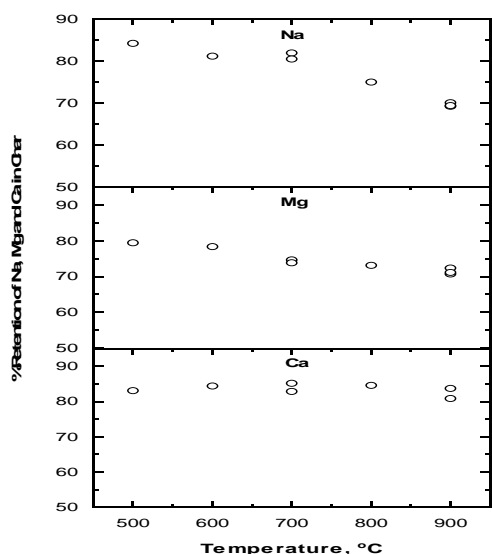


Fig 4. Retention of Na, Mg and Ca in char during the pyrolysis of raw coal in helium as a function of peak temperature (heating rate: $1000\text{ }^{\circ}\text{C s}^{-1}$; holding time: 0 s).

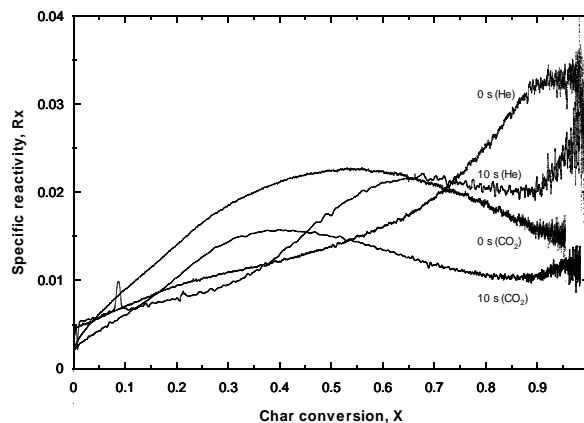


Fig 5. Specific reactivity in air at $400\text{ }^{\circ}\text{C}$ as a function of char conversion. The chars were prepared from the pyrolysis/gasification of raw Loy Yang coal sample at different holding times with a heating rate of $1000\text{ }^{\circ}\text{C s}^{-1}$ (peak temperature: $900\text{ }^{\circ}\text{C}$).

As can be seen in Fig. 5, at $900\text{ }^{\circ}\text{C}$ the reactivity of char decreased with increasing holding time. Fig. 6 shows the retention of AAEM species in the char as a function of holding time. The change in char reactivity is most likely due to char (carbon) structural changes together with the decrease of retention of AAEM species (particularly Na) in the char (Fig. 6). Fig. 6 shows at $900\text{ }^{\circ}\text{C}$ the volatilisation of AAEM species at '10' s holding time is enhanced relative to that at '0' s holding time, due to the production of free radicals in the nascent char/volatiles. Char structural changes may have also contributed to the lower reactivity of the chars at high temperature with longer holding times.

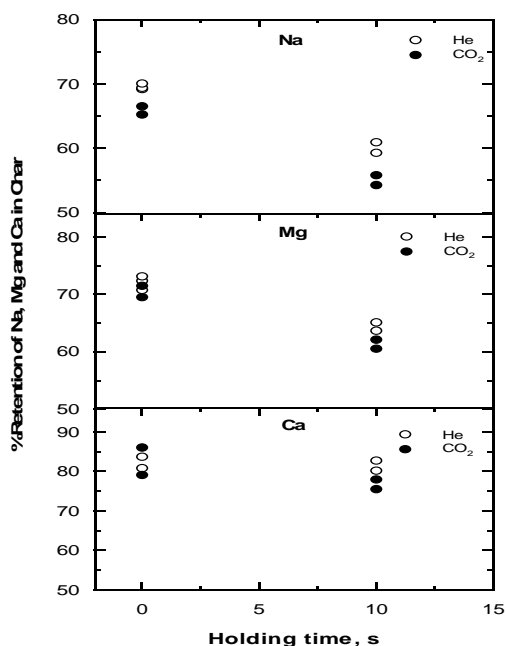


Fig 6. Retention of Na, Mg and Ca in char during the pyrolysis/gasification of raw coal sample as a function of holding time (heating rate: $1000\text{ }^{\circ}\text{C s}^{-1}$; peak temperature: $900\text{ }^{\circ}\text{C}$).

3.3 Effects of temperature and holding times on the reactivity of char from the pyrolysis/gasification of Na-form coal

Fig. 7 shows the specific reactivities of chars from the Na-form coal as a function of temperature. For chars prepared at different pyrolysis temperatures, the reactivity increased with increase in pyrolysis temperature from 500 to 900 °C even though the retention of Na in the char decreases with increasing temperature. It is believed that these “abnormal” effects are due to the changes in the dispersion of Na in char with increasing pyrolysis temperature. At low temperature (500 - 700 °C), the char still contained a very significant concentration of oxygen. The sodium in the char is likely to be preferentially bonded to the oxygen in the char throughout the char matrix [10]. The strong bonding between Na and O inside the char matrix would not favour the migration of Na to the char surface. In this case, a very significant proportion of Na retained inside the char and was not accessible to the gasifying agent, contributing little to the overall catalytic effects during the gasification of the char. Increasing pyrolysis temperature to 800 °C (or higher), the oxygen content of char would drastically decrease [11], leading to some degree of tendency for Na to concentrate on the char surface and thus to increases in char reactivity.

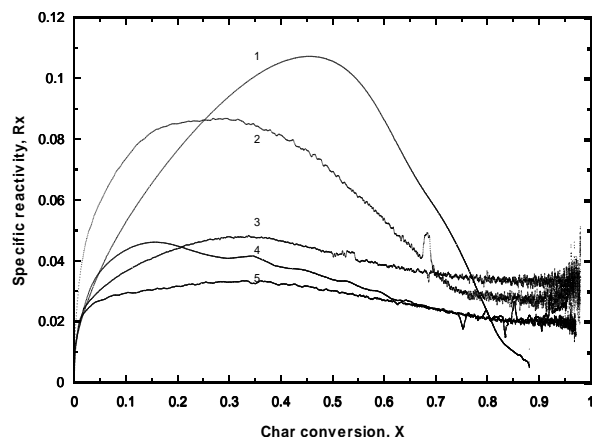


Fig 7. Specific reactivity in air at 400 °C as a function of char conversion. The chars were prepared from the pyrolysis of Na-form coal in helium at 1000 °C s⁻¹ (holding time: 0 s). The different pyrolysis temperatures were 900, 800, 700, 600 and 500 °C for curves 1-5, respectively.

Fig. 8 shows the specific reactivity of chars from the pyrolysis of Na-form coal at 900 °C with different holding times under the fast heating rate. Decreasing reactivity with increasing holding time may be due to the changes in char structure including the changes in the bonding between Na and char matrix. Holding time enhanced the heterogeneity of the char structure through ring condensation reactions, hence reactivity. Decrease in sodium concentration with increasing holding time could also lead to a decrease in active sites and thus reactivity.

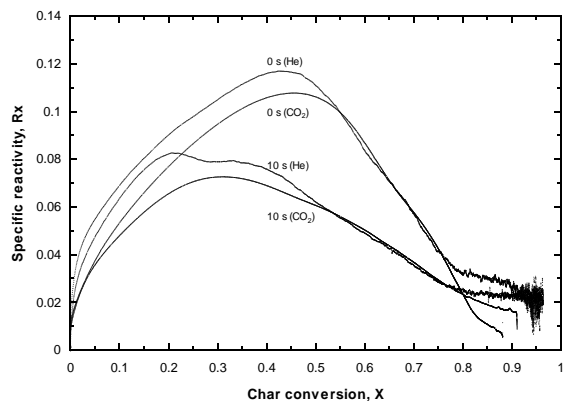


Fig 8. Specific reactivity in air at 400 °C as a function of char conversion. The chars were prepared from the pyrolysis/gasification of Na-form coal at different holding times with a heating rate of 1000 °C s⁻¹ (peak temperature: 900 °C).

3.4 Effects of temperature and holding times on the reactivity of char from the pyrolysis/gasification of Ca-form coal

Fig. 9 shows the reactivities of chars from the pyrolysis of Ca-form coal sample as a function of temperature. In agreement with the data in Fig. 1 for H-form coal and in Fig. 3 for raw Loy Yang coal sample, increases in pyrolysis temperature have led to decreases in char reactivity for the chars from the Ca-form coal. For chars from the Ca-form coal, the reduction in reactivity with increasing temperature is dependent not only upon the changes of char structure and is also dependent upon the activity of the catalytic species. Even at atomic/molecular level, ion-exchanged Ca is known to be highly dispersed, which is catalytically active during gasification [12].

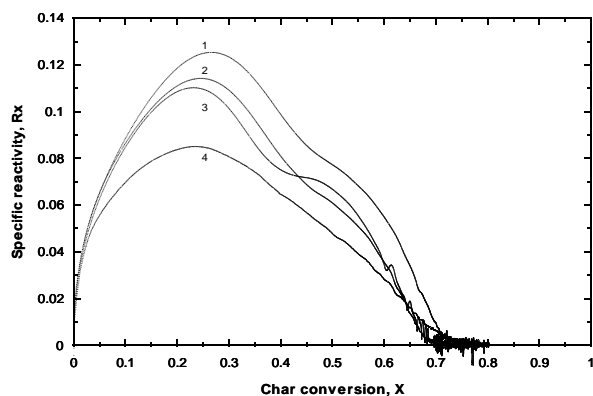


Fig 9. Specific reactivity in air at 400 °C as a function of char conversion. The chars were prepared from the pyrolysis of Ca-form coal in helium at 1000 °C s⁻¹ (holding time: 0 s). The different pyrolysis peak temperatures were 500, 700, 800 and 900 °C for curves 1-4, respectively.

During pyrolysis of Loy Yang coal up to 950 °C, Yamashita et al. [12] found that most of the Ca in the chars from Ca-exchanged coal remained highly

dispersed even though some CaO crystallites were formed between temperatures of 650 °C and 800 °C. Increasing pyrolysis temperature with increasing formation of catalytically inactive CaO crystallites would mean that a lower concentration of active CaO remains in the chars. At higher temperature, changes of char structure leading to lesser reactive char (LRC) and the increasing formation of CaO crystallites combined would lead to the decrease in char reactivity with increasing temperature.

Fig. 10 shows the reactivity of chars from the pyrolysis of Ca-form coal at 900 °C with different holding times under fast heating rate. Decreasing reactivity may be due to the carbon structure change with holding time. Increasing holding time the coal bond-breaking reactions and the condensation reactions of the aromatic-ring systems are more intensive, which increases the degree of alignment of aromatic-ring systems. As only the edge sites of the aromatic-ring system are reactive during reaction, the condensation of the aromatic-ring systems in char destroys the active sites, resulting in a loss in char reactivity.

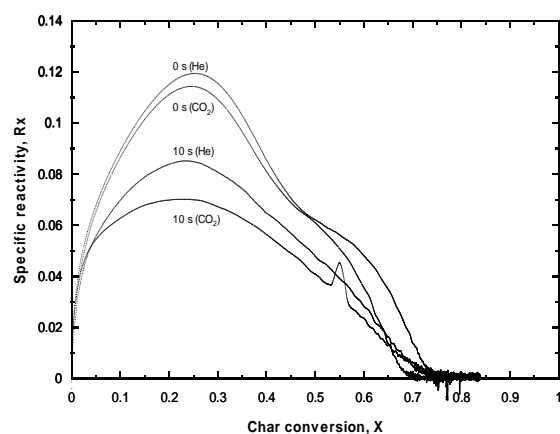


Fig 10. Specific reactivity in air at 400 °C as a function of char conversion. The chars were prepared from the pyrolysis/gasification of Ca-form coal at different holding times with a heating rate of 1000 °C s⁻¹ (peak temperature: 900 °C).

4. CONCLUSIONS

The reactivity of char is not solely dependent upon peak pyrolysis temperature. The concentration of AAEM species in the char and transformation of AAEM species during pyrolysis/gasification play important roles in determining the char reactivity. For chars from the Na-form coal, decreases in reactivity were mainly due to the volatilisation of catalyst (Na) and/or due to the changes in char structure. For chars from the Ca-form coal, decreases in reactivity can be ascribed as the dispersion and chemical forms of Ca in char as well as changes of char structure. For char from the H-form coal, decreases in reactivity were mainly due to the changes in char structure. The monovalent species (Na) was always

volatilised to a much larger extent than the divalent species (Mg and Ca) under similar pyrolysis/gasification condition.

5. ACKNOWLEDGEMENT

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