Volatilisation and Catalytic Effects of AAEM Species on Reactivity of Char from Pyrolysis and Gasification of Victorian Brown Coal

K. Jamil* and C. Z. Li**

School of Engineering & Technology, Deakin University, Geelong, VIC 3217, Australia
Department of Chemical Engineering, Monash University, Victoria 3800, Australia
Email: kawser.jamil@deakin.edu.au
(Received on 13 Sep 2005, revised on 4 Dec 2005)

Abstract

This study investigates the reactivity of chars prepared from a Victorian brown coal samples (a raw coal and a set of ion-exchanged coals). A series of pyrolysis/gasification experiments were carried out in helium and CO_2 atmospheres using a wire-mesh reactor at a wide range of temperatures from 500 °C to 900 °C. The reactivity of the resulting char was measured in air at 400 °C in a thermo-gravimetric analyser (TGA). For both raw and ion (H^+, Na^+, Ca^{++})-exchanged Loy Yang 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 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).

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 actual efficiency of a gasification combined power generation cycle would largely depend on the extent of char conversion achieved at the gasification/reforming stage. In a fluidised-bed gasifier, high char reactivity would mean that a high conversion level is achieved before char particles are elutriated out of the bed, or that a smaller number circulation is required to achieve a relatively high char conversion level. Maintaining high char reactivity is thus essential to achieving high char conversion level through gasification with a small gasifier volume, contributing to low capital and maintenance costs for the future power plants using coal. 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].

Compared with the black coals, Victorian brown coal has many unique properties and structural features [6], making the features of its high gasification reactivity to be very different from the chars of high rank coals. Firstly, Victorian brown coal features the presence of ion-exchangeable 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 volatilisation of

the AAEM species will greatly impact on the hot gas cleaning and the operation of downstream units such as the gas turbines. The retention of these AAEM species as catalysts will be an important factor for the gasification reactivity of the brown coal char [7]. Secondly, due to its as a low-rank fuel, the structure of the carbonaceous matter in brown coal char is susceptible to changes in the pyrolysis and gasification conditions [7] leading to changes in char reactivity. The susceptibility of the AAEM species and the carbonaceous structure in the char from Victorian brown coal requires the in situ measurement of char reactivity. The purpose of the present study is to trace the changes in char reactivity during pyrolysis/gasification, in particular, to gain insights into the individual effects of AAEM species and char structure on the reactivity of brown coal char during pyrolysis/gasification.

Experimental Procedure

Sample preparation

A Victorian brown coal from the Latrobe Valley, Victoria, Australia was used in the present 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/gasification 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. Na-form coal and Ca-form coal were prepared by ion-exchanging the H-form coal with aqueous solutions of sodium acetate and calcium acetate, respectively. They contained 2.80 wt% of Na and 3.27 wt% of Ca on the dry basis, respectively. The details of the sample preparation were given elsewhere [6, 8].

Pyrolysis/gasification experiments

Pyrolysis/gasification experiments were carried out in an electrically heated wire-mesh reactor [6, 8-9] using atmospheric flow of helium or CO_2 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. Four 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.

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 a Dionex DX-500 ion chromatograph consisted of a GP40 gradient pump equipped with an ED40 electromechanical detector. This ED40 detector was operated in conductivity mode for cation analysis and the pump was operated in isocratic mode. Separation of AAEM species was carried out on a Dionex CS12A ion exchange column using 0.02M MSA solution as an eluent. The retention of AAEM species in char was calculated by comparing the content of the AAEM species in the char with that in the raw substrate coal sample, considering the weight loss of the coal sample during pyrolysis or gasification experiments.

Char reactivity measurement

Char reactivity was measured using a Perkin Elmer Pyris-1 TGA following the procedure outlined previously [10]. Typically, about 3 mg of char sample was loaded into a sample pan and heated in the TGA from ambient to 105 ^{o}C in argon to remove the moisture from the char. The temperature was then increased at a heating rate of 50 ^{o}C min^{-1} to 400 ^{o}C. Once the final temperature was reached, air was then introduced to commence isothermal reactivity measurement. The specific reactivity (R_x) of char at any given time was calculated from the DTG data ($\frac{dW}{dt}$) provided by the TGA software.

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

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

The ash yield required for the calculation of reactivity on a dry-ash-free (daf) basis was obtained by increasing the temperature of TGA furnace to 600 ^{o}C with a holding period of 30 min to oxidise any possible carbonaceous residue left in the sample at the end of reactivity measurement at 400 ^{o}C.

Results and Discussion

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 reactivity decreases with increasing temperature. The H-form coal has very low cation (AAEM) content.
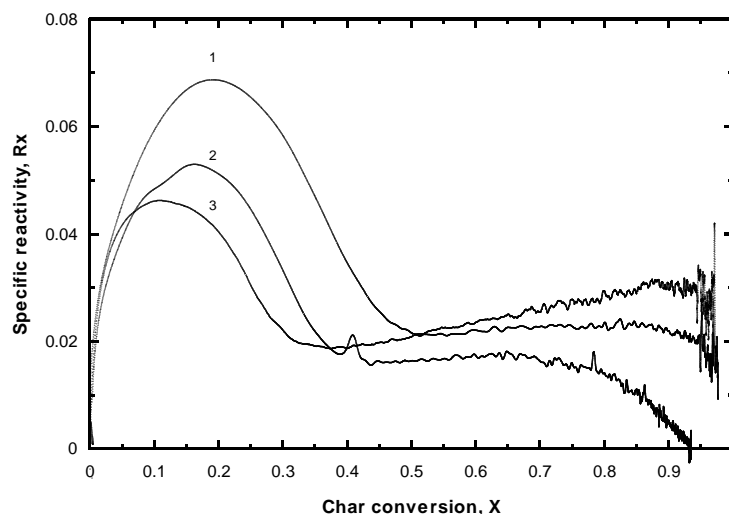

Fig. 1 Specific reactivity in air at 400 ^{o}C as a function of char conversion. The chars were prepared from the pyrolysis of H-form coal in helium at 1000 ^{o}C s^{-1} (holding time: 0 s). The different temperatures were 700, 800 and 900 ^{o}C for curves 1-3, respectively.

Therefore its char reactivity depends mainly on the char (carbon) structure. With increasing pyrolysis 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. 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 specific 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. At a low char conversion level (< 10%), increasing holding time from '0' s to '10' s reactivity dropped from 0.045 to 0.02 in helium atmosphere whereas in CO_2 atmosphere reactivity dropped from 0.045 to 0.006 and then levelled off at higher char conversion level. 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.
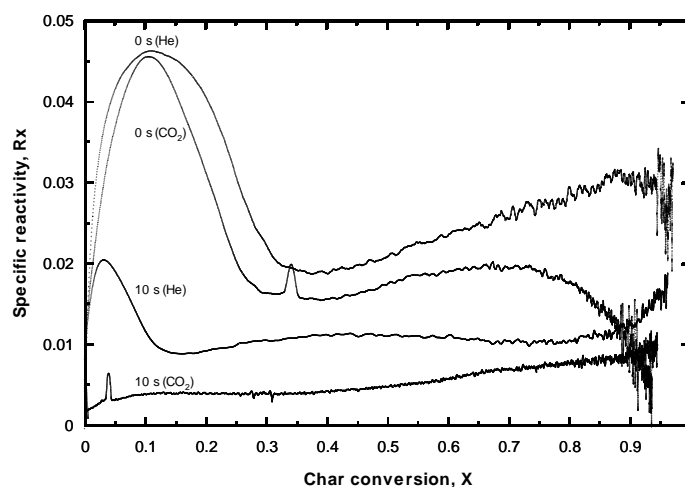

Fig. 2 Specific reactivity in air at 400 °C as a function of char conversion. The chars were prepared from the pyrolysis/gasification of H-form coal at different holding times with a heating rate of 1000 °C s^{-1} (peak temperature: 900 °C).

It is also noted that the increase of reactivity during the initial char conversion observed can only be due to the change in carbon (char) structure as a result of reaction during conversion. Firstly, new active sites could be created as a result of ring system rupture with the proceeding of char conversion. Secondly, with the char conversion, the pore structure could be changed; resulting an increase of active sites. The quality of the active sites may also become more reactive as the aromatic ring system becomes unstable due to the rupture of ring system. With the proceeding of char conversion, carbon was kept being removed. The pores in the char may be enlarged and finally collapsed. At high char conversion level, specific reactivity started to decrease due to loss of char porosity therefore the lack of active sites.

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 Loy Yang coal at 1000 $^{\circ}$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 $^{\circ}$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 $^{\circ}$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. Pyrolysis at 900 $^{\circ}$C would likely result in more Na on the char (pore) surface, the dominant effects however would be the volatilisation of Na and the condensation reactions inside the char to lead to the "deactivation" of char. Finally, at 900 $^{\circ}$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.
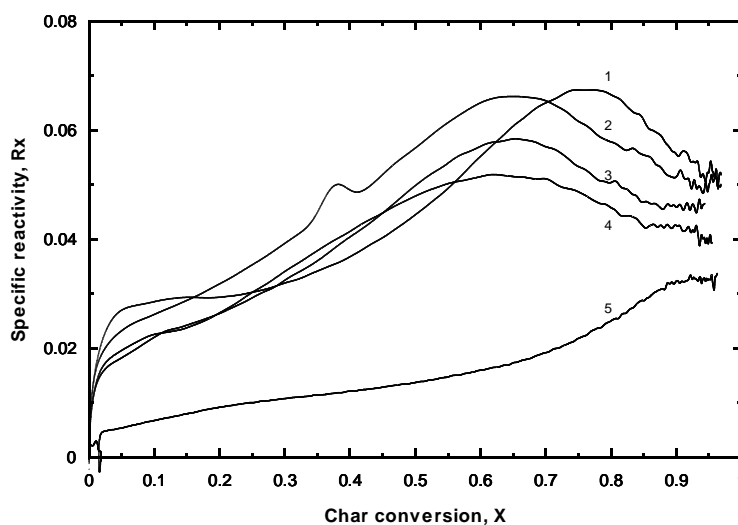

Fig. 3 Specific reactivity in air at 400 $^{\circ}$C as a function of char conversion. The chars were prepared from the pyrolysis of raw coal in helium at 1000 $^{\circ}$C s^{-1} (holding time: 0 s). The different temperatures were 500, 600, 700, 800 and 900 $^{\circ}$C for curves 1-5, respectively.
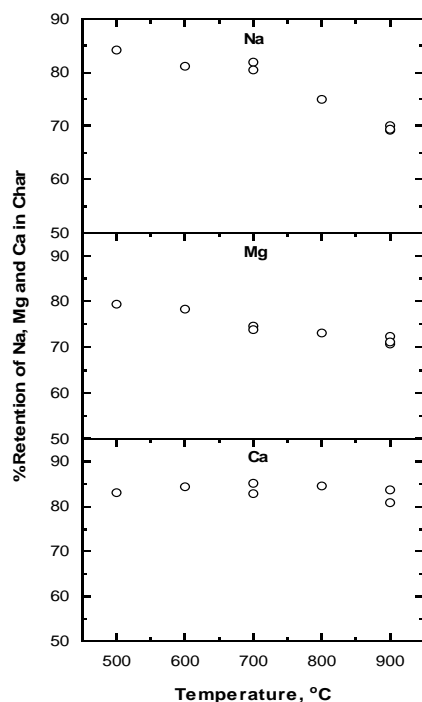
Fig. 4 Retention of Na, Mg and Ca in char during the pyrolysis of raw coal in helium as a function of peak temperature (heating rate: $1000\ ^oC\ s^{-1}$; holding time: 0 s).

As can be seen in Fig. 5, at 900 ^oC 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).
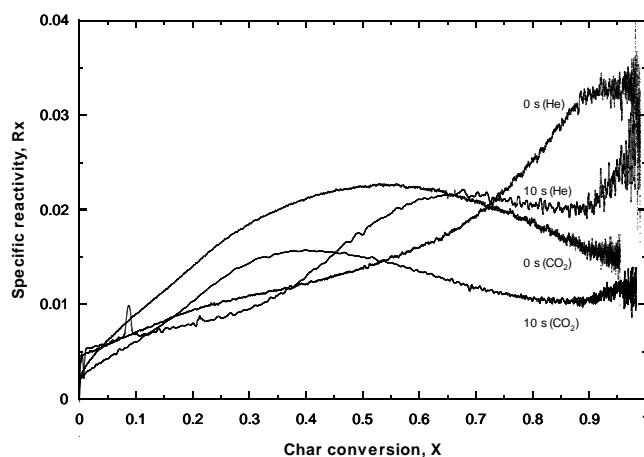

Fig. 5 Specific reactivity in air at 400 ^oC as a function of char conversion. The chars were prepared from the pyrolysis/gasification of raw Loy Yang coal sample at different holding times with a heating rate of $1000\ ^oC\ s^{-1}$ (peak temperature: 900 ^oC).

Examining the data in Fig. 5 showed that the reactivity was lower (at conversion level of 0.85) for chars prepared in CO_2 compared to that in helium atmosphere. As can be seen in Fig. 6 the retention of Na in the char is lower in CO_2 atmosphere than in helium. Previous studies reported a lower volatility of Na and K in inert atmospheres than during CO_2 gasification [1].
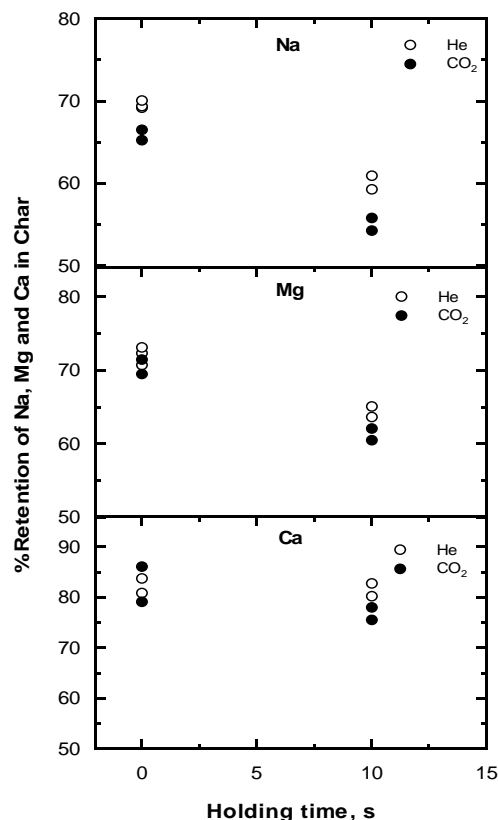

Fig. 6 Retention of Na, Mg and Ca in char during the pyrolysis/gasification of raw coal sample as a function of holding time (heating rate: 1000 ^{o}C s^{-1}; peak temperature: 900 ^{o}C).

During the pyrolysis of coal in CO_2, the retention of Na can be decreased in two ways. Na can be bonded to the char by the formation of surface oxygen complexes according to the following reaction:

CM-Na + O = CM-O-Na
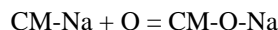
where, CM represents the coal/char matrix. The O is produced by the dissociation of a CO_2 molecule at the catalyst site. It is generally accepted [10] that the gasification of carbonaceous materials by CO_2 takes place by the chemisorption of CO_2 onto a catalytic site and the dissociation of CO_2 into CO and O.

The formation of surface oxygen complexes is known to be a precursor to the formation of catalytically active species [10], which have the ability to easily dissociate the CO_2 molecules. The Na bonded to the char as catalytically active surface oxygen complex is highly volatilised in CO_2 compared to helium atmosphere. The retention of Mg and Ca is almost identical in both helium and CO_2 atmospheres as shown in Fig. 6. The similar retention of Mg and Ca between the chars in helium and CO_2 indicates that the

difference in reactivity can be due to the catalytic effect of the Na retained in the char pyrolysed in CO_2. The second way in which the CO_2 can influence the retention of Na during pyrolysis is by the interaction with the reactive species in the volatiles. In other words, CO_2 increased the concentration of radicals surrounding the char and on the char surface so that there are more radicals to displace Na from the char according to the following reaction:

$$CM - X_s + R_f = CM - R_f + X_s-$$
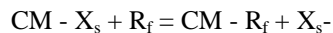
where, R_f denotes free radical, X_s represents the AAEM species (H, Na, Mg or Ca). The AAEM species displaced in this manner could either leave the char particle to be volatilised, or recombine with the char matrix to be retained in the char. Fig. 6 shows at 900 ^{o}C the volatilisation of AAEM species 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.

It can be seen in Figs. 3 to 5 that the specific reactivity increases initially with the char conversion and then decreases at high conversion levels. The main reason for the increases in the char reactivity at lower conversion levels is thought to be due to the increases in the Na concentration on the char (pore) surface. The increases in the Na concentration inside the reaction residue would increase the concentration of the catalytic active sites [10] on the internal reactive surface of the reaction residue, resulting in an increase of reactivity with the conversion. On the other hand, the reactivity decreases at higher char conversion are mainly attributed to the heterogeneity of the char structure. The highly condensed/graphitised carbonaceous matter in char, of lower reactivities, would tend to be concentrated in the char at higher conversion levels.

The structure of char from the pyrolysis of brown coal would greatly differ from that of graphite. Brown coal is a heterogenous material with a range of molecular structures present in petrographically different components. In particular, aromatic ring systems of varying sizes [11] are not uniformly distributed in the coal matrix. The heterogeneity of coal would also affect the condensation/graphitisation reactions during pyrolysis [12], with the larger aromatic ring clusters tending to be easier to condense than the smaller ones. It is thus reasonable to believe that the char from the pyrolysis of brown coal would be heterogenous and consists of aromatic ring systems of varying condensation extent. The more condensed/graphitised carbonaceous matter would be more difficult to gasify [10]. At higher char conversion levels in TGA, what was left in char must have been the more condensed/graphitised carbonaceous matter. The importance of char structure to the catalytic effects of Na has been discussed briefly elsewhere [13]. Due to the char heterogeneity (any heterogeneity in char would mean that the more reactive components are preferentially consumed first with the less reactive materials more concentrated in the char residue), the increased Na catalyst concentration was not enough to maintain the high char reactivity at high conversion levels.

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 specific reactivity increased with increase in pyrolysis temperature from 500 to 900 ^{o}C. 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 ^{o}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 ^{o}C (or higher), the oxygen content of char would drastically decrease [14], leading to some degree of tendency for Na to concentrate on the char surface and thus to increases in char reactivity.
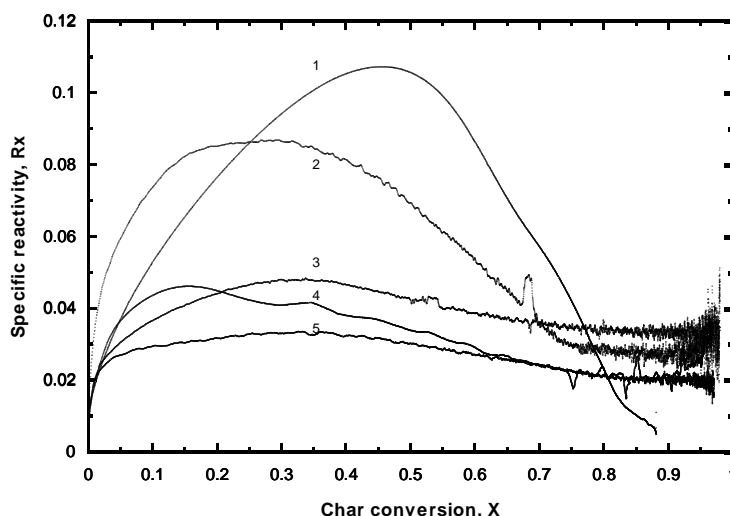

Fig. 7. Specific reactivity in air at 400 ^{o}C as a function of char conversion. The chars were prepared from the pyrolysis of Na-form coal in helium at 1000 ^{o}C s^{-1} (holding time: 0 s). The different temperatures were 900, 800, 700, 600 and 500 ^{o}C for curves 1-5, respectively.

In order to gain some insights into the relative contribution of volatilisation of catalyst (Na) and/or char structural changes, the char specific reactivities versus the Na concentration in char are plotted in Fig. 8 at 500 and 900 ^{o}C for char conversion levels at an increment of 5%. For the chars prepared at 500 ^{o}C, char reactivity increased linearly with Na concentration when the char conversion was < 40%. As the char is oxidised with air, the Na concentration in the char would increase. More importantly, more Na would likely be exposed on the pore surface [15] as a result specific reactivity of char would increase. At a high char conversion level (> 40%), the catalytic activity of Na decreased with increasing char conversion during the reactivity measurement. The possible reason for the decreases in the catalytic activity of Na with increasing char conversion is the deactivation of Na catalyst.

Fig. 9 shows the specific reactivity of chars from the pyrolysis/gasification of Na-form coal at 900 ^{o}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.
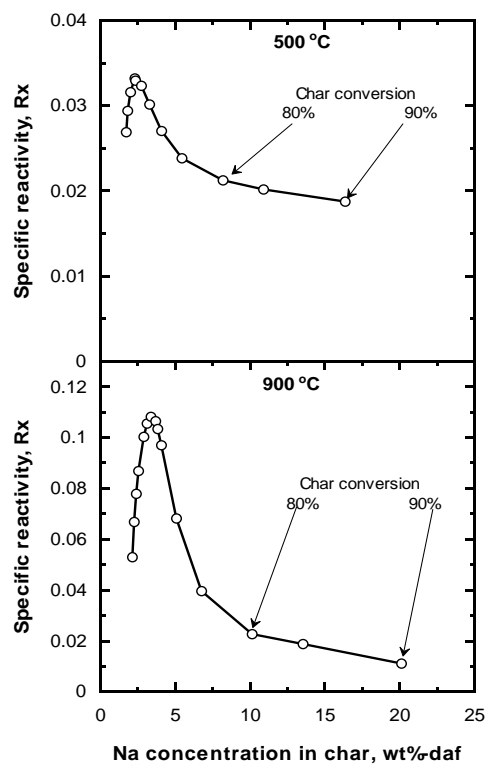
Fig. 8 Specific char reactivity in air at 400 ^{o}C as a function of Na concentration in the reacting chars. The chars were prepared from the pyrolysis of the Na-form coal in helium at 500 and 900 ^{o}C with a heating rate of 1000 ^{o}C s^{-1} (holding time: 0 s).
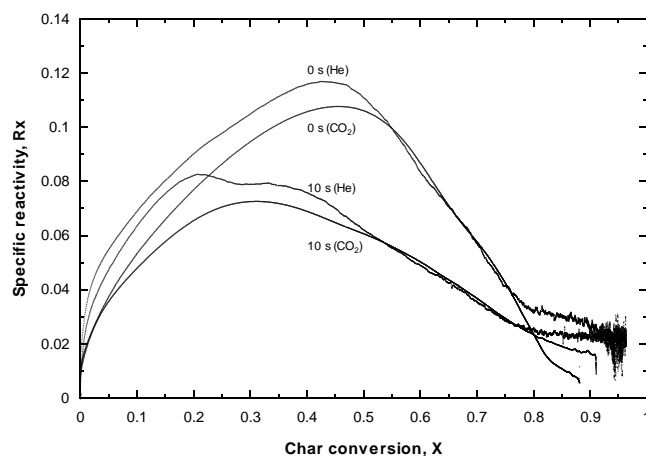

Fig. 9 Specific reactivity in air at 400 ^{o}C as a function of char conversion. The chars were prepared from the pyrolysis/gasification of Na-form coal sample at different holding times with a heating rate of 1000 ^{o}C s^{-1} (peak temperature: 900 ^{o}C).

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

Fig. 10 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.
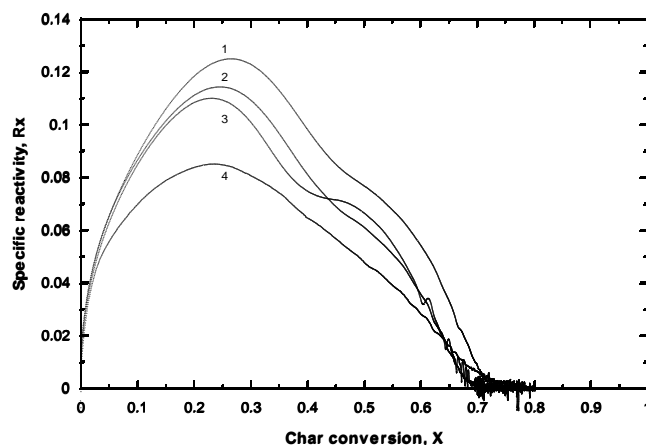

Fig. 10 Specific reactivity in air at 400 $^{\circ}$C as a function of char conversion. The chars were prepared from the pyrolysis of Ca-form coal in helium at 1000 $^{\circ}$C s^{-1} (holding time: 0 s). The different pyrolysis peak temperatures were 500, 700, 800 and 900 $^{\circ}$C for curves 1-4, respectively.

During the pyrolysis of Loy Yang coal sample up to 950 $^{\circ}$C, Yamashita et al. [16] 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 $^{\circ}$C and 800 $^{\circ}$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. 11 shows the reactivity of chars from the pyrolysis/gasification of Ca-form coal at 900 $^{\circ}$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. Examining the data in Figs. 10 and 11 closely it can be seen that 100% char conversion cannot be achieved. This phenomenon was also observed by Lizzio and Radovic [17] during the CO_2 gasification at temperature of 680 $^{\circ}$C of a Ca-exchanged North Dakota lignite in a quartz differential-flow reactor, and by Miura et al. [18] during the oxidation of a char from Canadian lignite at 450 $^{\circ}$C in a TGA. This suggests that regardless of pyrolysis conditions by which the chars were formed, the reactivities drop to 0 at ~80% char conversion. Recently, Li et al. [15] showed that the reactions of chars from the Ca-form coal with O_2

at 400 $^{\circ}$C was very hard to complete; the reactivity dropped close to 0 at char conversion levels higher than 0.7 or 0.9. On the other hand, the formation of a less reactive char (LRC) was not observed for Na-form coal samples. Figs. 7 to 9 confirms that all the char from Na-exchanged coal can be completely gasified, suggesting that the formation of LRC is dependent upon the valency of the carboxyl-bound cation in the coal.

The reason for the formation of the LRC is due to the role of Ca in bringing about a more compact char structure. Finely dispersed Ca is considered to be highly catalytically active and mobile in the char during oxidation. During char oxidation in the TGA, Ca may transform into other active forms at the same time as the carbonaceous matter is gasified: intermediates of Ca may include $CaCO_3$ [19], CaO [17] and CaO_2 [17]. Ca, being divalent, has the ability to react with the gasifying walls of the char matrix and link layers of carbon together, i.e., act as a cross-linking agent [10]. This would produce a close packing of the carbon layers, joined by well-dispersed Ca in the char. The LRC can be broken down at higher temperatures due to thermal breakage of some bonds between Ca and the char matrix, but can form again as long as there is enough well-dispersed Ca and carbonaceous matter. Therefore, the role of carboxyl-bound Ca is very different to that of carboxyl-bound Na. At low temperatures, well-dispersed Ca enhances the formation of LRC during char oxidation. Na does not exhibit such behaviour, due to the difference in valency between Na and Ca.
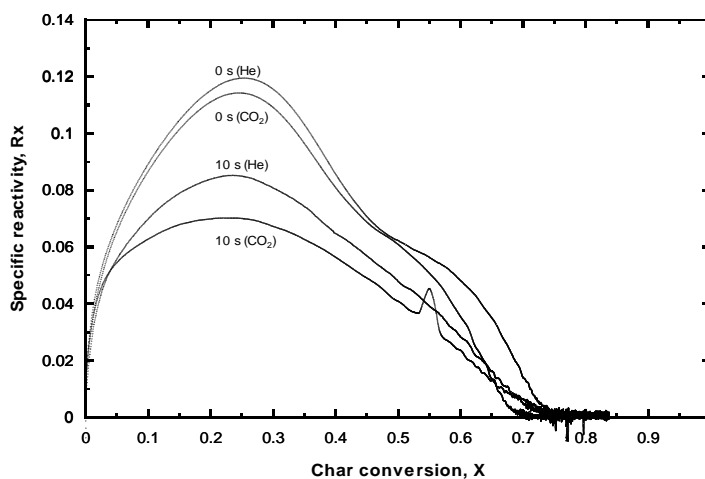

Fig. 11 Specific reactivity in air at 400 $^{\circ}$C as a function of char conversion. The chars were prepared from the pyrolysis/gasification of Ca-form coal sample at different holding times with a heating rate of 1000 $^{\circ}$C s^{-1} (peak temperature: 900 $^{\circ}$C).

Conclusion

The experimental results on the reactivity of char and volatilisation of AAEM species from the pyrolysis/gasification of Victorian brown coal in this study can be summarised as follows:

i) 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.

ii)   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.

iii)   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.

iv)   Significant proportion of AAEM species in raw Loy Yang as well as ion-exchanged coal samples were volatilised during pyrolysis/gasification.

v)   The monovalent species (Na) was always volatilised to a much larger extent than the divalent species (Mg and Ca) under similar pyrolysis/gasification condition.

Acknowledgment

References

[1]   T. Takarada, H. Ishikawa, H. Abe and Y. Nakaike, "Alkali volatilisation during pyrolysis and gasification of coal," In Proce., 8th International conference on coal science, Elsevier, Amsterdam, 1995, pp. 687-691.

[2]   L. R. Radovic, P. L. Walker and R. G. Jenkins, "Importance of catalyst dispersion in the gasification of lignite chars," J. Catalysis, Vol. 82, 1983, pp. 382-385.

[3]   T. G. Devi, M. P. Kannan and G. N. Richards, "Copper catalysis in the air gasification of cellulosic chars," Fuel, Vol. 69, 1990, pp. 1441-1445.

[4]   W. J. and S. D. Kim, "Catalytic activity of alkali and transition of metal salt mixtures for steam-char gasification," Fuel, Vol. 74, 1995, pp. 1387-1391.

[5]   P. L. Walker "Structure of coals and their conversion to gaseous fuels," Fuel, Vol. 60, 1981, pp. 801-804.

[6]   C. Z. Li, C. Sathe, J. R. Kershaw and Y. Pang, "Fates and roles of AAEM species during the pyrolysis of a Victorian brown coal," Fuel, Vol. 79, 2000, pp. 427-435.

[7]   D. M. Quyn, H. Wu, J. I. Hayashi and C. Z. Li, "Volatilisation and catalytic effects of AAEM species during the pyrolysis and gasification of Victorian brown coal," Part IV, Fuel, Vol. 82, 2003, pp. 587-593.

[8]   C. Sathe, Y. Pang and C. Z. Li, "Effects of heating rate and ion-exchangeable cations on the pyrolysis yields from a Victorian brown coal," Energy & fuels, Vol. 13, 1999, pp. 748-755.

[9]   J. R. Gibbins, R. A. V. King, R. J. Woods, and R. Kandiyoti, "Variable heating rate wire-mesh pyrolysis apparatus," Rev. Sci. Instrum., Vol. 60, 1989, pp. 1129-1136.

[10]   D. M. Quyn, H. Wu and C. Z. Li, "Volatilisation and catalytic effects of AAEM species during the pyrolysis and gasification of Victorian brown coal," Part I, Fuel, Vol. 81, 2002, pp. 143-149.

[11]   N. Kashimura, J. I. Hayashi, C. Z. Li, C. Sathe and T. Chiba, "Evidence of poly-condensed aromatic rings in a Victorian brown coal," Fuel, Vol. 83, No. 1, 2004, pp. 97-107.

[12]   H. Wu, J. I. Hayashi, D. M. Quyn and C. Z. Li, "Volatilisation and catalytic effects of AAEM species during the pyrolysis and gasification of Victorian brown coal," Part V, Combined effects of Na concentration and char structure on char reactivity, Fuel, Vol. 83, 2004, pp. 23-30.

[13]   H. Wu and C. Z. Li, "Effect of catalyst form and concentration on the reactivity of chars from a Victorian brown coal," In Proc., 18th Annual International Pittsburgh coal conference, 2001.

[14]   R. Meijer, M. Weeda, F. Kapteijn and J. A. Mouiln, "Catalyst loss and retention during alkali-catalysed carbon gasification in CO_2," Carbon, Vol. 29, No. 7, 1991, pp. 929-941.

[15]   X. Li, H. Wu, J. I. Hayashi, and C. Z. Li, "Volatilisation and catalytic effects of AAEM species during the pyrolysis and gasification of Victorian brown coal," Part VI, Further investigation into the effects of volatile-char interactions, Fuel, Vol. 83, 2004, pp. 1273-1279.

[16]   H. Yamashita, M. Nomura, and A. Tomita., "Local structures of metals dispersed on coal," Energy & fuels, Vol. 6, 1992, pp. 656-661.

[17]   A. A. Lizzio and L. R. Radovic, "Transient kinetics study of catalytic char gasification in CO_2," Ind. Eng. Chem. Res., Vol. 30, No. 8, 1991, pp. 1735-1744.

[18]   K. Miura, H. Zha and K. Kashimoto, "Effect of CaO dispersion on the appearance of a two-step reaction in air gasification of coal chars produced from a low-rank coal," Energy & fuels, Vol. 7, Vol. 5, 1993, pp. 669-673.

[19]   D. C. Amooros, A. L. Solano, F. H. M. Dekker and F. Kapteijn, "Isotopic steay-state and step-response study on carbon gasification catalysed by Ca," Carbon, Vol. 33, 1995, pp. 1147-1154.