PYROLYSIS AND IN-SITU GASIFICATION OF LOY YANG BROWN COAL UPON HEATING IN CO_2

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Abstract   Raw, acid-washed, Na-exchanged and Ca-exchanged Loy Yang brown coal samples were pyrolysed under atmospheric flow of helium or carbon dioxide in a wire-mesh reactor. The experimental results revealed negligible effects of atmosphere on the tar yield over the ranges of pyrolysis conditions: heating rate of 0.5 – 1000 $°C·s^{-1}$, holding temperature of 500 – 900 °C and holding time of 0 to 120 s. This was arisen from rapid intra-particle formation of tar precursors and their release out of the particles, which completed within a period of heating up to 500 – 600 °C preventing CO_2 from being involved therein. After the tar evolution, CO_2 commenced to react with nascent char at 700 – 800 °C. During the heating up period, the char formed under heating at 1000 $°C·s^{-1}$ was gasified by CO_2 at rate appreciably higher than that under heating at 0.5 $°C·s^{-1}$. Extended period of heating of the char at 700 °C or higher temperatures thus reduced the char reactivity with CO_2 probably due to the loss of catalytic activities of Na and Ca and thermal annealing of the char carbon structure.

Keywords: Wire-mesh reactor, CO_2 gasification, tar evolution, heating rate

INTRODUCTION

Pyrolysis is the initial step of combustion and reforming/gasification of coal. When introduced into a high temperature atmosphere containing reactive gases such as O_2, CO_2 and H_2O, coal particles are heated up at a rate of $10^3 – 10^5$ $°C·s^{-1}$ and undergoes so-called flash pyrolysis. Thermochemical reactions termed as the primary reactions take place inside the particles causing the evolution of tar, light hydrocarbon gases and inorganic gases as well as the formation of the solid product, char. Due to instantaneous completion of the primary reactions in terms of the volatiles evolution, in particular, the tar evolution [Unger and Suuberg, 1984; Fong *et al*., 1986; Xu and Tomita, 1987; Freihaut et al., 1989; Gibbins and kandiyoti, 1989; Sathe *et al*., 1999], it is believed that the reactive atmosphere around the particles is minimally involved in the primary reactions, although there has been no experimental proof thereof. Among the nascent products of the primary reactions, char would further experience oxidation(gasification) together with thermal annealing, while volatiles could

also be oxidised. In most existing studies on char gasification by CO_2 or H_2O [*eg*. Veraa and Bell, 1978; Linares-Solano *et al.*, 1979; Hashimoto *et al.*, 1983(a) and (b); Suzuki *et al.*, 1986; Ozaki *et al.*, 1986; Hashimoto *et al.*, 1987], the char samples were *ex-situ*

or *in-situ* prepared by pyrolysis mainly in inert atmospheres using heating rates from 0.05 to 25 $°C·s^{-1}$, which are orders of magnitudes lower than those in practical gasifiers. Hence, the reactivity of the nascent char formed under the practical conditions may be fairly different from the chars prepared as above [Messenböck *et al*., 1999; Hayashi *et al.*, 2000], which is due to the effects of the heating rate and/or atmosphere for the pyrolysis and, in addition, cooling prior to gasification (in case of *ex-situ* preparation). This could be particularly true for low-rank coals such as brown coals, since the chemical/physical structure of the char as well as the activity/abundance of the inherent catalysts such as Na and Ca may change during extended holding at elevated temperatures or when the char is cooled and re-heated for reactivity measurement. Continuing our previous studies [Sathe *et al.*, 1999; Li *et al.*, 2000], the pyrolysis of a Victorian brown coal has been performed in this study using a wire-mesh reactor. The reactor features the minimisation of the extents of extra-particle homogeneous reactions of nascent volatiles and heterogeneous reactions between the volatiles and coal/char particles, thus providing an extremely simplified reaction system. This paper reports the influence of CO_2, the flow of which was forced through the coal-particles-laden wire mesh, on the evolution of tar during pyrolysis and the subsequent mass release from the char due to gasification. The catalytic activities of Na and Ca in the nascent char during

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gasification will also be discussed based on the experimental results.

EXPERIMENTAL

Sample preparation

The same Loy Yang brown coal as that used in our previous studies [Sathe *et al.*, 1999; Li *et al.*, 2000] was employed in this study. Briefly, the as-mined coal from Letrobe Valley in Victoria, Australia, was dried at 35 °C and then pulverised and sieved to a particle size range from 106 to 150 µm. 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 washed with an aqueous solution of sulfuric acid to prepare an acid-washed (H-form) coal. The contents of Na, Ca and Mg in the H-form coal were 0.01 wt%-db or less. 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^{2+} on the dry basis, respectively. The details of the sample preparation were given elsewhere [Sathe *et al.*, 1999; Li *et al.*, 2000; Schafer, 1991].

Pyrolysis experiments

Pyrolysis of the coal samples were carried out in a wire-mesh reactor [Gibbins et al, 1989; Li *et al.*, 1993(a) and (b); Sathe *et al.*, 1999; Li *et al.*, 2000] using atmospheric He (purity > 99.999%) or CO_2 (Laser grade) as a carrier/reacting gas. About 5-7 mg of coal sample was used in each experiment. Under the carrier gas flow through the mesh at a constant rate of 3.4 L(STP)·min^{-1}, the mesh was heated at a rate of 1000 or 0.5 °C·s^{-1} from ambient to a prescribed temperature of

Fig. 1 Changes in the tar and char yields with holding time at 600 °C during the pyrolysis and/or gasification of the raw coal with a heating rate of 1000 °C·s^{-1}

500 – 900 °C with a pre-set holding period between 0 and 120 s, and then allowed to be cooled down to ambient temperature. Tar was collected in a trap that was either cooled with liquid nitrogen during pyrolysis in He or cooled with acetone/dry ice bath during pyrolysis/gasification in CO_2. Tar yield was determined by recovering the tar with a chloroform:methanol mixture (80:20 vol/vol) [Sathe *et al.*, 1999; Li *et al.*, 2000] and then determining the tar concentration in the solution. Char yield was determined by either weighing the coal/char-laden mesh before and after pyrolysis in He or weighing the char recovered from the smesh after pyrolysis/gasification in CO_2.

RESULTS AND DISCUSSION

Effects of CO_2 on tar and char yields from raw coal

Figure 1 shows the tar and char yields from the raw coal as a function of holding time at 600 °C with a heating rate of 1000 °C·s^{-1}. The data in this figure indicate that the release of the tar was almost instant since increasing the holding time from 0 to 20 s did not lead to any significant increase in the observed tar yield. The "0 s" holding time in fact corresponds to a holding time of about 0.3 s at temperatures above 500 °C as the coal/char particles were heated up and cooled down. The char yield gradually decreased with increasing holding time as the nascent char was thermally cracked, probably forming gases such as CO, CH_4 and H_2. The tar and char yields during the pyrolysis in He were in good agreement with those reported previously [Sathe *et al.*, 1999; Li *et al.*, 2000]. It is also noted in Fig.1 that the differences in the tar and char yields between the pyrolysis in He and pyrolysis/gasification in CO_2 were both within experimental errors. This suggests that CO_2 could hardly influence the tar evolution while gasify the nascent char to a negligible extent at 600 °C. At temperature as low as 600 °C, CO_2 seems to be unable to react with tar precursors inside the particles due to its low reactivity or otherwise extremely short period for tar precursors formation and subsequent tar evolution. The unchanged tar yields going from He to CO_2 also mean that the difference in the diffusivity between He and CO_2 did not seem to have significantly altered the mass transfer processes of tar precursors out of the abundant pore structure of the pyrolysing particles.
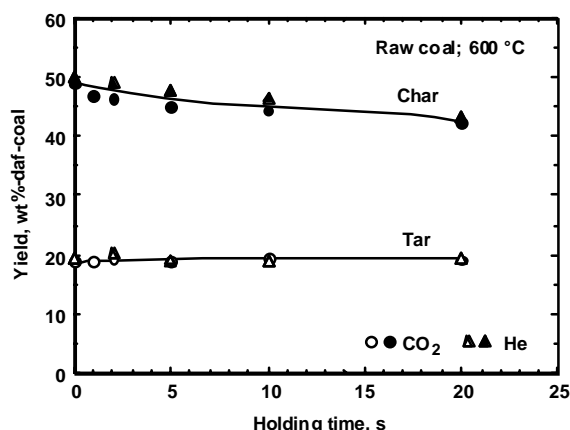
As can be seen in Fig.2, the tar yields from the pyrolysis in He and pyrolysis/gasification in CO_2 both remained unchanged over the range of the holding time at 900 °C and agreed well with each other. Moreover, the yields were also in good agreement with those at 600 °C (Fig.1). This result is explained by considering that the tar evolution under heating at 1000 °C·s^{-1} nearly completed as soon as the temperature reached 600 °C, and as a result, CO_2 brought about little additional formation of tar compared with that in He. On the other hand, at 900 °C the char yield was systematically lower

in CO_2 than in He. This should be arisen from the gasification of the char by CO_2. The difference in the char yield seemed to increase gradually with the holding time, from 6 wt%-daf at 0 s to 9 wt%-daf at 60 s. A major portion of the difference thus occurred as the temperature was raised to 900 °C. The effect of CO_2 on the char yield was also examined for the pyrolysis at 800 °C. The result is given in Fig.3, which reveals no significant effect of CO_2 on the char yield over the range of the holding time between 0 and 120 s. Combining the results shown in Figs. 1-3, it is strongly suggested that a portion of the nascent char, ca. 6 wt%-daf, was gasified by CO_2 within a period as short as 0.1 s as the particles were heated from 800 up to 900 °C. If the rate of the gasification is given as an average during this short period, it is about 60 wt%-daf·s⁻¹ on the coal basis.

The conversion of char by the gasification was estimated as the difference in the char yield between the pyrolysis in He and pyrolysis/gasification in CO_2. The char conversion at 900 °C is shown in Fig.4 as a function of holding time. The conversion seemed to increase with the time at an initial rate of about 0.1 wt%-daf·s⁻¹ on the coal basis, which was much lower than the average rate of gasification during heating-up period.

Heating rate effect on gasification reactivity of char from raw coal

Figure 5 illustrates the char and tar yields from the raw coal during the pyrolysis in He and the pyrolysis/gasification in CO_2 with heating rate and holding time of 0.5 °C·s⁻¹ and 10 s, respectively. As expected from the results of the fast-heating-rate pyrolysis, the tar yield was nearly constant over the temperature range from 500 up to 900 °C, and was hardly influenced by the atmosphere. Compared with the tar yield under heating at 1000 °C·s⁻¹ (Figs. 1 and 3), the yield at 0.5 °C·s⁻¹ was clearly lower, and this tendency is in broad agreement with those reported previously [Matsuo *et al.*, 1995; Sathe *et al.*, 1999; Li *et al.*, 2000; Hayashi *et al.*, 2000]. On the other hand, from the comparison of the char yield between CO_2 and He, the gasification was seen to commence around 700 °C. When defined as above, the char conversions by the gasification were 6 and 13 wt%-daf respectively at 800 and 900 °C. The difference between these conversions, 7 wt%-daf, corresponded to an average gasification rate of 0.035 wt%-daf·s⁻¹ during the period for heating from 800 up to 900 °C. This average rate was lower by orders of magnitudes than that during the fast heating at the same temperature range, although the ranges of the char yields under the slow and fast heating were not char formed under heating at 1000 °C·s⁻¹ may be farmore reactive with CO_2 than that at 0.5 °C·s⁻¹.
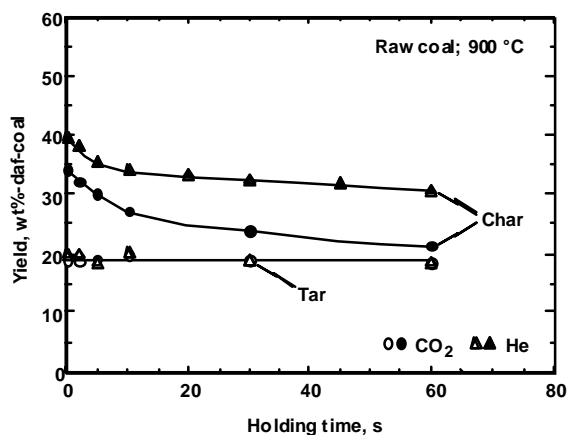

Fig. 2 Changes in the tar and char yields with holding time at 900 °C during the pyrolysis and/or gasification of the raw coal with a heating rate of 1000 °C·s⁻¹
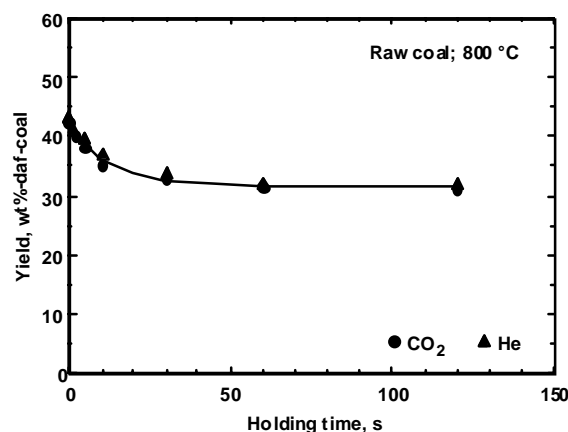

Fig. 3 Changes in the char yields with holding time at 800 °C during the pyrolysis and/or gasification of the raw coal with a heating rate of 1000 °C·s⁻¹
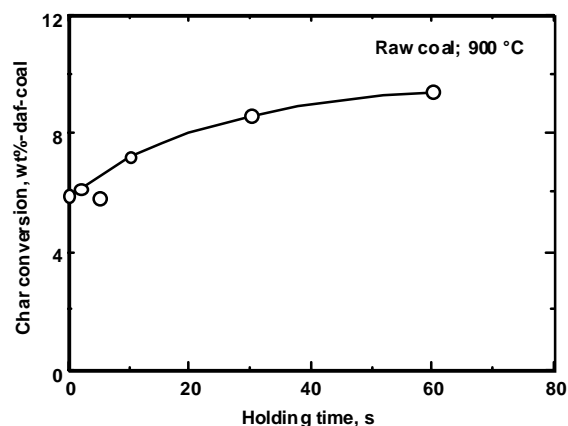

Fig. 4 Char conversion as a function of holding time at 900 °C during the gasification of the char formed from the raw coal at a heating rate of 1000 °C·s⁻¹
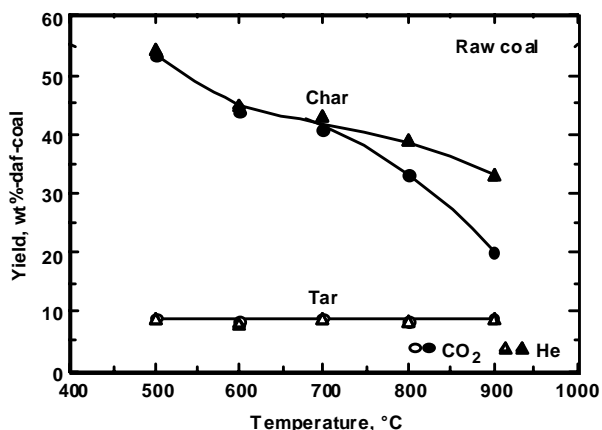
Fig. 5 Changes in the tar and char yields with temperature during the pyrolysis and/or gasification of the raw coal with a heating rate of 0.5 °C·s⁻¹ and a holding time of 10 s

Effect of CO_2 on tar and char yields in the presence and absence of metallic species

The H-form, Na-form and Ca-form coal samples were subjected to the pyrolysis in He and pyrolysis/gasification in CO_2. The results are summarised in Fig.6. Although not shown in the figure, the tar yield from every coal was affected insignificantly by the replacement of He with CO_2 over the ranges of temperature and heating rate examined. This result is attributed to the completion of major tar formation and release during heating up to 500 – 600 °C, as observed in the pyrolysis of the raw coal.

During heating of the modified Loy Yang coals, the gasification of the nascent chars became significant above 700°C. It is noted that the gasification of the char from the H-form coal occurred more slowly than the gasification of chars from the Na-form and the Ca-form coals as well as that of the char from the raw coal (Figs. 1-3 and s4). It is believed that the observed difference is mainly due to the catalytic effects of Na and Ca in the Na-form and Ca-form coal substrates, respectively, although the carbon structures of the chars from these ion-exchanged coal substrates may also differ slightly [Li *et al.*, 2000]. It also seems from Fig. 6 that the catalytic activity of Na in the char from the Na-form coal was higher than Ca in the char from the Ca-form coal under the same reaction conditions. This result is consistent with the data on the raw coal: the gasification conversion of the char from the raw coal (Figs. 1-3 and 4), containing some Na, was comparable to that of the char from the Ca-form coal.

However, it is surprising to note that the much higher concentration of Na in the Na-form coal (or Ca in the Ca-form coal) did not seem to make its reactivity much higher than that of the raw coal. The detailed reasons remain unclear. Firstly, it is known that the ion-exchanging processes to prepare the Na-form and Ca-

form coals caused irreversible changes to the coal
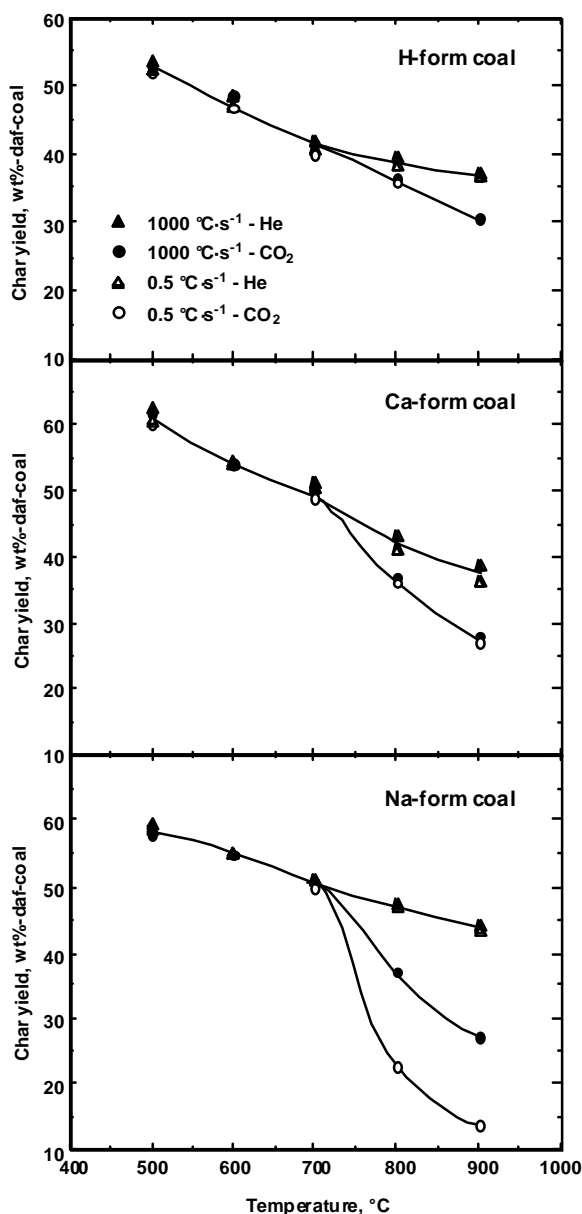

Fig. 6 Changes in the char yields with temperature during the pyrolysis and/or gasification of the H-form, Ca-form and H-form coals with a heating rate of 0.5 or 1000 °C·s⁻¹ and a holding time of 10 s

structure [Li *et al.*, 2000], which in turn may adversely affect the reactivity of the chars from the Na-form and Ca-form coals. Secondly, the Na and Ca in the coals go through considerable transformation upon heating, including their volatilisation [Li *et al.*, 2000]. The physical distribution and chemical forms of Na and Ca in the resulting chars, important factors influencing their catalytic activities during gasification, may differ considerably between the chars from the raw coal and the chars from the Na-form and Ca-form coals. Furthermore, the presence of high concentrations of Na

and/or Ca may also catalyse the changes of char structure during extended holding at elevated temperatures.

Under the current experimental conditions, the char was exposed to high temperatures for much longer time during pyrolysis at the heating rate of 0.5 $°C·s^{-1}$ than at 1000 $°C·s^{-1}$. In spite of this, the char yields from the Ca-form coal in CO_2 were comparable for both heating rates. In other words, the char prepared at the slow heating rate had much lower reactivities than its counterpart prepared at the fast heating rate. The lower reactivity of the slow-heating rate char is considered to be at least partially due to the (Ca-catalysed) changes in the char structure during the extended holding at elevated temperatures in the slow-heating-rate pyrolysis. On the other hand, for the chars from the Na-form coal, the char yield at the slow heating rate was clearly lower than that prepared at the fast heating rate. This implies that the structure of the char from the Na-form coal might have changed to a lesser extent than that of the char from the Ca-form coal when subjected to high temperatures for extended holding time at the slow heating rate.

Similar to the results of the Ca-form coal, the char yield from the H-form coal at the fast heating was nearly equivalent with that at the slow heating regardless of the atmosphere. This suggests that the char formed at the slow heating was much less reacstive with CO_2 than that at the fast heating. Hence, taken together with the results from the raw and Ca-form coals, the loss of the char reactivity along with extensive holding could involve not only catalytic but also non-catalytic processes.

CONCLUSIONS

During the pyrolysis and in-situ gasification of pulverised Loy Yang brown coal and its ion-exchanged coal samples over a range of heating rate from 0.5 to 1000 $°C·s^{-1}$, CO_2 surrounding the particles had negligible effects on the yield of tar, since the formation of its precursors and release out of the particles took place rapidly and completed at temperatures below 600 °C. After the completion of the tar evolution, CO_2 began to react with the nascent char at 700 – 800 °C even under a fast heating at 1000 $°C·s^{-1}$, causing gasification. During the heating up period, char formed under the fast heating was much more reactive with CO_2 than that under a slow heating at 0.5 $°C·s^{-1}$. The nascent char from the Na-form coal was more reactive in CO_2 than that from the Ca-form coal. Decreasing heating rate from 1000 to 0.5 $°C·s^{-1}$ led to more reduction in reactivity for the char from the Ca-form coal than for the char from the Na-form coal.

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