

## Pyrolysis of a Victorian Brown Coal in Helium and CO<sub>2</sub> Atmosphere

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### Abstract

Pyrolysis of a Victorian brown coal was performed in helium and CO<sub>2</sub> atmosphere under atmospheric flow in a wire-mesh reactor. Experiments were carried out over the ranges of pyrolysis conditions: heating rate of 0.5–1000 °C s<sup>-1</sup>, holding temperature of 500–900 °C, and holding time at peak temperature of 0 to 60 s. The experimental results revealed that the tar yield increased with the increase of heating rate in both helium and CO<sub>2</sub>, however negligible effect of gas atmosphere on the tar yield was observed. The char yield was not very sensitive to changes in heating rate at temperature lower than 800 °C in both helium and CO<sub>2</sub>. At higher temperatures, the gasification of nascent char by CO<sub>2</sub> led to significant decreases in the char yields. Decreasing heating rate from 1000 to 0.5 °C s<sup>-1</sup> 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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### Introduction

In the combustion and reforming/gasification process for coal the pyrolysis normally takes place in atmospheres containing reactive gases such as O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O. However, the pyrolysis of coal has largely been studied in inert atmosphere. The effects of reactive gas on the pyrolysis behaviour remain unclear. Thermochemical reactions termed 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 solid product, char. Among the volatiles, tar is evolved so rapidly that its evolution is completed before the particles temperature reaches 600 - 700 °C [1-6]. It is therefore believed that the reactive atmosphere around the particles is minimally involved in the primary reactions. Among the nascent products of the primary reactions, char would further experience oxidation (gasification) together with thermal annealing, while volatiles could also be oxidized/reformed. In most of the studies on char gasification by CO<sub>2</sub> or H<sub>2</sub>O [7-9], 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<sup>-1</sup>, 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 [10-11], 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.

In continuation of the previous studies [6, 12], the pyrolysis of a Victorian brown coal has been performed using a wire-mesh reactor. The reactor features the minimization of the extents of extra-particle homogenous 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<sub>2</sub>,

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 gasification have been discussed based on the experimental results.

## Experiment

### *Sample preparation*

The sample used in the study was a Victorian brown coal from the Latrobe Valley, Victoria, Australia. A bulk of as-mined coal was dried at temperature lower than 35 °C, crushed and sieved to collect the 106-150  $\mu\text{m}$  fraction. The fraction, which will be referred to as the raw coal, was then sealed in bottles and 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 dry-and-ash-free 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 sulfuric acid to prepare an acid-washed (H-form) coal. The contents of Na, Ca and Mg in the H-form coal were less than 0.001 wt%-db. 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, 12-13].

### *Pyrolysis experiments*

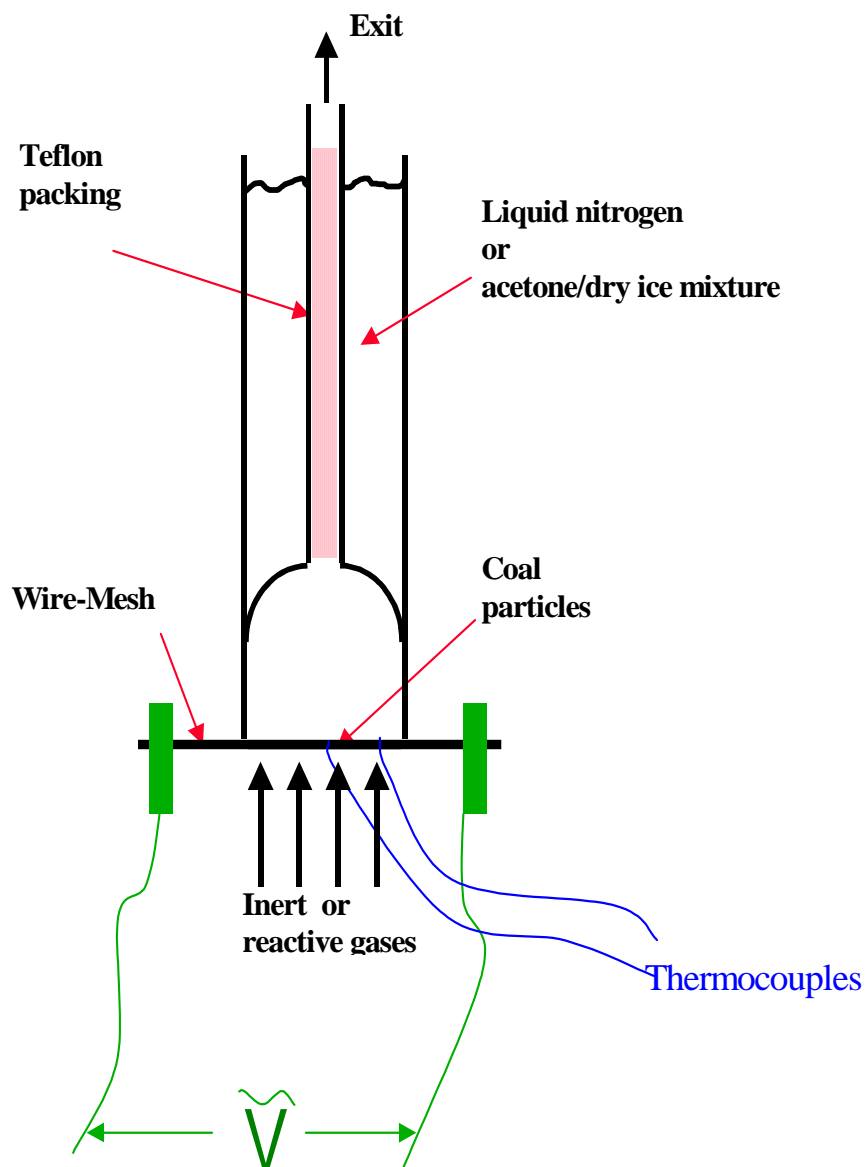
Pyrolysis experiments were carried out in a wire-mesh reactor (Fig. 1) similar to that used in previous studies [6, 12, 14-15] using atmospheric flow of helium (Ultra high purity > 99.999%) gas or CO<sub>2</sub> (Laser grade) as a carrier/reacting gas. Details of the pyrolysis experiments were described previously [6, 12]. In brief, the coal particles (less than 10 mg) were tightly sandwiched in a monolayer form by two mesh (stainless steel wire-mesh) layers. The wire-mesh was 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  $\mu\text{m}$  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. During an experiment in helium, a stream of helium gas flows through the sample holder, removing volatiles away from the vicinity of the reaction zone into a liquid nitrogen cooled tar trap which was packed with Teflon. However, during an experiment in CO<sub>2</sub>, an acetone/dry ice in place of liquid nitrogen was used as coolant for the tar trap. In both helium and CO<sub>2</sub> experiments, a gas flow rate of 3.4 L min<sup>-1</sup> (measured at 25 °C and 1 bar) was used. When the required holding time had elapsed, the heating current was stopped and the sample (and the sample-laden wire-mesh sample holder) allowed to cool naturally in the flowing helium/CO<sub>2</sub> gas stream.

### *Char and tar yields*

The weighing of the char sample after pyrolysis experiment was carried out after the char sample was considered to have reached equilibrium with ambient air. Char yield was determined by either weighing the coal/char-laden mesh before and after pyrolysis in helium or weighing the char recovered from the mesh after pyrolysis in CO<sub>2</sub>.

At the end of a pyrolysis experiment, tar was recovered by washing the tar trap with a chloroform (CHCl<sub>3</sub>): methanol (CH<sub>3</sub>OH) mixture (80:20 vol/vol) [6, 12]. For the quantification of tar, a portion or all of the tar

solution from a pyrolysis experiment was transferred onto an aluminum dish. The solvents were then evaporated in a nitrogen-swept oven controlled at 35 °C. Tar yield was determined by the weight uptake of the dish during the process.



**Fig. 1** Wire-mesh reactor system

#### *Characterization of tar*

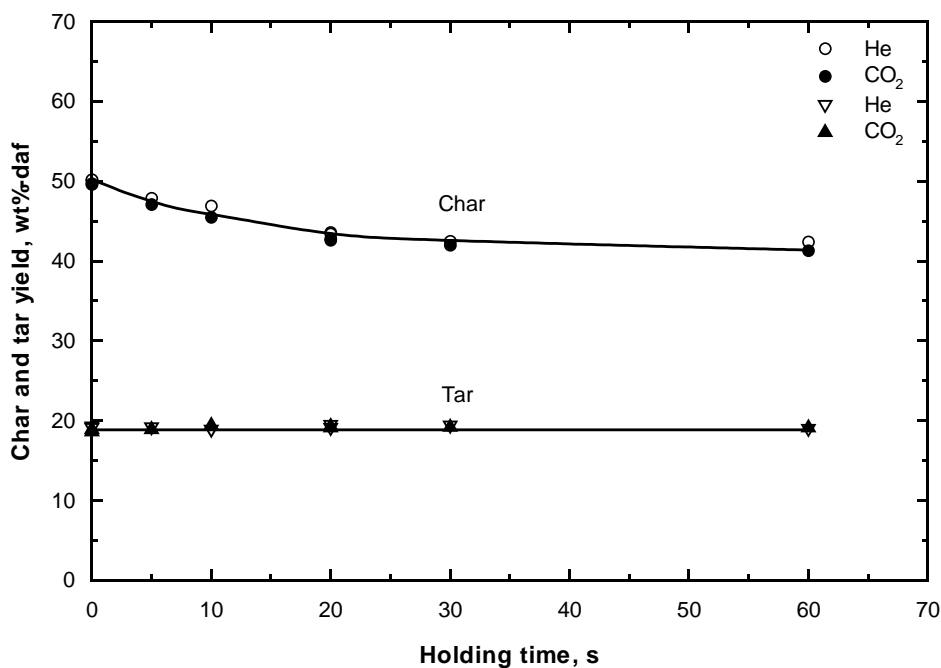
Tar solutions were analysed by UV fluorescence spectroscopy. The tar solutions obtained from the earlier mentioned pyrolysis experiments were diluted with Spectrosol grade methanol (from BDH) until the effects

of self-absorption due to bulk concentration were negligible. This was normally below  $10^{-6}$  g ml $^{-1}$ . Synchronous spectrum of the diluted solution was then recorded on a Perkin-Elmer LS50B luminescence spectrometer over a wavelength range from 280 to 600 nm with a constant energy difference corresponding to a wavelength difference of 2800 cm $^{-1}$  between the excitation and emission monochromators. A UV/visible cell of 1 cm light path length was used. Narrow emission and excitation monochromators were used to maximize selectivity. A slit width 2.5 nm was used for both monochromators for tar from the pyrolysis experiment. A scan speed of 200 nm min $^{-1}$  was used and each spectrum shown in this paper represents the average of four scans. The spectrometer featured automatic correction for changes in source intensity as a function of wavelength. The fluorescence intensity expressed on the basis “per g of coal” was calculated by multiplying the fluorescence intensity of the tar sample, at the same concentration, by tar yields from the pyrolysis experiments. Other details of the analysis were reported elsewhere [12, 16].

## Results and Discussion

### *Effects of CO<sub>2</sub> on tar and char yields from raw coal at different holding times*

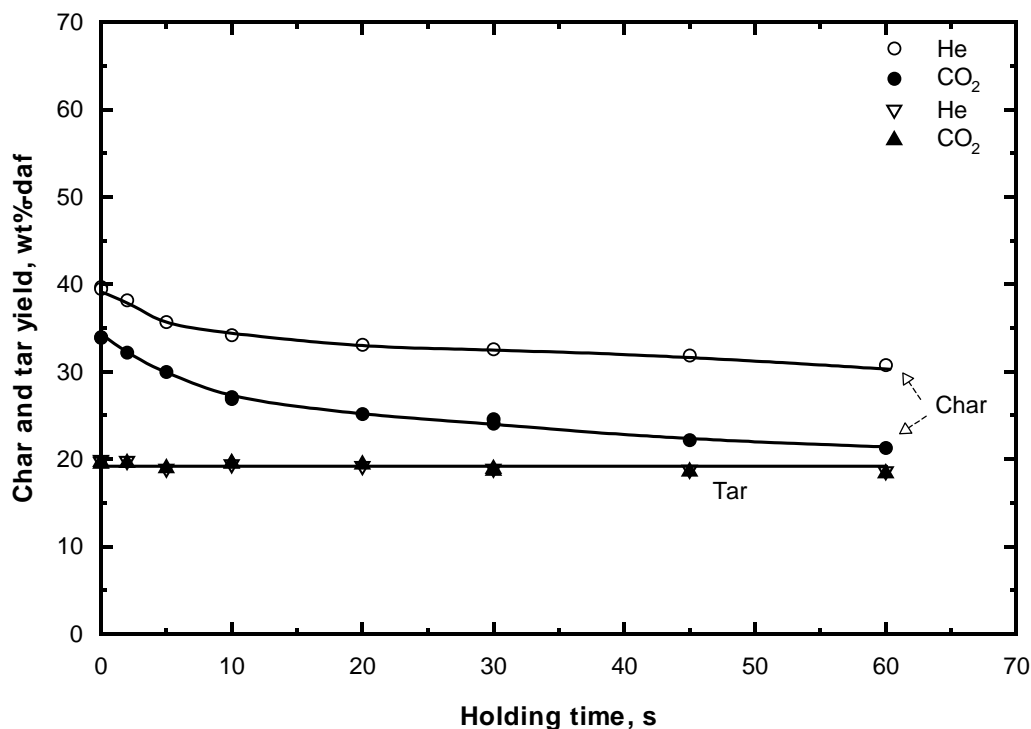
Fig. 2 shows the tar and char yields from the raw coal as a function of holding time at 600 °C with a heating rate of 1000 °C s $^{-1}$ . When the coal was heated at 1000 °C s $^{-1}$  to 600 °C, the data in Fig. 2 indicate that the release of the tar was almost instant. Increasing the holding time from “0 s” to 20 s did not lead to any significant increase in the observed tar yield. The “0 s” holding time at 600 °C in Fig. 2 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 slowly, probably forming gases such as CO, CH<sub>4</sub> and H<sub>2</sub>. The tar and char yields during the pyrolysis in helium were in good agreement with those reported previously [6, 12].



**Fig. 2** Effects of holding time on the tar and char yields from the pyrolysis of raw coal at 600 °C (Heating rate: 1000 °C s $^{-1}$ )

It is also noted in Fig. 2 that the differences in the tar and char yields between the pyrolysis in helium and pyrolysis/gasification in  $\text{CO}_2$  were both within the experimental errors. This suggests that  $\text{CO}_2$  could hardly influence the tar evolution and gasify the nascent char to a negligible extent at 600 °C.

As can be seen in Fig. 3, the tar yields from the pyrolysis in helium and pyrolysis/gasification in  $\text{CO}_2$  also 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. 2). This result is explained by considering that the tar evolution under heating at 1000 °C  $\text{s}^{-1}$  nearly completed as soon as the temperature reached 600 °C, and as a result,  $\text{CO}_2$  brought about little additional formation of tar compared with that in helium. On the other hand, at 900 °C the char yield was systematically lower in  $\text{CO}_2$  than in helium. This should be arisen from the gasification of the nascent char by  $\text{CO}_2$ . 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 during the process when the temperature was raised to 900 °C.

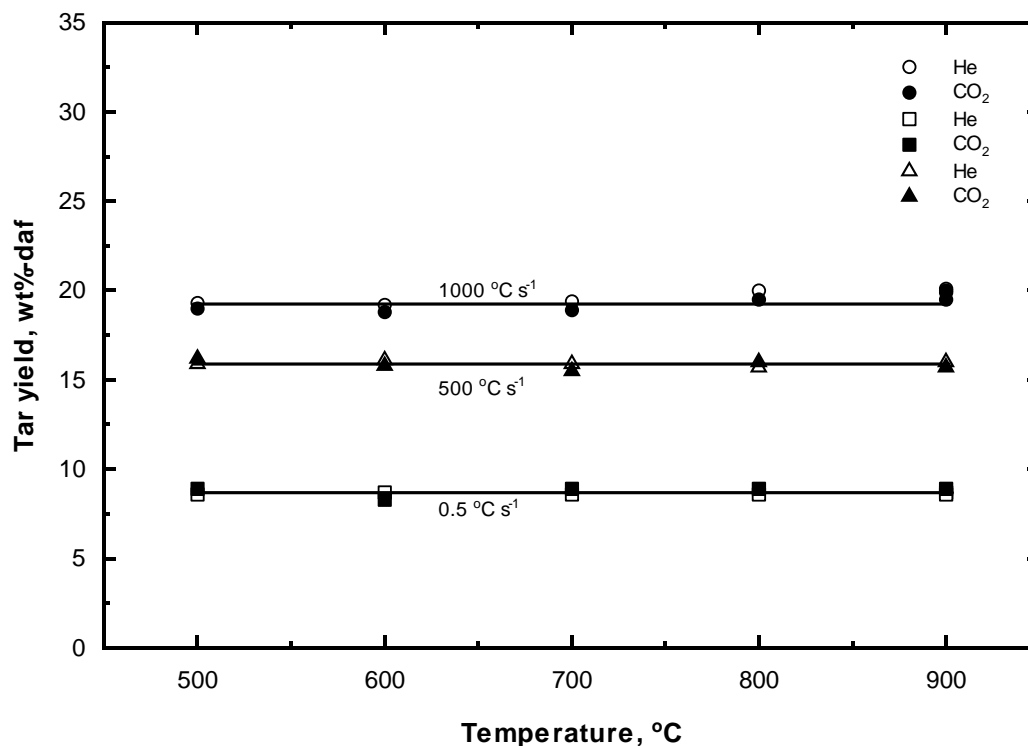


**Fig. 3** Effects of holding time on the tar and char yields from the pyrolysis of raw coal at 900 °C. (Heating rate: 1000 °C  $\text{s}^{-1}$ )

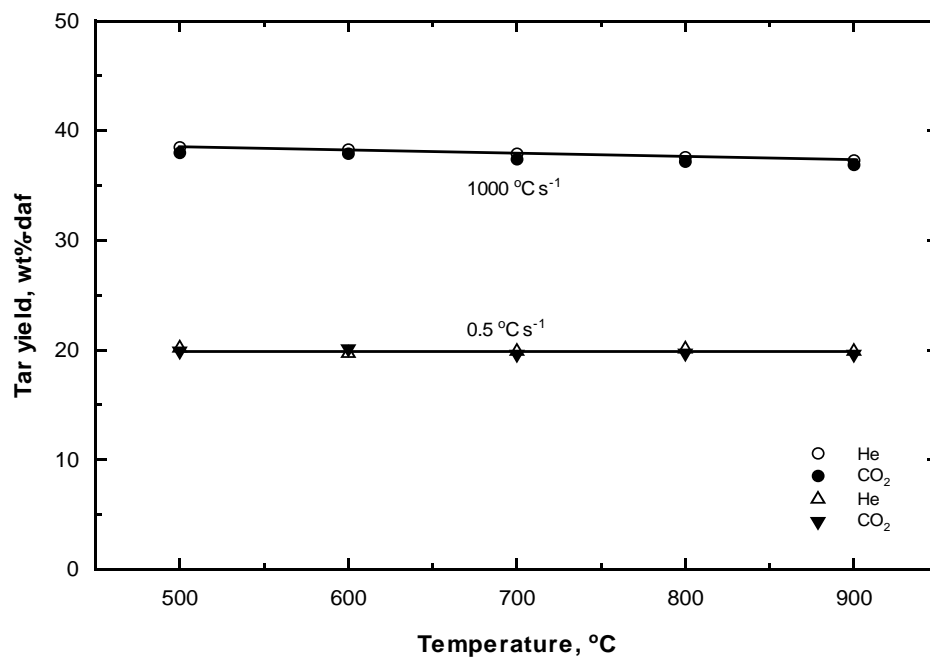
#### *Effects of $\text{CO}_2$ on the tar yields from pyrolysis of raw and ion-exchanged coals at different heating rates*

Figs. 4–7 show the tar yields from the raw Loy Yang, H-form, Ca-form and Na-form coal samples during pyrolysis in helium and pyrolysis/gasification in  $\text{CO}_2$  with a heating rate of 0.5 - 1000 °C  $\text{s}^{-1}$ . The data in Figs. 4–7 indicate that the tar yields increased when the heating rate was increased from 0.5 to 1000 °C  $\text{s}^{-1}$ . The tar yield was found to be very sensitive to changes in heating rate. The heating rate sensitivity of tar yield is believed to be partly related to the presence of carboxyl/carboxylate groups and other bulky substitution groups in the coal samples. As shown in Figs. 6–7, the tar yields from the Ca-form and Na-

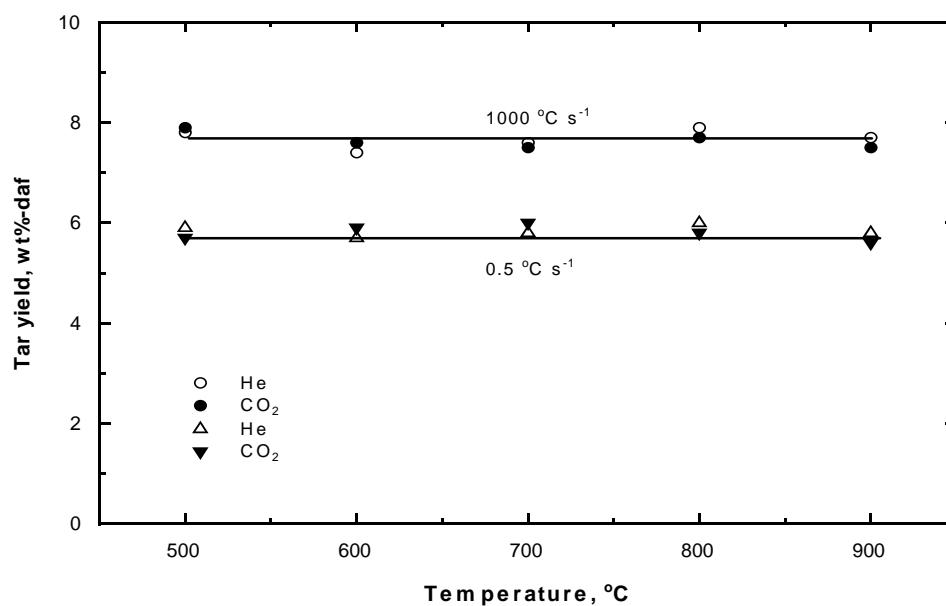
form coal samples are much lower than those from the raw (Fig. 4) and H-form (Fig. 5) coal samples. The loss of humic material and the rearrangement of the coal macromolecular network during ion-exchanging process are thought to be responsible for the lower tar yields. Although the tar yields were not affected significantly by the replacement of helium and CO<sub>2</sub> over a range of temperature (up to 900 °C) and heating rate (0.5 °C s<sup>-1</sup> and 1000 °C s<sup>-1</sup>). Taken together, these data (Figs. 4-7) indicate that the reactivity of CO<sub>2</sub> at the temperatures (up to 900 °C) of major tar formation and release was not high enough to break down the tar precursors inside the particles to cause any observable changes in the tar yields. At a slow heating rate of 0.5 °C s<sup>-1</sup>, the release of tar components was virtually complete at very low temperature (e.g. 500-600 °C). Clearly at this low temperature, CO<sub>2</sub> was not able to react significantly with the tar precursors inside the particles. Similarly, the data in Figs. 4-7 suggest that CO<sub>2</sub> was not reactive enough to interfere with the tar-forming reactions involving **radicals**. At high temperatures (>700 °C) the in situ gasification of the nascent char did not produce any significant amount of large fragments to cause a detectable increase in the tar yield for both fast and slow heating rates used. The unchanged tar yields going from helium to CO<sub>2</sub> also mean that the difference in the diffusivity between helium and CO<sub>2</sub> did not seem to have significantly altered the mass transfer processes of tar precursors out of the abundant pore structure of the particles. The UV-fluorescence spectroscopy of the tars also confirmed the similarity between the tars proposed in CO<sub>2</sub> and in helium at both heating rates.



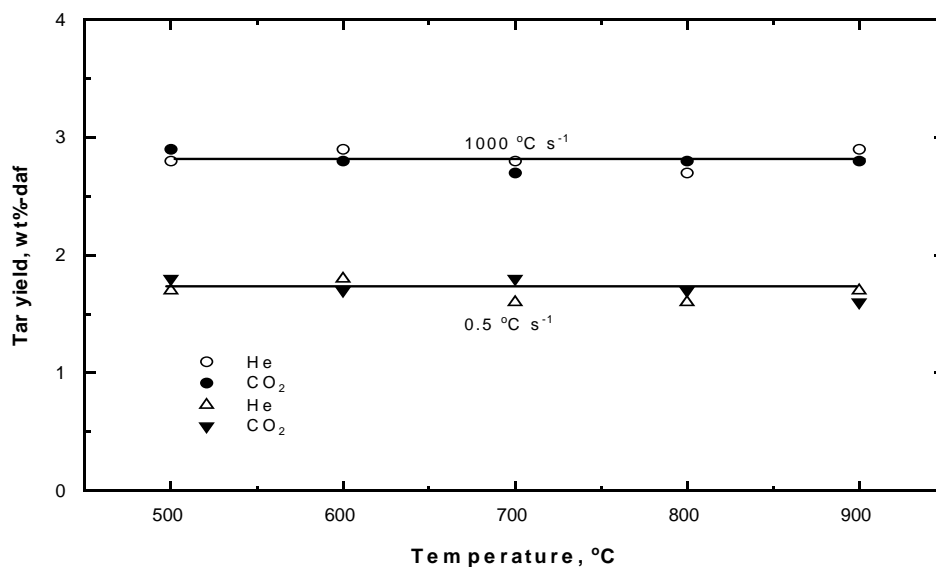
**Fig. 4** Effects of heating rate on the tar yield from the pyrolysis of raw coal (Holding time: 10 s for 1000 °C s<sup>-1</sup> and 20 s for 0.5 °C s<sup>-1</sup>)



**Fig. 5** Effects of heating rate on the tar yield from the pyrolysis of H-form coal (Holding time: 10 s for 1000 °C s<sup>-1</sup> and 20 s for 0.5 °C s<sup>-1</sup>)



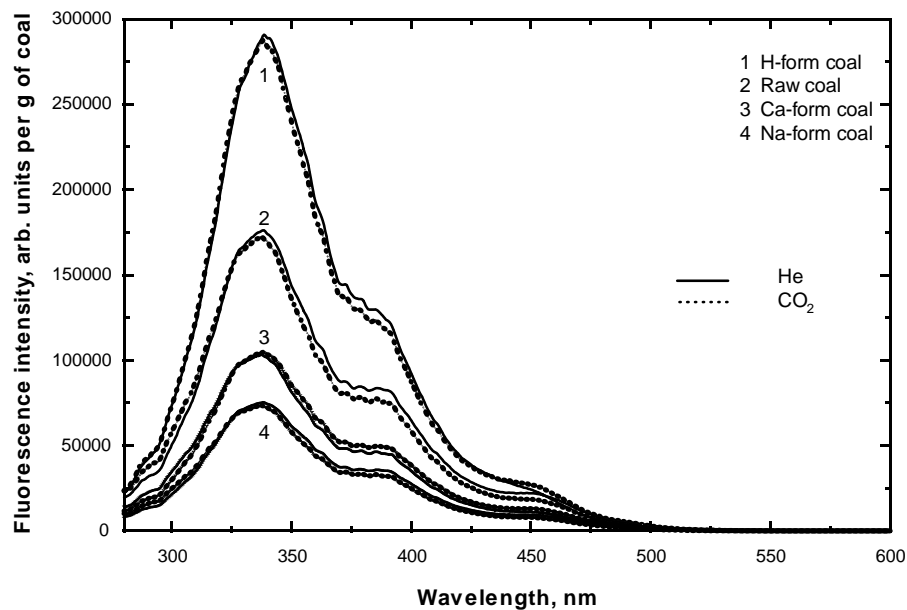
**Fig. 6** Effects of heating rate on the tar yield from the pyrolysis of Ca-form coal (Holding time: 10 s for 1000 °C s<sup>-1</sup> and 20 s for 0.5 °C s<sup>-1</sup>)



**Fig. 7** Effects of heating rate on the tar yield from the pyrolysis of Na-form coal (Holding time: 10 s for 1000 °C s<sup>-1</sup> and 20 s for 0.5 °C s<sup>-1</sup>)

*Effects of CO<sub>2</sub> on the synchronous spectra of tars from the pyrolysis of raw and ion-exchanged coals*

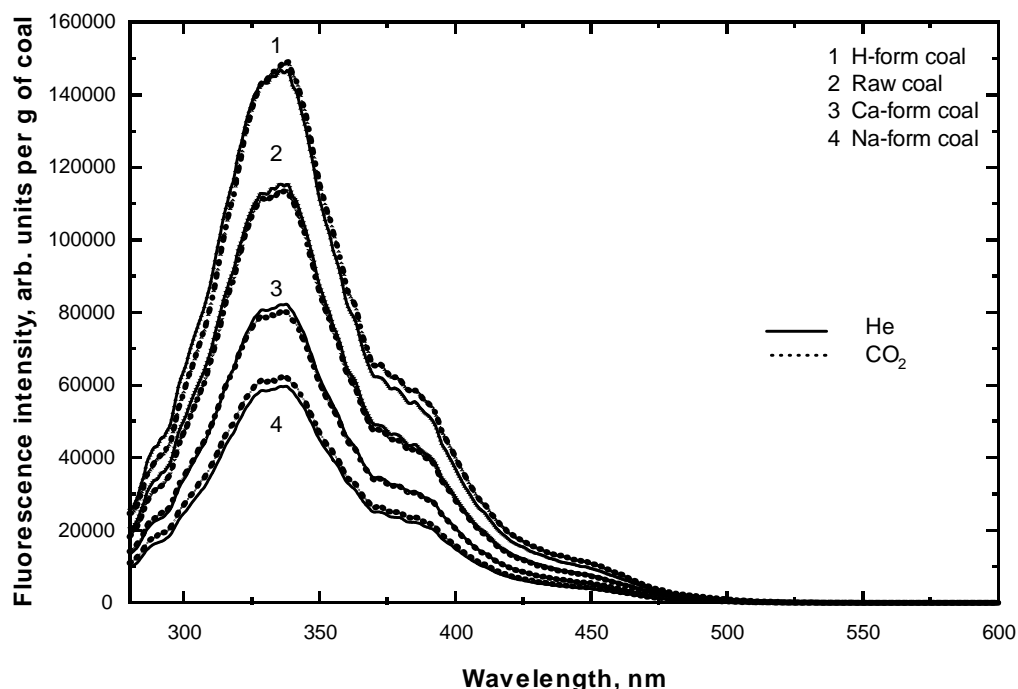
Figs. 8-9 show the synchronous spectra of the tars produced from the pyrolysis of raw and ion-exchanged coal samples at both fast (1000 °C s<sup>-1</sup>) and slow (0.5 °C s<sup>-1</sup>) heating rates.



**Fig. 8** Effects of CO<sub>2</sub> on the synchronous spectra of tar yield from the pyrolysis of raw and ion-exchanged coal samples (Heating rate: 1000 °C s<sup>-1</sup>)



The data in Figs. 8-9 indicate that the increasing temperature from 500 °C to 900 °C did not seem to have significant effects on the release of larger aromatic ring systems not only in helium but also in CO<sub>2</sub> atmosphere. On the other hand the spectra of tar yields from both the raw and ion-exchanged coal samples at a slow heating rate of 0.5 °C s<sup>-1</sup> were significantly lower than those from the same samples at fast heating rate (1000 °C s<sup>-1</sup>) indicating the yields of larger aromatic ring systems are much higher at fast heating rates than at slow heating rates. In other words, fast heating rate resulted in more aromatic volatile products than the slow heating rate. The fluorescence intensities of the tars from the Na-form and Ca-form coal was always much lower than those from the raw and H-form coal samples. The presence of Na and Ca in the coal structure has played a much more important role.

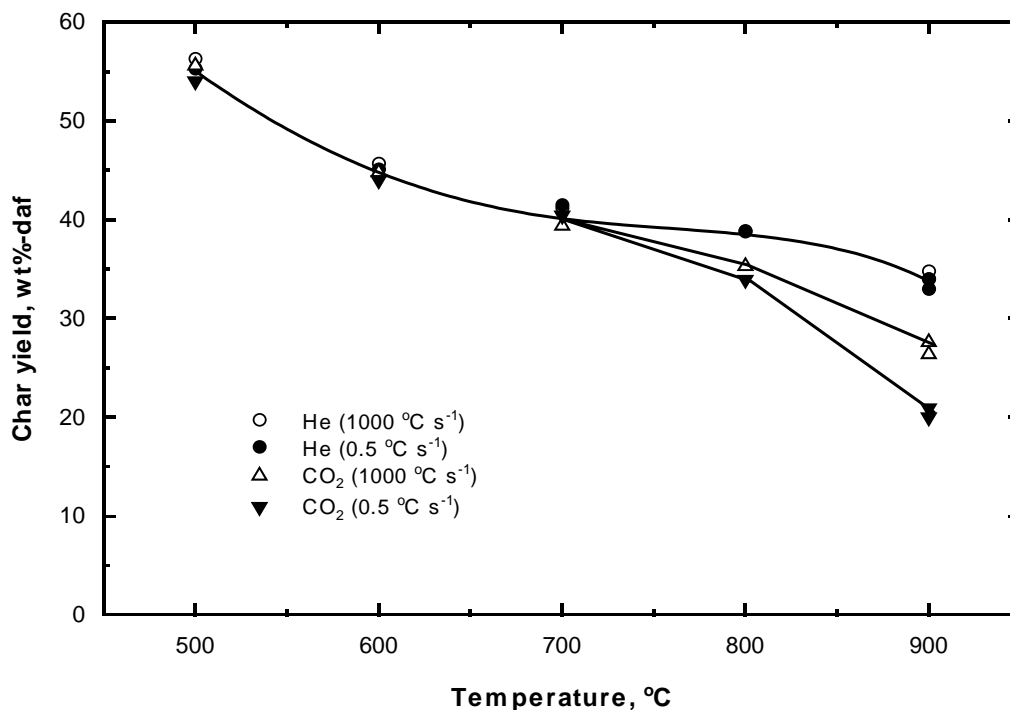


**Fig. 9** Effects of CO<sub>2</sub> on the synchronous spectra of tar yield from the pyrolysis of raw and ion-exchanged coal samples (Heating rate: 0.5 °C s<sup>-1</sup>)

#### *Heating rate effect on gasification reactivity of char from raw coal*

Fig. 10 illustrates the char yield from the raw coal during the pyrolysis in helium and the pyrolysis/gasification in CO<sub>2</sub> with heating rates and holding times of 1000 °C s<sup>-1</sup> and 0.5 °C s<sup>-1</sup> and 10 s and 20 s, respectively. As expected from the results (Figs. 4-7) of the both fast and slow 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 yields under heating at 1000 °C s<sup>-1</sup> (Figs. 4-7), the tar yield at 0.5 °C s<sup>-1</sup> was clearly lower. On the other hand, the char yield shown in Figure 10 was not very sensitive to changes in both heating rates (from 1000 °C s<sup>-1</sup> to 0.5 °C s<sup>-1</sup>) at temperatures lower than 800 °C in both helium and CO<sub>2</sub>. It is believed that heating the coal particles rapidly at fast heating rate enhances the chance of simultaneous bond breaking, leading to the release of volatiles within a very short period of time. As was discussed in more detail elsewhere [12, 16-17], this would reduce the residence time of tar precursors inside the coal/char particles. Therefore, the tar precursors are more likely to be released without

being cracked at a fast heating rate than at a slow heating rate. At a slow heating rate, the tar precursors would likely be cracked to form char and light gas. Due to the low aromatic content of the tar precursors [17], only a very little char would be formed. Thus, the amount of char formed as a result of thermal cracking of tar precursors is so small that it may not be observed in terms of char yield increase. The main products of the thermal cracking are light gases [12]. In other words, the char yields obtained at slow heating rates may not be much smaller than that obtained at fast heating rates. But temperature above 700 °C, the char yield decreased at slow heating rate than that at fast heating rates in CO<sub>2</sub>, mainly due to the reaction of CO<sub>2</sub> gas either with the nascent char or less likely with the tar precursors.

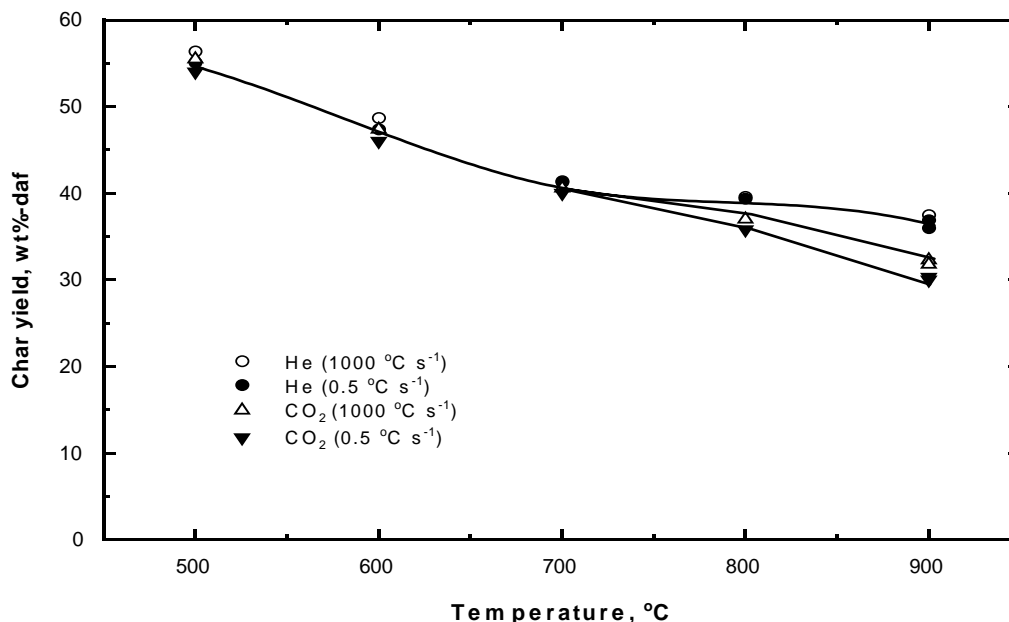


**Fig. 10** Effects of temperature and gas atmosphere on the char yield from the pyrolysis of raw coal. (Holding time: 10 s for 1000 °C s<sup>-1</sup> and 20 s for 0.5 °C s<sup>-1</sup>)

#### *Effect of CO<sub>2</sub> on the char yields in the presence and absence of metallic species*

The H-form, Ca-form and Na-form coal samples were subjected to the pyrolysis in helium and pyrolysis/gasification in CO<sub>2</sub>. The results are given in Figs. 11-13. In Figs. 4-7, the tar yield from every coal was affected insignificantly by the replacement of helium with CO<sub>2</sub> over the ranges of temperature and heating rate examined. In contrast to the tar yield, the char yield was seen to decrease as the gas atmosphere surrounding the particles was changed from helium to CO<sub>2</sub>. The difference between the char yield in helium and that in CO<sub>2</sub> can be considered as a result of the gasification of the nascent char. For the raw coal (Fig. 10), significant gasification could be observed above 700 °C. It is noted that the gasification of the char from the H-form coal (Fig. 11) occurred more slowly than the gasification of chars from the Ca-form (Fig. 12) and the Na-form (Fig. 13) coals as well as the gasification of the char from the raw Loy Yang coal (Fig. 10). It is believed that the observed difference is mainly due to the catalytic effects of Na

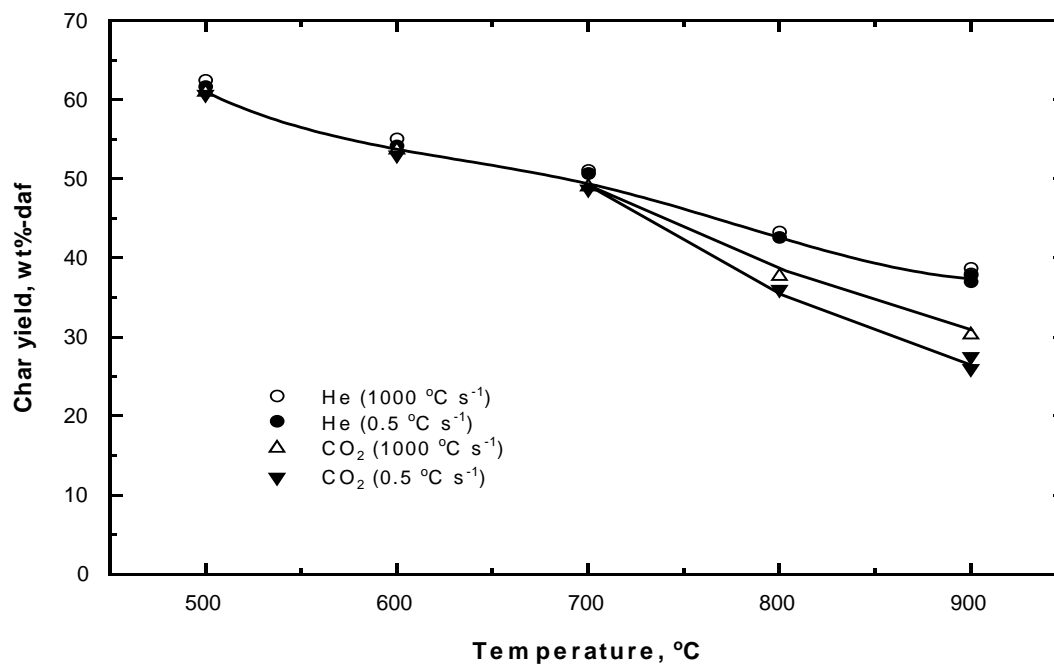
and Ca in the Na-form and Ca-form coal substrates, respectively, although the carbon structures of the chars from these ion-exchanged coal substrates may also differ slightly [12].



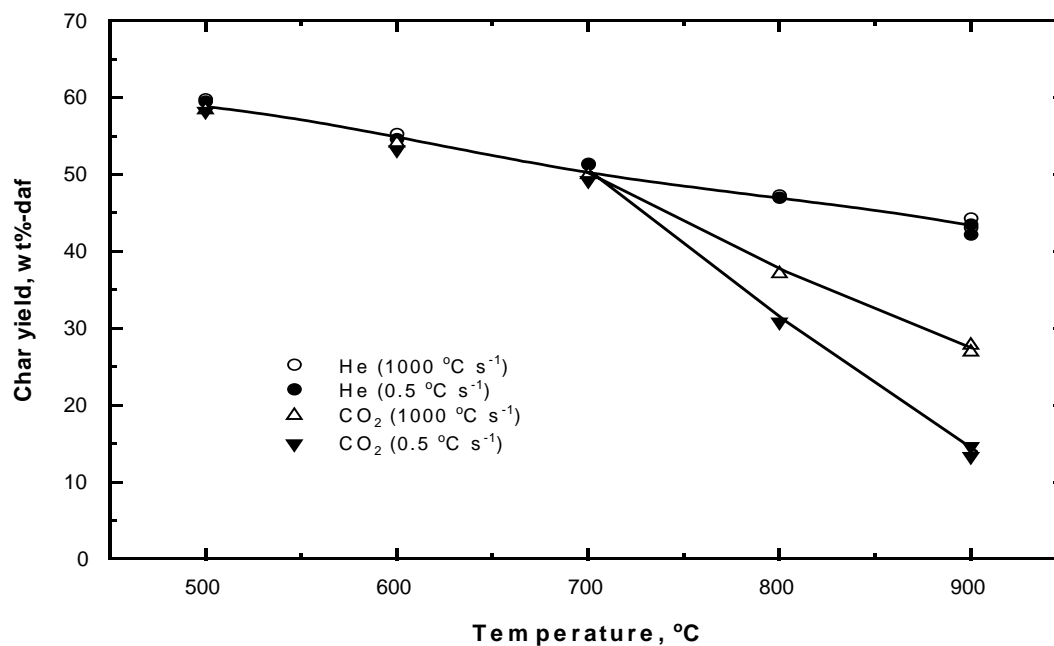
**Fig. 11** Effects of temperature and gas atmosphere on the char yield from the pyrolysis of H-form coal (Holding time: 10 s for 1000 °C s<sup>-1</sup> and 20 s for 0.5 °C s<sup>-1</sup>)

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 structure [12], 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 [12]. Their physical distribution and chemical forms in the resulting chars, important factors influencing their catalytic activities of Na and Ca 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 shown in Figs. 11-13, the char was exposed to high temperatures for much longer time during pyrolysis at slow heating rate of 0.5 °C s<sup>-1</sup> than at fast heating rate of 1000 °C s<sup>-1</sup>. For the chars from the Na-form coal (Fig. 13), 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 (Fig. 12) when subjected to high temperatures for extended holding time at the slow heating rate. The char yield from the H-form coal (Fig. 11) as well as from Ca-form coal (Fig. 12) at the fast heating was not too much difference with that at the slow heating rate regardless of the atmosphere. This suggests that the char formed at the slow heating was much less reactive with CO<sub>2</sub> than that at the fast heating. Hence, 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.



**Fig. 12** Effects of temperature and gas atmosphere on the char yield from the pyrolysis of Ca-form coal (Holding time: 10 s for 1000 °C s<sup>-1</sup> and 20 s for 0.5 °C s<sup>-1</sup>)



**Fig. 13** Effects of temperature and gas atmosphere on the char yield from the pyrolysis of Na-form coal (Holding time: 10 s for 1000 °C s<sup>-1</sup> and 20 s for 0.5 °C s<sup>-1</sup>)

## Conclusion

Pyrolysis experiments on a Victorian brown coal were carried out in a wire-mesh reactor using atmospheric flow of helium (Ultra high purity > 99.999%) gas or CO<sub>2</sub> (Laser grade) as a carrier/reacting gas. The salient observations are as follows.

- i) The tar yield was found to increase with increasing heating rate in both helium and CO<sub>2</sub> atmosphere. However, CO<sub>2</sub> surrounding the particles had negligible effects on the tar yield over a range of heating rate from 0.5 to 1000 °C s<sup>-1</sup> for both raw and its ion-exchanged coal samples.
- ii) The fluorescence intensities of the tars from the Na-form and Ca-form coal were always much lower than those from the raw and H-form coal.
- iii) In both helium and CO<sub>2</sub>, the char yield was not very sensitive to changes in heating rate up to temperature of 700 °C. At higher temperatures, the gasification of the nascent char by CO<sub>2</sub> led to significant decreases in the char yields.
- iv) During the heating up period, char formed under the fast heating was much more reactive with CO<sub>2</sub> than that under a slow heating at 0.5 °C s<sup>-1</sup>.
- v) The nascent char from the Na-form coal was more reactive in CO<sub>2</sub> than that from the Ca-form coal. Decreasing heating rate from 1000 to 0.5 °C s<sup>-1</sup> led to more reduction in reactivity for the char from the Ca-form coal than from the Na-form coal char.

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