Changes in nascent char structure during the gasification of low-rank coals in CO₂

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Abstract

The purpose of this study is to investigate the structural changes in nascent chars during the gasification of two low-rank coals in CO$_2$ at 1000 °C and 1200 °C. Western Australian Collie sub-bituminous coal and Victorian Loy Yang brown coal were heated up at 1000 K s$^{-1}$ in He/CO$_2$ in a wire-mesh reactor. FT-Raman spectroscopy was applied to understand the key structural features of nascent chars. For comparison, the Raman data of the chars produced in a drop tube furnace in N$_2$/CO$_2$ at 1200 °C for Loy Yang coal were also included in this study. The results showed that the evolution of char structure was determined by the counteracting effects of thermal annealing and oxygenation during the initial holding at 1000 °C ($< 1$ s).

With further holding at 1000 °C or holding at 1200 °C, the rapid formation of O-containing functional groups and the selective consumption of small aromatic rings took place. For each coal, there was no significant change in reaction pathway between gasification at 1000 and 1200 °C. Combining the data from FT-Raman and FT-IR spectroscopy, there appears to be more than one type of O-containing functional groups formed during the gasification in CO$_2$. Some are more sensitive to Raman scattering but some are more sensitive to FTIR absorption.

*Keywords:* Raman spectroscopy; IR spectroscopy; Fast pyrolysis; Gasification; Char structure; Sub-bituminous coal; Brown coal.
1. Introduction

Gasification is an important technology for the utilisation of low-rank coals due to their high gasification reactivity [1]. Through gasification, low-rank coals are converted to syngas (mainly consists of CO and H₂) that can be used to produce hydrogen and to synthesise chemicals or liquid fuels. Unlike in pulverised-fuel combustion technology, CO₂ is partially consumed as a gasification agent to produce CO in gasification technology. This is a more economical way to reduce CO₂ emissions than the conventional CO₂ capture technologies [2]. It is essential to understand the reaction mechanism of coal/coal char-CO₂ for further development of gasification technologies.

Recently, the transformation of inorganic species and char structures has been recognised as an important factor during the gasification in CO₂ [3-5]. The quantitative analysis of catalysts is relatively easy but the direct quantification of char structural features is a challenge. Raman spectroscopy has been used as a powerful technique to obtain information about the carbon skeleton in char during the pyrolysis/gasification of low-rank coals [6-22] and biomass [23-27]. The reaction pathways between gasification in O₂, CO₂ and H₂O are different at 800 °C [9, 18, 19]. Su and co-workers [12] studied the structural changes during the gasification of a Chinese bituminous coal in CO₂. With a fast heating rate, significant changes in char structure (distribution of ring systems and O-containing functional groups) already took place with “0 minutes” holding (end of the coal feeding) during gasification in CO₂. It seems that the previous research concerning the changes in char structure during gasification in CO₂ was mainly carried out at the magnitude of a few minutes. There is still a lack of experimental evidence about the structural evolution of nascent char during the initial gasification (seconds
or less than 1 s) in CO₂. Therefore, it is necessary to find an accurate method to study the initial (a few seconds or shorter) changes in the structure of nascent chars during gasification.

A wire-mesh reactor (WMR) that was frequently used in the investigation of primary pyrolysis [28-31] and gasification [32, 33] can provide a wide range of heating rate from 0.1 to 5000 K s⁻¹ and high time resolution (increment of 10 ms). It is very suitable for the production of nascent char with even milliseconds holding at a pre-set peak temperature. In addition, a fast flow of carrier gas (at 0.1 m s⁻¹) continuously passes through the sample particles, which immediately cools down the volatiles and takes them away from the coal/char particles. In other words, a WMR that can minimise volatile-char interactions is appropriate to be employed to investigate the initial char structure evolution only due to the gasification and thermal cracking.

Jamil and co-workers [32] studied the mechanism of the gasification of Loy Yang brown coal in CO₂ in a WMR at 600 to 900 °C. They found that rapid weight losses due to the gasification of char happened during the heating process from 700 to 900 °C. The gasification rate strongly depended on the rate of thermal cracking in this temperature range. However, the structural evolution of nascent char during the gasification in CO₂ is still unclear.

In this study, a brown coal and a sub-bituminous coal were heated up rapidly to 1000 and 1200 °C with holding times up to 30 s in CO₂ and in He, respectively. The brown coal was also pyrolysed (pure N₂) and gasified (5.3% CO₂ balanced with N₂) in a drop tube furnace (DTF) at 1200 °C with the holding time from 2.3 to 3.9 s. All chars were then analysed by FT-Raman spectroscopy and FTIR spectroscopy to gain insight into the evolution of the char structure during initial holding in CO₂ at relatively high temperatures.
2. Experimental

2.1 Sample preparation

For the experiments in the WMR, two low-rank coals (Collie sub-bituminous coal from Western Australia and Loy Yang brown coal from Victoria) were used. The sample preparation of two coals can be found elsewhere [14, 30]. Briefly, “as mined” coal was dried at low temperature (<35 °C). The air-dried coal was ground and screened to the size of 106-150 μm. The properties of the two coals are shown in table 1.

For experiments in the DTF, the air dried Loy Yang coal was crushed by a blender (Hamilton Beach, Magnum Blender MB-911) to the size < 125 μm. The sample was further dried in a vacuum oven at 60 °C. The moisture in coal to be used in the DTF varied from 0.78 to 1.1%.

2.2 Pyrolysis and gasification

The details of the operating procedure for the WMR can be found elsewhere [30]. Briefly, ~10 mg sample particles were sandwiched between two layers of stainless steel mesh. Two electrodes clamped two ends of mesh and supplied an alternating current to heat the samples. A high flow of ultra-high purity helium/CO₂ passed through the sample particles at a rate of 0.1 m s⁻¹ (measured under ambient conditions). K type thermocouples were used in He and S type thermocouples were used for the experiments in CO₂.

For the DTF experiments [34], the Loy Yang coal sample was continuously fed into the 1200 °C hot furnace through a water-cooled feeding tube. After a few seconds in an
atmosphere of 5.3-5.4 vol% CO₂ balanced with N₂ or pure N₂, solid products were collected through a water-cooled probe. Large char particles dropped straight in a filter, while the fine char/soot particles were taken away with carrier gas through a bypass. The large char particles in the filter were collected for further analysis. The absolute pressure in the DTF was 0.5 MPa for gasification and pyrolysis.

2.3 FT-Raman/IR spectroscopy for char characterisation

A Perkin-Elmer Spectrum GX FT-Raman/IR spectrometer was used to acquire the FT-Raman/IR spectra of chars. All the char samples were mixed and ground with spectroscopic grade potassium bromide (KBr). The concentration of char in char-KBr mixture was chosen to be 0.25% [35]. A 10-band deconvolution method was used to analyse the Raman spectra between 800 and 1800 cm⁻¹ [15]. The total Raman area, Raman band ratios and FTIR intensity (600 to 1800 cm⁻¹) were applied to characterise the char structural features in this study.

3. Results and discussion

3.1 Char yields of Loy Yang coal during fast pyrolysis and gasification

The changes in char yield as a function of holding time during the pyrolysis/gasification of Loy Yang brown coal in the WMR at 1000 and 1200 °C are illustrated in Fig. 1. The char yield and Raman data of the chars pyrolysed in WMR have been published in Ref. 36 and used here for comparison purposes. The “0 s” holding means the char that only underwent the heating process with no holding at peak temperatures. At 1000 °C, compared with pyrolysis
in He at 1000 °C, the char yield had an additional 3-4% weight loss during the initial 1.5 s gasification in CO$_2$. With further stay at 1000 °C, a large decrease in char yield was observed from ~33 to ~7% from 1.5 to 10 s. At 1200 °C, weight loss (~2.5%) occurred during fast heating (in 0.2 s) in CO$_2$ from 1000 to 1200 °C. The rate of the weight loss was 12.5 wt%-db s$^{-1}$ (equal to 12.64 wt%-daf s$^{-1}$). It is worth emphasising that only ~1.2% weight loss was observed during heating from 1000 to 1200 °C in He. This indicates that the rate of weight loss due to thermal cracking is 6 wt%-db s$^{-1}$ (6.07 wt%-daf s$^{-1}$). Therefore, the gasification rate due to CO$_2$ was 6.57 wt%-daf s$^{-1}$ which is similar to the thermal cracking rate 6.07 wt%-daf s$^{-1}$. This indicates that the initially high gasification rate of char is strongly related to the thermal cracking during heating from 1000 to 1200 °C, which is consistent with the work done by Jamil and co-workers who carried out gasification experiments in CO$_2$ at 700 to 900 °C [32]. During holding at 1200 °C, a very significant decrease in char yield took place within 1.7 s from ~32 to ~7%. The gasification reaction between nascent char and CO$_2$ at high temperatures was significant, which might result in the corresponding changes in char structure, as will be discussed in the following section.

3.2 Structural changes in Loy Yang coal char during gasification in CO$_2$

Figures 2 and 3 show the changes in the total Raman area from 800 to 1800 cm$^{-1}$ and the band area ratio of $I_{(G_r+V_l+V_r)}$ to $I_D$ as a function of holding time in He/CO$_2$. The total Raman area is mainly determined by two factors: the O-containing functional groups that would enhance the total Raman intensity [15] and aromatic ring systems that would increase the light absorptivity and reduce the total Raman intensity. The ratio of $I_{(G_r+V_l+V_r)}$ to $I_D$ mainly reflects the ratio of small aromatic rings (3-5 fused benzene rings) to large ones (≥ 6 rings) [15].
As is shown in Fig. 2, the total Raman area of Loy Yang coal char during the gasification in CO$_2$ was overall higher than that during pyrolysis in He at 1000 °C. The increase in total Raman area after reaction with CO$_2$ should be mainly due to the formation of O-containing functional groups and/or the consumption of ring systems. In Fig. 3, it is clear that the ratio between small and large aromatic rings during gasification is overall lower than that during pyrolysis at 1000 °C, which indicates that the ring systems are more condensed during the gasification in CO$_2$ than during pyrolysis. The more condensed ring systems would have caused the lower total Raman area, which was opposite to the observed higher total Raman area in CO$_2$ than in He. Because of that, the higher total Raman area (Fig. 2) in CO$_2$ should be mainly due to the formation of O-containing functional groups in CO$_2$ rather than the changes in aromatic ring systems.

A minimum in the total Raman intensity was observed for char produced at 1 s holding at 1000 °C in Fig. 1. For the char produced by pyrolysis at 1000 °C, the total Raman area significantly decreased within 1 s holding, which should be mainly due to the thermal annealing (aromatic ring condensation and loss of O-containing functional groups). Therefore, the minimal total Raman area at 1 s should be mainly attributed to the counteraction of two opposite effects: oxygenation and thermal annealing. As the thermal annealing during pyrolysis is almost completed within 1 s, the total Raman area gradually increased from 1 to 3 s in CO$_2$ with the continuous formation of O-containing functional groups at 1000 °C. Very slow increases in total Raman area were observed with further holding from 3 to 10 s in CO$_2$. The nearly constant total Raman area from 3 to 10 s holding in CO$_2$ should be due to the dynamic balance between the thermal cracking and the formation of O-containing functional groups.
When the temperature was increased to 1200 °C, the total Raman area of nascent char during holding in CO$_2$ was overall higher than that of nascent char during holding in He. The total Raman area rapidly increased within 0.5 s in CO$_2$ and then became roughly constant during holding from 0.5 to 1.7 s. It is clear that the formation of O-containing functional groups at 1200 °C is much quicker to reach a plateau than at 1000 °C, which might be related to the higher gasification rate [20] at 1200 °C as shown in Fig. 1.

The total Raman areas of the Loy Yang coal chars produced from the DTF at 1200 °C are illustrated in Fig. 2 by the symbols of $\blacklozenge$ (pyrolysis) and $\times$ (gasification). Similar to the chars produced from the WMR, the chars from the gasification in CO$_2$ gave higher total Raman peak areas than those from the pyrolysis in He, confirming the rapid formation of O-containing functional groups in CO$_2$ at 1200 °C. The total Raman areas of the pyrolysed chars from the DTF were nearly the same as those from WMR, while the total Raman area of the chars gasified in the DTF were lower than those of the chars gasified in the WMR. As the concentration of CO$_2$ was 100 vol% in WMR but 5.3 vol% balanced with N$_2$ in the DTF, the lower total Raman area should be mainly due to the slower gasification rate in a lower CO$_2$ concentration atmosphere, which caused less formation of O-containing functional groups in the DTF than in the WMR with the similar reaction time.

In Fig. 3, the distribution of ring systems also changed significantly during the holding in CO$_2$. During pyrolysis in He at 1000 °C, the ratio of small to large rings showed a rapid decrease within 0.5 s, with insignificant changes in char yield shown in Fig. 1. This can be mainly due to aromatic ring condensation. This fast enhancement of ring condensation also resulted in a rapid decrease in the ratio during the initial gasification of Loy Yang coal in CO$_2$. 

at 1000 °C (Fig. 3). With further holding at 1000 °C, the $I_{(G_r+V_l+V_r)}/I_D$ ratio gradually decreased in CO$_2$ with little reduction during pyrolysis. It indicates that large changes in char structure took place due to the reaction between char and CO$_2$. As a continuous decrease in char yield was observed during holding at 1000 °C in CO$_2$ (Fig. 1), the decrease in the ratio of small to large aromatic rings in CO$_2$ can be mainly due to the selective consumption of the active small aromatic rings. With the temperature increase to 1200 °C in CO$_2$, the ratio of small to large rings rapidly decreased within 1 s, while the distribution of ring systems had insignificant change after the further holding from 1 to 1.5 s. As there was large decrease in char yield (from ~16 to ~7%) during this period of holding in CO$_2$ at 1200 °C shown in Fig. 1, it indicates that the reaction pathway changed from the selective consumption of small rings to the unselective consumption of small and large rings with the increasingly stable char structure.

The chars from the DTF also showed large decreases in the ratio of small to large rings during gasification in CO$_2$ compared with those during pyrolysis. It confirmed the selective consumption of small ring systems during initial gasification in CO$_2$. Insignificant changes in the $I_{(G_r+V_l+V_r)}/I_D$ of DTF char during holding from 2.3 to 3.2 s also confirmed that the changes in ring systems mainly happened during initial holding (at least < 2.3 s in the DTF).

### 3.3 Changes in char yield during the pyrolysis/gasification of Collie coal

Fig. 4 shows the changes in char yield during the pyrolysis/gasification of Collie coal at 800, 1000 and 1200 °C in the WMR. It is clear that, similar to Loy Yang brown coal [33], insignificant differences in the char yield between gasification in CO$_2$ and pyrolysis in He were observed during holding at 800 °C. When the temperature was increased to 1000 °C,
contrary to the insignificant changes in char yield during pyrolysis, there were large decreases in char yield from ~57 to ~33% within 20 s holding in CO$_2$. At 1200 °C, a rapid decrease in char yield from ~53 to ~15% within 5 s in CO$_2$ was observed. Compared with the decrease in char yield in Fig. 1, it is clear that the gasification rate of Collie sub-bituminous coal is lower than that of Loy Yang brown coal. This was expected from the differences in coal rank between the brown coal and the sub-bituminous coal.

3.4 Changes in char structure during the pyrolysis/gasification of Collie coal

Figures 5 and 6 show the changes in the total Raman areas between 800 and 1800 cm$^{-1}$ and the band area ratio of I$_{(Gr+Vl+Vr)}$ to I$_D$ as a function of holding time during the fast pyrolysis/gasification of Collie coal. In Fig. 5, similar to Loy Yang coal, Collie coal also showed a generally higher total Raman area during the gasification in CO$_2$ than the pyrolysis in He. It indicates the formation of O-containing functional groups during holding in CO$_2$ at 1000 and 1200 °C. However, at 1000 °C, the increase in total Raman area for Collie coal was from ~450 (in He) to ~900 (in CO$_2$), which was much less than that for Loy Yang coal from ~450 (in He) to ~1650 (in CO$_2$). The difference can be mainly due to the relatively slow gasification rate at 1000 °C for Collie coal, which formed less O-containing functional groups with the same holding time [20]. When the temperature was increased to 1200 °C in CO$_2$, the total Raman area increased rapidly within 2.5 s and then levelled off during further holding from 2.5 to 5 s. It suggests that the rapid formation of O-containing functional groups in CO$_2$ occurs at 1200 °C and reaches a dynamic balance with the breakage of O-containing functional groups during holding from 2.5 to 5 s.
In Fig. 6, it is clear that there were large decreases in the ratio between $I_{(Gr+Vl+Vr)}$ and $I_D$ during the gasification in CO$_2$ compared with the changes in the ratio during the pyrolysis in He at 1000 and 1200 °C, which should be mainly owing to the selective consumption of small aromatic rings. The decrease in the ratio of small to large rings mainly occurred < 5 s holding at 1000 °C. When the temperature was increased from 1000 to 1200 °C, the difference in the ratio between gasification and pyrolysis was ~0.3 with 0 s holding and, similarly, the difference was ~0.3 with 5 s holding between two atmospheres. It suggests that the changes in ring systems due to the gasification mainly took place during heating from 1000 to 1200 °C with little changes in ring systems during holding at 1200 °C.

In the discussion presented above, temperature has been shown as an important parameter to influence the char structure as shown by Raman spectroscopic data. Therefore, it would be interesting to observe if the gasification pathway would also drastically change from 1000 to 1200 °C. This is investigated by plotting the Raman spectroscopic data as a function of char yield (conversion). Figure 7 shows the changes in $I_{(Gr+Vl+Vr)}/I_D$ as a function of char yield during gasification in CO$_2$. With an increase in temperature from 1000 to 1200 °C, the ratio of small to large rings showed insignificant change. It suggests that temperature has little effect on the reaction pathway during gasification in CO$_2$ for two coals.

3.5 The changes in char structure based on FTIR spectrum

The FTIR spectra (600 to 1800 cm$^{-1}$) of the two coals during pyrolysis/gasification are shown in Figs. 8 and 9. The concentration of char in KBr was identical. The spectra had two strong peaks. One peak was located from ~1500 to ~1600 cm$^{-1}$ that should be mainly due to the aromatic ring (C=C) stretching vibrations and/or carbonyl functional groups [37]. Tay and
co-workers [18] used 0.2 M H$_2$SO$_4$ to remove the AAEM species from Loy Yang coal chars prepared in CO$_2$ at 800 °C. There was no band shift from ~1600 (COO$^-$) to ~1700 cm$^{-1}$ (COOH). It indicates that the strong peak at 1500 to 1600 cm$^{-1}$ should be mainly attributed to the aromatic ring (C=C) stretching vibrations. Another strong peak was located at from ~900 to ~1300 cm$^{-1}$, which should mainly represent the C-O stretching [38, 39].

In Fig. 8, it is clear that the chars from the pyrolysis of Loy Yang coal at 1000/1200 °C and Collie coal at 1000 °C showed gradual decrease in the IR intensity region from ~600 to ~1800 cm$^{-1}$, due to the thermal cracking of O-containing functional groups and enhancement of aromatic ring condensation. The chars from the Collie coal showed insignificant changes at 1200 °C, which indicates the very stable structure of Collie coal char at 1200 °C at even 0 s holding.

In Fig. 9, at 1000 °C, the chars from two coals showed decreases in IR intensity (600 to 1800 cm$^{-1}$) during the initial 1 s holding and then increase during the further holding in CO$_2$. This initial reduction in IR intensity was the same as the changes in total Raman area (Figs. 2 and 5), which should be mainly due to the dominant effect of thermal annealing during the initial holding at 1000 °C. The increase in the intensity of C-O stretching (~900 to ~1300 cm$^{-1}$) might be partially responsible for the increase in total Raman area during holding at 1000 °C (> 1 s) and at 1200 °C (in Figs. 2 and 5). However, unlike the total Raman area that gradually levelled off during holding at 1000 °C and 1200 °C for two coals (Figs. 2 and 5), the formation of O-containing functional groups (C-O bond) continuously increased during holding according to the FTIR data. It suggests that there might be more than one type of O-containing functional group that formed during gasification in CO$_2$; some are sensitive in the Raman scattering but some are sensitive in FTIR absorption. Additionally, it was noted that
the absorbance intensity at 1500-1600 cm\(^{-1}\) (C=C stretching in aromatic rings) increased corresponding to the intensity at 900 to 1300 cm\(^{-1}\) (C-O stretching) during gasification. It implies that the formation of O-containing functional groups that mainly attached to the aromatic rings such as phenolic groups would enhance the dipole moment of the aromatic rings vibration and subsequently increase the intensity of C=C stretching in aromatic rings [39, 40].

During gasification in CO\(_2\) at 1200 °C, Collie coal char showed a sharp peak at \(~\)1100 cm\(^{-1}\) and a shoulder at \(~\)1180 cm\(^{-1}\) while Loy Yang coal char only had a broad peak at \(~\)1180 cm\(^{-1}\). The peak at \(~\)1180 cm\(^{-1}\) should be mainly due to the formation of aromatic ether and/or phenol [38]. However, the sharp peak at \(~\)1100 cm\(^{-1}\) might be due to the formation of O-containing functional groups and/or due to another possibility: the higher mineral content in Collie coal than in Loy Yang coal (ash content in dry basis for Collie coal is 5.7 wt%; Loy Yang coal is 1.1 wt%, which shown in table 1). With the increase in char conversion during gasification, the concentration of minerals relatively increased with the continuous consumption of organic matters, which caused the continuous increase in the intensity at \(~\)1100 cm\(^{-1}\) [41, 42]. In order to clarify the contribution of minerals to the band at 1100 cm\(^{-1}\), a Collie char sample was ashed in the TGA, following the procedure described by Li and co-workers [43]. The char sample was produced through gasifying Collie coal in CO\(_2\) at 850 °C with 50 minutes holding in a fluidised-bed/fix-bed reactor [14]. As is shown in Fig. 10, the shape of the FTIR spectrum of the Collie coal char produced in fluidised-bed/fix-bed reactor is similar to the FTIR spectra of the Collie coal chars produced in WMR (Fig. 9). As for the FTIR spectrum of ash, it showed a strong peak at 1100 cm\(^{-1}\). It is clearly suggested that the very high intensity of Collie coal char at 1100 cm\(^{-1}\) (FTIR spectra) should be due to the ash in char as well as the formation of O-containing functional groups.
4. Conclusions

The structural changes in nascent char were investigated during the fast gasification in CO$_2$/pyrolysis in He for two coals at 1000 and 1200 °C. The results in this study show that:

1. A minimal total Raman area was observed with 1 s holding at 1000 °C for two coals in CO$_2$. It indicates the counteracting effects of thermal annealing and oxygenation during the initial holding at 1000 °C.

2. With holding at 1000 °C (> 1 s) and 1200 °C, the formation of O-containing functional groups (total Raman area) and the change in ring systems [I$_{\text{Irr}}$+I$_{\text{Vl}}$+I$_{\text{Vr}}$]/I$_D$] rapidly took place and then gradually tended to be steady with a few seconds residence at 1000 or 1200 °C.

3. For each coal, although the temperature influenced the gasification rate significantly, the reaction pathway changed little between gasification at 1000 and 1200 °C.

4. There appears to be more than one type of O-containing functional groups formed during gasification in CO$_2$. Some are sensitive to Raman scattering but some are sensitive to FTIR absorption.

5. The sites where the O-containing functional groups (in terms of FTIR spectroscopy) formed in chars are likely associated with aromatic rings and increase the intensity of C=C stretching in aromatic rings accordingly. The strong peak at 1100 cm$^{-1}$ (FTIR spectrum) for Collie coal char should be due to the ash in char as well as the formation of O-containing functional groups.
Acknowledgements

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• Nascent char undergo rapid transformation in the initial stages of gasification in CO$_2$.

• Annealing and oxygenation have opposite effects on char structural transformation.

• More than one type of O-containing structures were formed during the gasification in CO$_2$. 
Fig. 1. Changes in char yield as a function of holding time at 1000 °C and 1200 °C during the pyrolysis in He or the gasification in CO₂ in wire-mesh reactor for Loy Yang coal. The data for pyrolysis in He were published in Ref. 36 and are shown here for comparison purposes.
Fig. 2. Changes in total Raman area as a function of holding time at 1000 °C and 1200 °C during the pyrolysis in He or the gasification in CO$_2$ of Loy Yang coal. ✶ (pyrolysis) and ✫ (gasification) represent the chars produced in the drop tube reactor. ♠, ●, ▲ and ■ represent the chars produced in the wire-mesh reactor. The data for pyrolysis in He were published in Ref. 36 and are shown here for comparison purposes.
Fig. 3. Changes in $I_{(Gr+Vl+Vr))/D}$ as a function of holding time at 1000 °C and 1200 °C during the pyrolysis in He or the gasification in CO$_2$ of Loy Yang coal. *(pyrolysis) and × (gasification) represent the chars produced in the drop tube reactor. ■, ●, ▲, and ▼ represent the chars produced in the wire-mesh reactor. The data for pyrolysis in He were published in Ref. 36 and are shown here for comparison purposes.
Fig. 4. Changes in char yield as a function of holding time at 1000 °C and 1200 °C during the pyrolysis in He or the gasification in CO$_2$ for Collie coal. All chars were produced in the wire-mesh reactor. The data for pyrolysis in He were published in Ref. 36 and are shown here for comparison purposes.
Fig. 5. Changes in total Raman area as a function of holding time at 1000 °C and 1200 °C during the pyrolysis in He or the gasification in CO₂ for Collie coal. All chars were produced in the wire-mesh reactor. The data for pyrolysis in He were published in Ref. 36 and are shown here for comparison purposes.
Fig. 6. Changes in $I_{\text{Gr+Vl+Vr}}/I_D$ as a function of holding time at 1000 °C and 1200 °C during the pyrolysis in He or the gasification in CO$_2$ for Collie coal. All chars were produced in the wire-mesh reactor. The data for pyrolysis in He were published in Ref. 36 and are shown here for comparison purposes.
Fig. 7. Changes in $I_{(G+V_l+V_r)}/I_D$ as a function of char yield at 1000 °C and 1200 °C during the gasification in CO$_2$ for the two coals. All chars were produced in the wire-mesh reactor.
Fig. 8. FTIR spectra from 600 to 1800 cm\(^{-1}\) as a function of holding time at 1000 °C and 1200 °C during the pyrolysis in He of two coals. All chars were produced in the wire-mesh reactor. The holding time at each peak temperature is shown. The concentration of char in KBr was identical.
Fig. 9. FTIR spectra at 600 to 1800 cm$^{-1}$ as a function of holding time at 1000 °C and 1200 °C during the gasification in CO$_2$ of two coals. All chars were produced in the wire-mesh reactor. The holding time at each peak temperature is shown. The concentration of char in KBr was identical.
Fig. 10. FTIR spectra of a Collie coal char and its ash from 600 to 1800 cm\(^{-1}\). The char was produced through gasifying Collie coal in CO\(_2\) at 850 °C with 50 minutes holding in a fluidised-bed/fix-bed reactor [14]. The concentration of ash in ash-KBr mixture equals the concentration of ash in char-KBr mixture.
Table 1 Properties of two coals [14,18]

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<th>Proximate analyses (wt%)</th>
<th>Ultimate analyses (wt%)</th>
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<td></td>
<td>Ash(^a)</td>
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(a, dry basis; b, dry and ash-free basis; c, by difference)