

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

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Lei Zhang^a, Shiro Kajitani^b, Satoshi Umemoto^b, Shuai Wang^a, Dimple Quyn^a,
Yao Song^a, Tingting Li^a, Shu Zhang^a, Li Dong^a, Chun-Zhu Li^{a*}

^aFuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Perth,
10 WA 6845, Australia

^bEnergy Engineering Research Laboratory, Central Research Institute of Electric Power Industry
(CRIEPI), 2-6-1 Nagasaka, Yokosuka-City, Kanagawa 240-0196, Japan

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* Corresponding author:

E-mail address: chun-zhu.li@curtin.edu.au (Chun-Zhu Li)

Phone: +61 8 9266 1131

Fax: +61 8 9266 1138

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25 **Abstract**

The purpose of this study is to investigate the structural changes in nascent chars during the gasification of two low-rank coals in CO₂ 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/CO₂ 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 N₂/CO₂ 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 CO₂. 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.

45 **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
50 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.

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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
60 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
65 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
70 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
75 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
80 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
85 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
90 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

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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 ($< 35\text{ }^{\circ}\text{C}$). 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 $< 125\text{ }\mu\text{m}$. The sample was further dried in a vacuum oven at $60\text{ }^{\circ}\text{C}$. 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, $\sim 10\text{ mg}$ 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/ CO_2 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 CO_2 .

For the DTF experiments [34], the Loy Yang coal sample was continuously fed into the $1200\text{ }^{\circ}\text{C}$ 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
120 though 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.

125 **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
130 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.

135 **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
140 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
145 gasification in CO₂. 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 CO₂ 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
150 loss due to thermal cracking is 6 wt%-db s⁻¹ (6.07 wt%-daf s⁻¹). Therefore, the gasification
rate due to CO₂ 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 CO₂ at 700 to
155 900 °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 CO₂ at
high temperatures was significant, which might result in the corresponding changes in char
structure, as will be discussed in the following section.

160 3.2 Structural changes in Loy Yang coal char during gasification in CO₂

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_(Gr+Vl+Vr) to I_D as a function of holding time in He/CO₂. The total Raman
area is mainly determined by two factors: the O-containing functional groups that would
165 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_(Gr+Vl+Vr) to I_D mainly
reflects the ratio of small aromatic rings (3-5 fused benzene rings) to large ones (≥ 6 rings)
[15].

170 As is shown in Fig. 2, the total Raman area of Loy Yang coal char during the gasification in
CO₂ was overall higher than that during pyrolysis in He at 1000 °C. The increase in total
Raman area after reaction with CO₂ 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
175 pyrolysis at 1000 °C, which indicates that the ring systems are more condensed during the
gasification in CO₂ 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 CO₂ than in He. Because of that, the higher total Raman area (Fig. 2) in CO₂ should
be mainly due to the formation of O-containing functional groups in CO₂ rather than the
180 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
185 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 CO₂ with the continuous formation of O-containing functional groups at 1000 °C. Very
190 slow increases in total Raman area were observed with further holding from 3 to 10 s in CO₂.
The nearly constant total Raman area from 3 to 10 s holding in CO₂ should be due to the
dynamic balance between the thermal cracking and the formation of O-containing functional
groups.

195 When the temperature was increased to 1200 °C, the total Raman area of nascent char during holding in CO₂ was overall higher than that of nascent char during holding in He. The total Raman area rapidly increased within 0.5 s in CO₂ 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
200 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 ✱ (pyrolysis) and ✕ (gasification). Similar to the chars produced from the WMR, the chars from the gasification in CO₂ gave higher total Raman
205 peak areas than those from the pyrolysis in He, confirming the rapid formation of O-containing functional groups in CO₂ 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 CO₂ was 100 vol% in WMR but 5.3 vol% balanced with N₂ in the DTF, the
210 lower total Raman area should be mainly due to the slower gasification rate in a lower CO₂ 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
215 CO₂. 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 CO₂

at 1000 °C (Fig. 3). With further holding at 1000 °C, the $I_{(Gr+Vl+Vr)}/I_D$ ratio gradually
220 decreased in CO₂ with little reduction during pyrolysis. It indicates that large changes in char
structure took place due to the reaction between char and CO₂. As a continuous decrease in
char yield was observed during holding at 1000 °C in CO₂ (Fig. 1), the decrease in the ratio
of small to large aromatic rings in CO₂ can be mainly due to the selective consumption of the
active small aromatic rings. With the temperature increase to 1200 °C in CO₂, the ratio of
225 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 CO₂ 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
230 structure.

The chars from the DTF also showed large decreases in the ratio of small to large rings
during gasification in CO₂ compared with those during pyrolysis. It confirmed the selective
consumption of small ring systems during initial gasification in CO₂. Insignificant changes in
235 the $I_{(Gr+Vl+Vr)}/I_D$ 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

240 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 CO₂ 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
245 in char yield from ~57 to ~33% within 20 s holding in CO₂. At 1200 °C, a rapid decrease in
char yield from ~53 to ~15% within 5 s in CO₂ 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.

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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
255 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 CO₂ than the pyrolysis
in He. It indicates the formation of O-containing functional groups during holding in CO₂ 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 CO₂), which was much less than that for Loy Yang coal from
260 ~450 (in He) to ~1650 (in CO₂). 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
CO₂, 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
265 in CO₂ 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 H₂SO₄ to remove the AAEM species from Loy Yang coal chars prepared in CO₂ 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 CO₂. 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 CO₂; 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
320 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].

325 During gasification in CO_2 at 1200 °C, Collie coal char showed a sharp peak at $\sim 1100 \text{ cm}^{-1}$ and a shoulder at $\sim 1180 \text{ cm}^{-1}$ while Loy Yang coal char only had a broad peak at $\sim 1180 \text{ cm}^{-1}$. The peak at $\sim 1180 \text{ cm}^{-1}$ should be mainly due to the formation of aromatic ether and/or phenol [38]. However, the sharp peak at $\sim 1100 \text{ cm}^{-1}$ might be due to the formation of O-containing functional groups and/or due to another possibility: the higher mineral content in
330 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 $\sim 1100 \text{ cm}^{-1}$ [41, 42]. In order to clarify the contribution of minerals to the band at 1100 cm^{-1} , a
335 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
340 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

345 The structural changes in nascent char were investigated during the fast gasification in CO₂/
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
CO₂. It indicates the counteracting effects of thermal annealing and oxygenation during the
350 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 [$I_{(Gr+Vl+Vr)}/I_D$] rapidly took place
and then gradually tended to be steady with a few seconds residence at 1000 or 1200 °C.

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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
360 gasification in CO₂. 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
365 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.

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