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Chemical structure transformation during the later stage of plastic layers during coking using Synchrotron infrared microspectroscopy technique

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Abstract

During the coking process, the carbon structure of coal evolves after the re-solidification of the plastic layers to form a solid residue, i.e., semi-coke, which is known to determine the structure and quality of the final coke product. This paper reports the chemical structural transformations of various Australian coking coals during the later stage of the plastic layers that may be related to the evolution of the carbon structures. The plastic layers and semi-coke/coke samples were prepared from four Australian coking coals of different ranks and vitrinite contents in a lab-scale coke oven. The synchrotron attenuated total reflection Fourier transform infrared (ATR-FTIR) microspectroscopy (Synchrotron IR) was used in combination with the X-ray photoelectron spectroscopy (XPS). The Synchrotron IR, as a nondestructive analytical technique, proved to be a useful tool to examine the

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change in functional groups in the semi-coke samples. The XPS analysis was employed to study the conversion of sp^2 - and sp^3 -bonded carbons. The results suggested that a dramatic chemical structure change took place during the stages following the plastic layers through to the coke/semi-coke regions. These chemical structure changes were strongly impacted by the properties of the parent coals. The carbon state changes observed in XPS spectra were in good agreement with the aromatic ring condensation degree, which was indicated by the ratio of out-of-plane aromatic C-H to C=C bonds in aromatic rings. The results showed that carbon structure evolution took place during the later stages of the thermoplastic ranges, forming the solid the semi-coke.

Keywords: Coke making; Synchrotron IR; Semi-coke; Chemical Structural Transformation.

1. Introduction

During the coking process, a coal charge undergoes a thermoplastic stage when heated to approximately 350-550 °C in a reducing atmosphere, which is referred to as the plastic layers. It has been numerously investigated in the literature [1-4]. The plastic layer re-solidifies into a fresh semi-coke after around 500 °C through which complex chemical reactions and devolatilization take place. When the temperature at the oven center reaches 1000 °C, coal converts into metallurgical cokes. Coke is used as permeable skeleton support and reductant in iron-making [5, 6]. In the transitional stage following the re-solidification of the plastic layer through to coke, the finally interconnected 3D carbon structures are formed through cross-linking, aromatization, and ring condensation reactions [7, 8]. The carbon structures formed during this stage are believed to determine the properties and strength of the product coke. However, the underlying mechanisms of the carbon structure evolution and transformation during coking have not been well understood.

Some previous studies have reported chemical structure changes in semi-cokes. Pusz et al. [9, 10]

43 found that the coke formed close to the heating wall had more ordered texture with more radicals.
44 Butuzova et al. [11] found that the “high concentration of paramagnetic centers in the fluid-like non-
45 volatile” products determines a level of coking capacity by using electron spin resonance (ESR) and
46 IR analysis. The ESR results showed that the spin concentrations showed maxima around 400-500 °C.
47 The results suggested that the concentrations of free radicals firstly increased during the formation of
48 the plastic layers, then declined during re-solidification to produce semi-coke as a result of re-
49 polycondensation reactions [12]. Öner et al. [13] investigated the structures of semi-cokes “produced
50 from the pyrolysis of petroleum pitches” by using FTIR and “solid-state carbon-13 nuclear magnetic
51 resonance (^{13}C NMR)”. There existed more aromatic structures in the semi-cokes, and the aromaticity
52 of carbonaceous semi-cokes increased with the increment of the pyrolysis temperature.

53 Synchrotron IR, which has a higher resolution than the ordinary FTIR, has been widely used in
54 biosciences to study the chemistry of biological samples on microscale, and their infrared imaging
55 does not cause any destruction to the samples [14]. The technique has been widely used for imaging
56 biochemical composition in a diverse range of biological samples at a micron-scale resolution [15, 16].
57 In the Synchrotron IR technique, the ATR-FTIR microspectroscopy, coupled with Ge crystal brought
58 into the focus of the synchrotron IR beam below the 20× IR objective, can scan the visible micro-level
59 images and obtain IR spectra [17]. However, this technique also has a potential capacity in observing
60 micromorphology, and chemical structure transitions across the whole coke-making process [18], and
61 thereby was used in this study. Therefore, this technique has been employed in this research. In order
62 to study the plastic layer chemical structure changes, a “4 kg double-heated wall coke oven equipped
63 with a sampling probe was employed to collect the semi-coke samples under simulated practical oven
64 heating” [19]. Four Australian coking coals as a comparison of different vitrinite contents and various

65 ranks were selected to produce samples at a continuous temperature gradient in the specific coke oven.
 66 Australian coals are accepted to contain less sulfur and ash contents, which would provide a purer
 67 environment to investigate the carbon skeleton transformation [20]. Combined with XPS analysis, the
 68 Synchrotron IR was used to analyze the chemical structure changes of the semi-coke samples aiming
 69 at a better understanding of the underlying chemistry for the chemical structure changes in the semi-
 70 coke region during coking.

71 2. Materials and methods

72 2.1. Materials and sample preparation

73 Table 1 shows the proximate and ultimate analysis results of the four Australian coking coals used
 74 in this study for the preparation of semi-coke samples. Set 1 (YC1 and YC2) samples vary in their
 75 vitrinite contents, ranging from 35.8% to 55.3% but with similar rank. Set 2 samples (YC3 and YC4)
 76 have similar vitrinite content (63.1 and 66.6) but vary in their ranks, as indicated by their different
 77 mean maximum vitrinite reflectance (1.16, and 1.45, respectively).

78 **Table 1**

79 Sample properties of four Australian coals used in this study.

Coal samples		YC1	YC2	YC3	YC4
Proximate Analysis	Inherent Moisture (wt.%, air dried basis (ad))	1.1	0.6	0.9	1
	Ash (wt.%, dry basis (db))	8.9	9	10.7	8.9
	Volatile Matter (wt.%, db)	20	23.3	18.7	24.5
	Fixed Carbon (wt.%, db)	70	67.1	69.7	65.6
Ultimate Analysis	Carbon (%daf)	87.4	87.9	89	87.6
	Hydrogen (%daf)	4.61	5.08	4.8	5.1
	Nitrogen (%daf)	1.68	1.94	2	1.4
	Total Sulfur (%daf)	0.27	0.62	0.72	0.5
	Oxygen (%daf)	6	4.4	3.5	5.4

Gieseler Fluidity	Initial Softening Temperature (°C)	440	416	436	421
	Max Fluidity Temperature (°C)	458	456	470	457
	Solidification Temperature (°C)	478	492	497	485
	Plastic Range (°C)	38	76	61	64
	Max Fluidity (ddpm)	2	340	50	60
	Max Fluidity (Log 10)	0.3	2.53	1.7	1.78
Mean Maximum Reflectance (%)		1.31	1.21	1.45	1.16
Vitrinite (%)		35.8	55.3	63.1	66.6
Maceral analysis (v%, mmf)	Liptinite (%)	0.3	0.2	0	0.6
	Inertinite (%)	60.8	41	36.9	32.8

80

81 The parent coals were charged to prepare partially carbonized samples, including the plastic layer
82 and coke/semi-coke layer in a 4 kg laboratory-scale coke oven. The details of the 4 kg coke oven have
83 been reported in previous studies [19]. The total length of the sampling tube is 100 mm. The coal
84 sample in the sample tube was extracted when the temperature at 75 mm position to the heating wall
85 reached 400 °C. This allows the partially coked samples to contain various characteristic coal bed
86 sections, including loose coal, plastic layers, and semi-coke and coke regions (as shown in Fig. 1). For
87 Synchrotron IR scanning, each semi-coke sample was resined and cross-sectioned in half to expose
88 the surface of interest. The cross-sectioned area was polished, as shown in the lower-left figure in Fig.
89 2. The temperature histories of 4 coals in the sampling tube, shown in Fig. 2, were recorded by five
90 thermocouples. The 25 mm position to the heating wall eventually reached approximately 800 °C, and
91 the plastic layers were left between 50-85 mm.

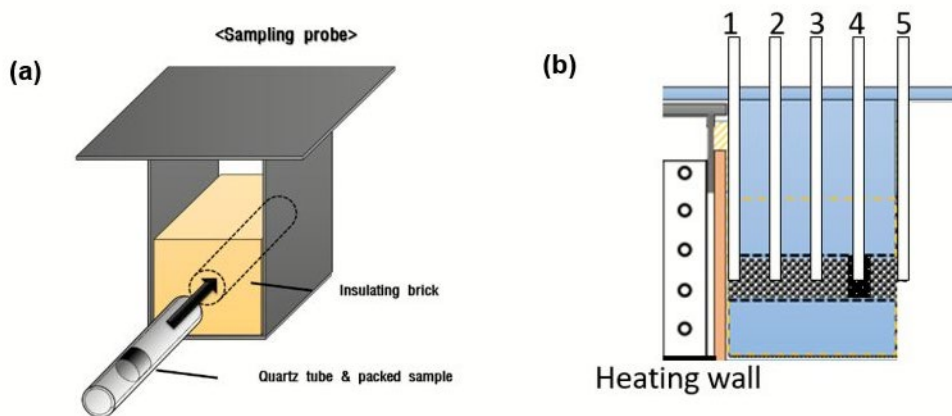


Fig. 1. Schematic diagram of (a) the sampling module, and (b) the cross-section image for plastic layer and semi-coke sampling.

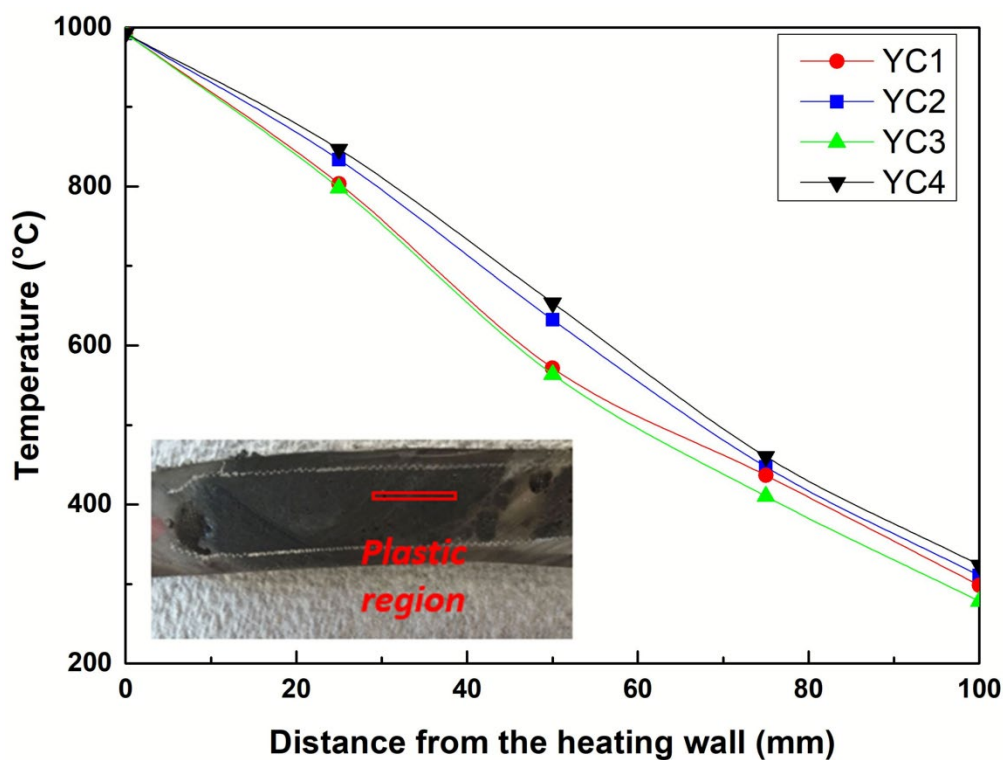


Fig. 2. Temperature profiles of the coal bed during heating.

2.2. Spectral analysis of samples using Synchrotron IR

The measurements were done using the Australian Synchrotron IRM Beamline (Melbourne, Australia). The machine uses a Bruker Vertex 80v spectrometer attached to a Hyperion 3000 FTIR microscope. The facility has a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector

(Bruker Optik GmbH, Ettlingen, Germany). The IR scanning was done on the in-house adapted macro ATR-FTIR device. The machine is equipped with a Ge ATR using a 20× IR objective (NA = 0.60; Bruker Optik GmbH, Ettlingen, Germany). The diameter of the Ge ATR tip is 100 μm. The sampling area (or focused beam size) at each measurement point using pinhole size 0.75 mm is 9.38 μm. More detailed information about the parameters of this technique has been reported by Vongsvivut et al. [17]. The semi-coke samples prepared were mounted on a micro-vice mounting device (S.T. Japan-Europe GmbH, Cologne, Germany) and were placed onto the microscope stage. Before commencing ATR-FTIR mapping, microscopic images were taken to overview the macrostructural appearance from the plastic layers to coke/semi-coke regions, which enabled identifying measurement points for the IR spectral data collection. The semi-coke samples prepared were mounted on the micro-vice mounting device and were placed on the sample stage of the macro ATR-FTIR unit. Before the macro ATR-FTIR scanning, microscopic images were taken to overview the macrostructure changes from the plastic layers to coke/semi-coke regions, which enabled identifying measurement points for the IR scanning. Fig. 3 shows the macrostructure change in the transitional region of the YC1 sample. The dark grey parts are the pores filled with resin, while the black areas are the pores. It can be seen that light grey regions assigned to the structure of semi-cokes became more condense with micropores inside after 500 °C.

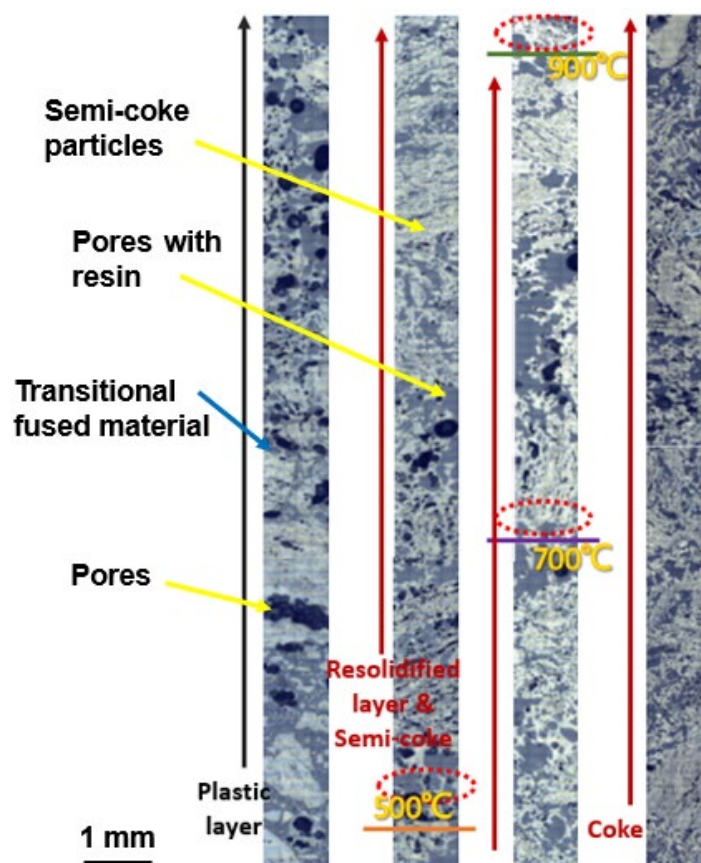


Fig. 3. Microscopic image of the macrostructure of YC1 samples.

In order to acquire spatially resolved chemical information in the transitional regions, sixty-four scans per spectrum were performed over the range of 4000-700 cm^{-1} . Fig. 4 shows that the deconvolution and integration of spectra of interest were achieved using OPUS 8.0 software suite (Bruker Optik GmbH, Ettlingen, Germany) by following the procedures presented in the literature [21-23]. Characteristic bands of the functional groups used in this study are shown in Table 2, with which the calculation enables to acquire several structural parameters, including $A_{\text{aro-H}}/A_{\text{ali-H}}$ (3100-3000 cm^{-1} /3000-2800 cm^{-1}), $A_{\text{CH}_2}/A_{\text{CH}_3}$ (2920 cm^{-1} /2950 cm^{-1}), aromatic ring condensation degree (900-700 cm^{-1} /1610-1490 cm^{-1}), based on previous studies [22, 24].

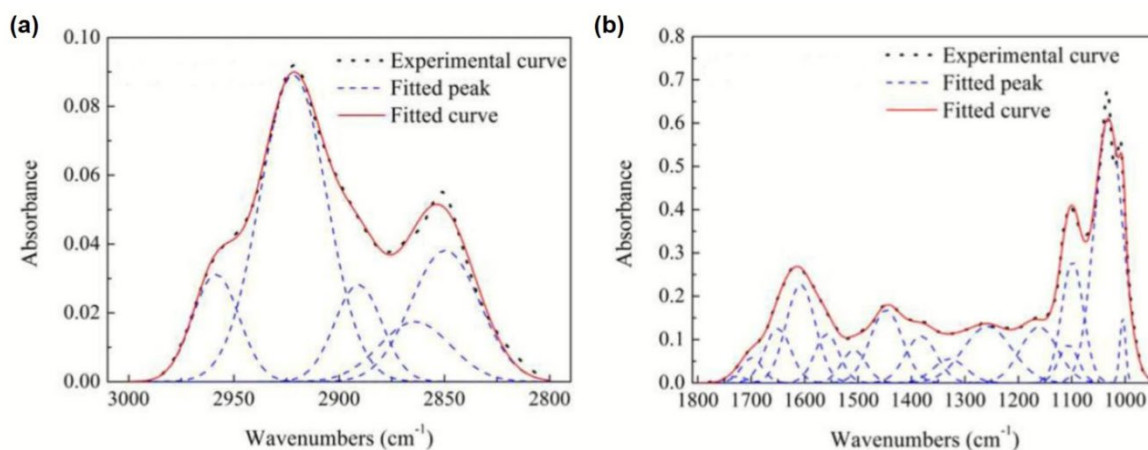


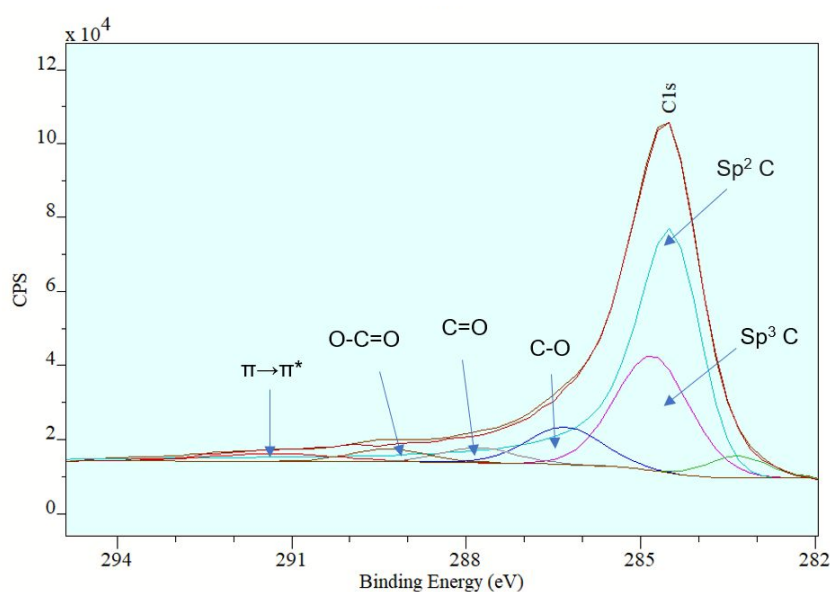
Fig. 4. Graphical representation of curve-fitting in the ranges of: (a) 3000–2800 cm⁻¹, and (b) 1800–1600 cm⁻¹ with FTIR [23].

2.3. XPS analysis on the state of carbon

In order to clarify the form of existence of carbon, oxygen, and nitrogen in the semi-cokes, XPS analysis was carried out. The samples were a series of coals and coke, ground into powers. The powders were pressed into the indium foil (“Advent Research Materials part number IN159616”) using a stainless-steel spatula. The foil itself was mounted to a sample holder via the carbon dot (“Ted Pella part number 16084-4”). The XPS spectra were collected by illuminating the samples with a non-monochromatic x-ray source (Omnivac) using Al K α ($h\nu=1486.6$ eV) radiation. The photoemission was collected by the SES2002 analyzer (Scienta). The scanning of areas of interest was performed using a pass energy of 20 eV and 100 meV steps. Working pressure in the analysis chamber with the sample under x-ray illumination was $\sim 3 \times 10^{-9}$ mBar, with a base pressure of 3×10^{-10} mBar. CaseXPS was employed to deconvolve the C 1s peak and obtain the contribution of each state of carbon.

Four or five samples of each semi-coke samples were prepared for XPS experiments in order to investigate the atomic identification change, especially the chemical state of carbon. Survey scans were aligned by setting the C1s peak to 284 eV to match the CASA internal reference. Satellite peaks were

145 then subtracted from the data using CASA's internal tool, followed by a 5-point SG Quadratic
 146 smoothing function across each dataset. The deconvolution of the C 1s spectra yielded six peaks [25],
 147 each representing a certain carbon bound state. Peak 1 (284.6 eV) represents the graphitized carbon
 148 (sp^2). The peak 2 (284.8 eV) represents the aliphatic C (sp^3). The peak 3 (286.3 eV) represents the
 149 carbon in phenolic, alcohol or ether. The peak 4 (287.6 eV) represents the carbon in carbonyl or quinone
 150 groups. The peak 5 (289.1 eV) represents the carbon in carboxyl or ester groups. Moreover, peak 6
 151 (291.3 eV) represents the $\pi \rightarrow \pi^*$, as shown in Fig. 5. The relative contents of peak 1 and peak 2 were
 152 investigated in more detail to achieve a better understanding of how the carbon bonds would change
 153 in the semi-cokes.



154
 155 **Fig. 5.** Deconvolution of C 1 s spectra of semi-coke sample at the position of 2 mm to the coke oven
 156 wall using YC2 coal.

157 3. Results and discussion

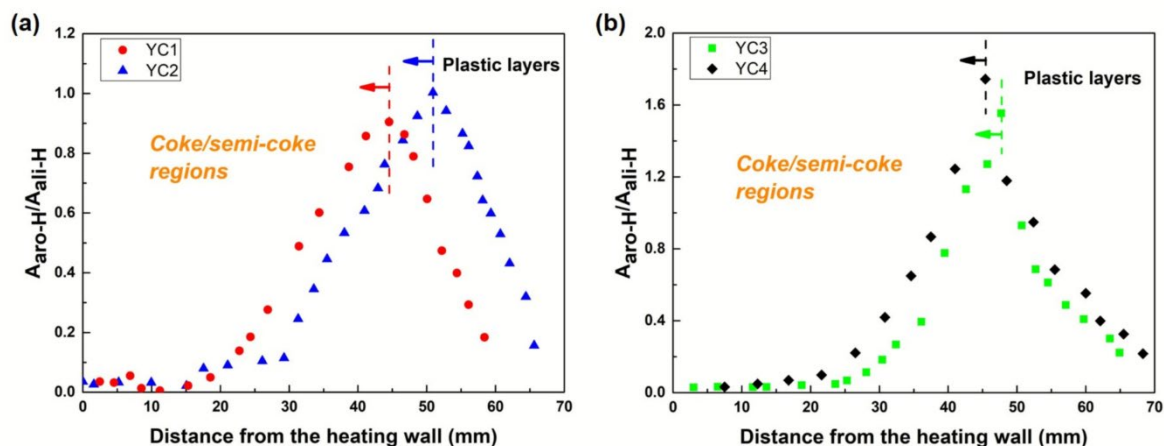
158 3.1. Chemical structure transition as analyzed by Synchrotron IR

159 The ratio $A_{\text{aro-H}}/A_{\text{ali-H}}$ represents the “relative abundance of aromatic and aliphatic functional groups”

[23]. Firstly, the trend of the ratio of YC1 was compared to that of YC2 to explore the impacts of vitrinite content on the chemical structure transformation in the semi-coke to coke regions. As shown in Fig. 6(a), this ratio increased to the end of the plastic layers. It was estimated that the thermoplastic region of YC1 was in 46-59 mm, and that of YC2 was from 52 mm to 66 mm. The progressive changes in the values of $A_{\text{aro-H}}/A_{\text{ali-H}}$ during the plastic layer region are consistent with our previous studies by Lee et al. [19, 26]. YC2 coal with higher vitrinite content generated more significant amounts of the plastic mass than YC1. It is assumed that this was attributed to the removal of amounts of methyl and methylene from side chains as pyrolysis gas, CH_4 , in the thermoplastic region [27]. The $A_{\text{aro-H}}/A_{\text{ali-H}}$ for both two coals reached maxima at the end of the plastic layers. At this stage, YC2 showed a relatively higher proportion of aromatic hydrogen. This may correspond to the higher vitrinite contents in YC2 coals suggesting more aliphatic groups since more aliphatic H would transfer into aromatic H or release as saturation with other radicals at the later stage of the plastic layer. The ratio commenced to dramatically decrease from the ends of the plastic layers to semi-coke regions. This trend indicates that the release of hydrogen gas is a result of the dehydrogenation of aliphatic rings and the dominant condensation of aromatic structures [28]. The ratios decreased to below 0.1 from 25 mm to 0 mm (800-1000 °C). This indicated that the graphitization of the cross-linked aromatic structures might have become dominant.

Fig. 6(b) shows the changes in the $A_{\text{aro-H}}/A_{\text{ali-H}}$ of YC3 and YC4 coals with different ranks. The maximum ratio of YC4 with a lower rank at the end of the plastic layers is slightly higher than that of YC3 with a higher rank indicating that lower rank coals maintained to have a relatively higher proportion of aromatic H. However, their trends and amounts seemed similar, probably suggesting that the effect of ranks on the chemical structure evolution is in good agreement with that on the coke

182 quality since the range of rank in this study is relatively narrow, i.e., 1.16 to 1.45 [29]. The results
 183 implied that the same trend was revealed during the coke/semi-coke region for the medium to high-
 184 rank coals converging to the same value at a temperature of 700 °C.



185
 186 **Fig. 6.** Changes in Aaro-H/Aali-H of semi-coke from (a) YC1 and YC2 coals, and (b) YC3 and YC4
 187 coals.

188 A_{CH2}/A_{CH3} is a parameter that represents the “length and degree of branching aliphatic side chains”
 189 [30]. This ratio significantly decreased in the plastic layers of four samples (see Fig. 7). The result
 190 suggests the cleavage of the aliphatic bridge bonds and the detachments of the aliphatic side-chains in
 191 the thermoplastic region. A slight increase in the ratio has been observed near the end of the plastic
 192 layers for all coals. This decrease may be attributed to the demethylation through the elimination of
 193 the side chains and due to a large extent of the cross-linking reactions [31]. As close to the heating wall
 194 side, the ratio continued to decline, probably resulted from the removal of large amounts of hydrogen
 195 from methylene for further condensation and cross-linking [32].

196 Fig. 7(a) shows the changes in the A_{CH2}/A_{CH3} of coals with different vitrinite contents. The ratio of
 197 YC1 with lower vitrinite contents showed a faster downward trend attributed to the amounts of
 198 aliphatic groups is favorable to transfer into aromatics or serve as bridges between molecules in an
 199 inertinite-rich atmosphere. Additionally, the ratio of coals with different ranks and similar vitrinite

200 contents showed the same trend at the beginning of the plastic layer and inside the semi-coke region,
 201 as shown in Fig. 7(b). However, the increase in the ratio was higher with YC4 during the later stage of
 202 the plastic layer, indicating a higher level of the cross-linking reactions with releasing a more
 203 significant amount of methane.

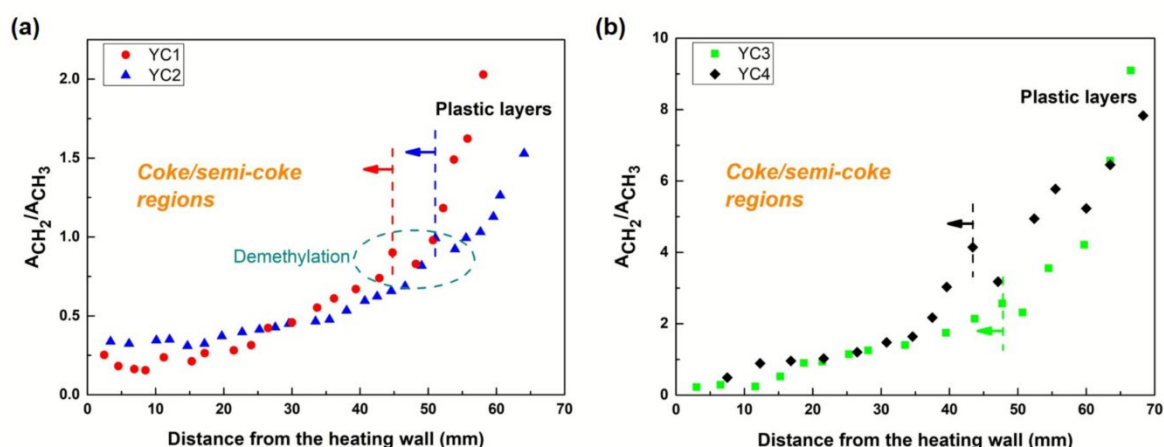
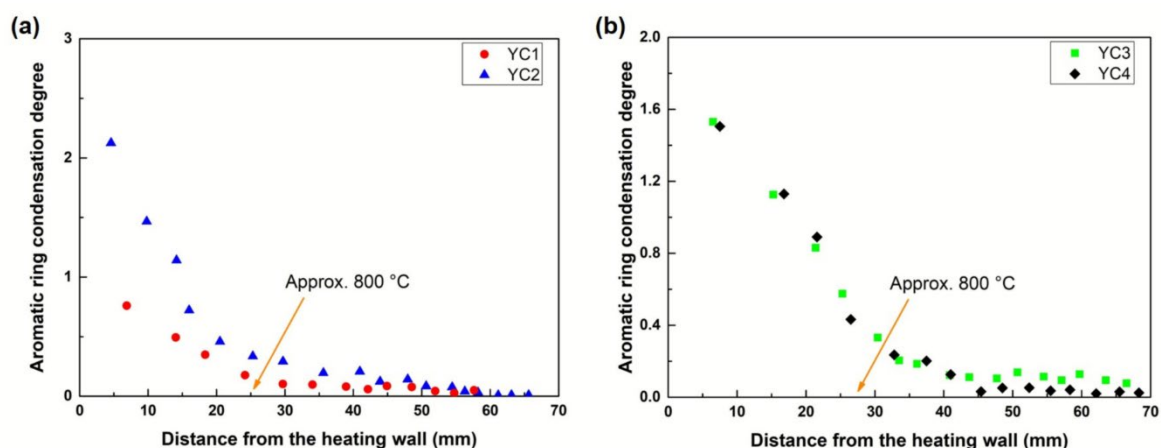


Fig. 7. Changes in the ACH_2/ACH_3 of semi-coke obtained from (a) YC1 and YC2 coals, and (b) YC3 and YC4 coals.

207 The characteristic band at $900-700\text{ cm}^{-1}$ is assigned to the out-of-plane aromatic hydrogen
 208 substituted by other functional groups [33], and the band of $1610-1490\text{ cm}^{-1}$ represents the aromatic
 209 $C=C$ bonds in aromatic rings. The ratio of $900-700\text{ cm}^{-1}$ to $1610-1490\text{ cm}^{-1}$ is known to represent the
 210 aromatic ring condensation degree (see Fig. 8) [24]. The ratios of all the samples rose during the whole
 211 coking process, and they rapidly increased from 20 mm to the heating wall side ($800\text{ }^{\circ}\text{C}$ to $1000\text{ }^{\circ}\text{C}$),
 212 indicating that higher degrees of aromatic ring condensation took place during the transitional stage
 213 from the semi-cokes to cokes. Odeh et al. [34] reported that an increase in the “degree of aromatic
 214 condensation with increasing char formation temperature.” They attributed this increase to the
 215 “removal of aliphatic side chains from the coal macromolecular structure.” The dramatic increase
 216 during the semi-coke region was possibly related to the amounts of transferable hydrogens that are
 217 substituted by other macromolecules. This is achieved through the intensive cross-linking reactions

218 and ring condensations of aromatic macromolecules. The increment in the amounts of out-of-plane
 219 hydrogen is corresponding to the decrease in aromatic hydrogen, which may have the potential
 220 capacity to be substituted by ordered aromatic sheets during re-polymerization. In the meantime, the
 221 decrease in smaller molecular aromatic rings to a greater extent. At the same time, aromatic H
 222 decreased due to the formation of highly condensed aromatics, and stacks of aromatic sheets also have
 223 an impact on the increase of this ratio.

224 Also, as shown in Fig. 8(a), YC1 coal showed a higher increasing rate of the ratio than YC2, which
 225 may be favorable to the formation of isotropic structures composed by domains [35, 36]. The coke can
 226 be regarded as porous and partially graphitized carbon, which is a 3D carbon matrix with isotropic and
 227 anisotropic structures, resulting in a relatively high mechanical strength [37, 38]. Therefore, the coke
 228 with more isotropic structures leads to its higher strength. YC3 and YC4 showed a similar increasing
 229 rate of the aromatic ring condensation degree from 30 mm to the coke side. In previous studies [10,
 230 34], it was concluded that coals with medium and high ranks would behave similarly, like a highly
 231 carbonized coal regardless of their difference in rank. They would also exhibit similar aromaticity at
 232 700 °C.



233 **Fig. 8.** Degree of aromatic ring condensation represented by the ratio of 900–700 cm⁻¹/1610–1490
 234 cm⁻¹ observed for (a) YC1 and YC2 coals, and (b) YC3 and YC4 coals.
 235

Niu et al. [39] suggested that the absorptions at $\sim 1600\text{ cm}^{-1}$, $\sim 1570\text{ cm}^{-1}$, and 1490 cm^{-1} represent “the aromatic C=C bonds in a single ring”, and the two or three rings in the network structures, respectively. This type of structure may ascribe to the shift of the absorption frequency from 1610 cm^{-1} to 1490 cm^{-1} to the growing number of aromatic rings, which corresponds to the increased degree in the aromatic ring condensation [40].

3.2. XPS characteristics of semi-cokes

Fig. 9 shows the changes in the proportion of sp^2 - and sp^3 -bonded carbon during the formation of coke/semi-cokes from 4 coals. The relative amount of the sp^3 -bonded carbon decreased toward the heating wall and even rapidly in the semi-coke region, indicating the elimination of aliphatic groups through cross-linking and condensation of large aromatic molecules. The fact that the graphitized carbon significantly increased nearer the heating wall following the later stage of the plastic layer suggests that there might have been significant growth in the size of the aromatic sheets as a result of the ring condensation and graphitization. It seems that condensation dominates in the transitional region from the later stage of a plastic layer to coke, which is corresponding to the increase in the degree of aromatic ring condensation, indicative from IR results shown in Fig. 8.

Besides, YC2 showed a higher increase rate of sp^2 carbon than that of YC1 (as shown in Fig. 9(a) and (b)). This result implies that a greater extent of graphitization for YC2 might have been achieved during the formation of coke/semi-coke. This is also reflected in the faster increase in the aromatic ring condensation degree. Furthermore, the overall trends of two coals with different ranks seem quite similar, which are in good agreement with the similar changes in the functional groups from IR, as shown in Fig. 9(c) and (d).

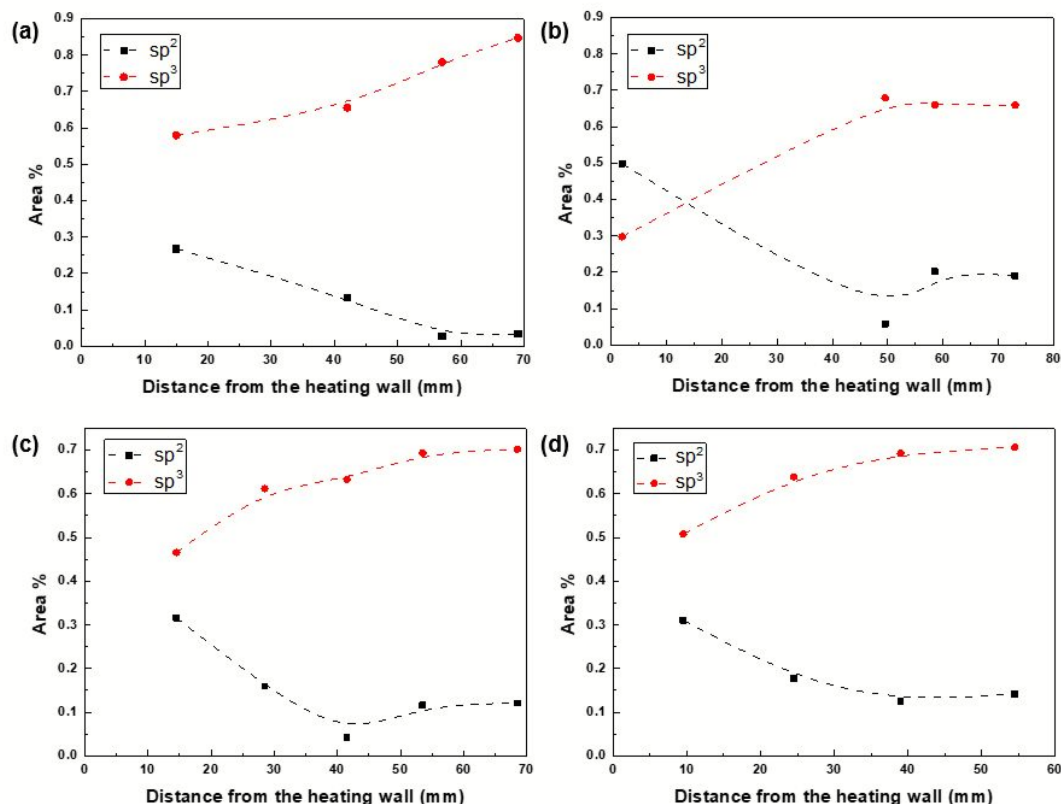


Fig. 9. Changes in relative contents of sp^2 and sp^3 -bonded C from XPS spectra of semi-coke from (a) YC1; (b) YC2; (c) YC3 and (d) YC4.

4. Conclusions

- A decrease in the $A_{\text{aro-H}}/A_{\text{ali-H}}$, an increase in sp^2 C, and the degree of aromatic ring condensation from semi-coke to coke coincide with the hydrogen gas release profile. The cross-linking, re-polymerization and ring condensation reactions are the dominant mechanisms for the chemical structural transition during the semi-coke stage following the re-solidification of the thermoplastic mass.
- The increase in the out-of-plane hydrogen, indicated by the IR shift at $900\text{--}700\text{ cm}^{-1}$, suggests that the three-dimensional structure evolution during this stage is a critical stage of carbon structures in semi-coke and coke.

- 269 • The employment of Synchrotron IR combined with the XPS technique provides a better insight
270 into the underlying mechanism of the coking process, in particular, the semi-coke structure
271 following the re-solidification of the plastic layer.
- 272 • During the later stage of the plastic layer, the vitrinite content in parent coals has a significant
273 influence on the chemical structure transformation from aliphatic groups to graphitized carbon.
274 The coal ranks seem to have a limited impact on the chemical structure transformation with the
275 limited number of coals studied.

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369 **List of Tables:**

370 **Table 2**

371 Sample properties of four Australian coals used in this study.

Coal samples		YC1	YC2	YC3	YC4
Proximate Analysis	Inherent Moisture (wt.%, air dried basis (ad))	1.1	0.6	0.9	1
	Ash (wt.%, dry basis (db))	8.9	9	10.7	8.9
	Volatile Matter (wt.%, db)	20	23.3	18.7	24.5
	Fixed Carbon (wt.%, db)	70	67.1	69.7	65.6
Ultimate Analysis	Carbon (%daf)	87.4	87.9	89	87.6
	Hydrogen (%daf)	4.61	5.08	4.8	5.1
	Nitrogen (%daf)	1.68	1.94	2	1.4
	Total Sulfur (%daf)	0.27	0.62	0.72	0.5
	Oxygen (%daf)	6	4.4	3.5	5.4
Gieseler Fluidity	Initial Softening Temperature (°C)	440	416	436	421
	Max Fluidity Temperature (°C)	458	456	470	457
	Solidification Temperature (°C)	478	492	497	485
	Plastic Range (°C)	38	76	61	64
	Max Fluidity (ddpm)	2	340	50	60
	Max Fluidity (Log 10)	0.3	2.53	1.7	1.78
Mean Maximum Reflectance (%)		1.31	1.21	1.45	1.16
Maceral analysis (v%, mmf)	Vitrinite (%)	35.8	55.3	63.1	66.6
	Liptinite (%)	0.3	0.2	0	0.6
	Inertinite (%)	60.8	41	36.9	32.8

372

373 **Table 3**

374 Bands assignment of FTIR absorption peaks used in this study [22, 23].

Band position/cm ⁻¹	Functional groups
3000-3100	Stretching aromatic C-H
3000-2800	Stretching aliphatic C-H, R-CH ₃ asymmetric stretching (2960), R-CH ₂ , asymmetric stretching (2920), R ₃ CH stretching (2890), symmetric stretching vibration of CH ₃ (2860), R-CH ₃ symmetric stretching (2850)
1610-1490	aromatic C=C stretching
900-700	Aromatic C-H out-of-plane deformation

375

376 **List of Captions of Figures:**

377 **Fig. 1.** Schematic diagram of (a) the sampling module, and (b) the cross-section image for plastic layer
378 and semi-coke sampling.

379 **Fig. 2.** Temperature profiles of the coal bed during heating.

380 **Fig. 3.** Microscopic image of the macrostructure of YC1 samples.

381 **Fig. 4.** Graphical representation of curve-fitting in the ranges of: (a) 3000-2800 cm^{-1} , and (b) 1800-
382 1600 cm^{-1} with FTIR [23].

383 **Fig. 5.** Deconvolution of C 1s spectra of semi-coke sample at the position of 2 mm to the coke oven
384 wall using YC2 coal.

385 **Fig. 6.** Changes in Aaro-H/Aali-H of semi-coke from (a) YC1 and YC2 coals, and (b) YC3 and YC4
386 coals.

387 **Fig. 7.** Changes in the $A_{\text{CH}_2}/A_{\text{CH}_3}$ of semi-coke obtained from (a) YC1 and YC2 coals, and (b) YC3
388 and YC4 coals.

389 **Fig. 8.** Degree of aromatic ring condensation represented by the ratio of 900-700 $\text{cm}^{-1}/1610-1490 \text{ cm}^{-1}$
390 observed for (a) YC1 and YC2 coals, and (b) YC3 and YC4 coals.

391 **Fig. 9.** Changes in relative contents of sp^2 and sp^3 -bonded C from XPS spectra of semi-coke from (a)
392 YC1; (b) YC2; (c) YC3 and (d) YC4.