

# **A Mechanistic Study Of The Formation Of Plastic Layers During The Heating Of Coking Coal**

**Soonho Lee**

**BSc(MechEng); MSc(MechEng) (PNU)**

A thesis submitted in fulfilment of the requirements for the degree of  
Doctor of Philosophy in Chemical Engineering



The University of Newcastle  
Australia

February, 2019

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## **Acknowledgements**

I would firstly like to express my sincere gratitude to my principal supervisor, Professor Jianglong Yu, for his continuous support for my PhD research and for his patience, motivation and immense knowledge. His invaluable guidance has assisted me immensely with my research and in my writing of this thesis. I could not imagine having a better mentor for my PhD study.

I would also like to thank my co-supervisors, Emeritus Professor Terry Wall, Associate Professor John Lucas and Doctor Rohan Stanger, for their encouragement and insightful comments and questions. They gave me the incentive to approach my research from various perspectives.

I would like to thank my Master's degree supervisor, Professor Chung-Hwan Jeon, at Pusan National University in Korea for his tremendous support, without which I would not have had the opportunity to study for a PhD in Australia.

I would like to extend my sincere thanks to my industrial mentors, Associate Professor Merrick Mahoney at the University of Newcastle, Kim Hockings from BHP, and Doctor Dave Osborne, the ACARP Coordinator, for their technical advice through ACARP and BHP supported research projects.

I would also like to extend my sincere thanks to Jim Todhunter for his assistance and advice in developing the 4 kg coke oven and in assisting me with my daily activities in the K100 laboratory from my first day at the University of Newcastle. I extend my deep gratitude to Doctor Arash Tahmasebi who helped me immensely in the revision of my papers and thesis. I also extend my gratitude to the other PhD students in our group (Yunze Hui, Doctor Fengkui Yin, S. M. Ashiqur Rahman, Faridul Islam, Joshua Oliveira, Yixin Chen and Rou Wang) and Shaolei Gai in another group for their encouragement and support during my studies.

I gratefully acknowledge Key Laboratory of Advanced Coal and Coking Technology of Liaoning Province at University of Science and Technology Liaoning in China and its members (Doctor Jinxiao Dou, Tian Lu) for their support with my research. I would like to extend my thanks to the visiting scholars from China (Associate Professor Huan Zhao, Doctor Guiyun Yi, Xiuzhen Geng, Zixuan Wang) for their contribution to my experimental work.

I also wish to thank Doctor Priscilla Tremain and Doctor Monica Rossignoli for their training and permission to use their analytical equipment.

I would also like to thank PhD fellows, Doctor Quang Anh Tran, Doctor Xie Wei, Doctor Hui Song and Doctor Liza Elliott for their valuable comments on my research, thus adding further enhancement to the quality of my research work.

I also offer sincere thanks to the fourth-year students Jiayu Sun, Xintong Zhang, Malachi Gairdner, Alexander Tai, Shin Rui How and Juan Monroy with whom I had the pleasure to work during their honours research projects.

I gratefully acknowledge ACARP for the funding of my PhD research under project c24054. I also acknowledge the financial support from the University of Newcastle for my PhD scholarship under the University of Newcastle Postgraduate Research Scholarship (UNRSC 50:50) scheme.

I would particularly like to acknowledge the access I had to the Imaging and Medical Beamline (IMBL) at the Australian Synchrotron, part of ANSTO, for the micro-CT imaging analysis. I extend my thanks to Doctor Anton Maksimenko, IMBL, Australian Synchrotron, for his assistance and support in recording micro-CT images. My thanks also go to Lauren North for her assistance in teaching me how to reconstruct the micro-CT images.

Finally, I would thank my parents and maternal relatives who have always cared for me during my overseas study. I would specifically like to thank my younger brother, Seungho Lee, who has looked after my parents during my time away. Without their support, I would never have been able to complete my PhD.

# Table of Contents

Acknowledgements .....	ii
Table of Contents .....	iv
List of Figures.....	vii
List of Tables .....	x
Nomenclature.....	xi
Abstract .....	xii
Chapter 1. Introduction.....	1
1.1 Role of coke in a blast furnace .....	1
1.2 Formation of the plastic layer in a coke oven.....	2
1.3 Outline of the thesis .....	5
Chapter 2. Literature Review.....	7
2.1. Coke making process .....	7
2.1.1 Coking coal .....	7
2.1.2 Carbonization in industrial coke ovens.....	9
2.1.2.1 Coke oven batteries and the overall coke-making process .....	9
2.1.2.2. Carbonization in a coke oven.....	11
2.1.3 Coke applications .....	12
2.1.3.1 Role of coke in the blast furnace.....	12
2.1.3.2 Requirements for the physical and chemical properties of coke.....	13
2.1.3.3 Factors affecting the strength of coke .....	15
2.2. Phenomena of carbonization in industrial coke ovens .....	17
2.2.1. Heat transfer in a coke oven.....	17
2.2.2 The path of the volatile matter released in a coke oven .....	18
2.2.3 Internal gas pressure (IGP) and oven wall pressure (OWP) .....	19
2.2.3.1 Generation of IGP and OWP .....	19
2.2.3.2 Factors affecting IGP and OWP .....	21
2.2.4 Fissuring .....	22
2.3 Pyrolysis characteristics of coking coal .....	24
2.3.1 Devolatilization of coking coal during pyrolysis .....	24
2.3.2 The structural transformation of coking coal during pyrolysis .....	25
2.3.3 Extrinsic factors modifying thermoplasticity .....	28
2.3.4 Analytical techniques to measure the thermoplasticity of coals .....	30
2.3.6.1 Gieseler Plastometer.....	31
2.3.6.2 Audibert-Arnu Dilatation.....	31

2.4 Formation and chemistry of the plastic layer during coking .....	32
2.4.1 Characteristics of the plastic layer .....	33
2.4.1.1 Pore structures in the plastic layer .....	33
2.4.1.2 Permeability of the plastic layer .....	35
2.4.2 Factors modifying the properties of the plastic layer .....	37
2.4.2.1 Effects of the particle size and packing density .....	37
2.4.2.2 Effects of the heating rate .....	37
2.4.2.3 Effects of maceral concentrates .....	38
2.5 Experimental techniques for studying the plastic layers .....	38
2.5.1 Sole-heated coke ovens .....	38
2.5.2 Thermogravimetric-plastometer-swelling pressure (TG-P-SP) apparatus .....	41
2.5.3 4 kg double-heated wall coke oven .....	43
2.6 Modelling of the plastic layers .....	44
2.6 Summary of the literature .....	46
2.6.1 Thermoplasticity of coking coals .....	46
2.6.2 Formation of the plastic layer .....	47
2.6.3 Influences of the plastic layer .....	47
2.6.4 Research activities on the plastic layer .....	48
2.7 Knowledge gaps .....	49
2.7 Objectives .....	50
Chapter 3. Experimental .....	52
3.1 Coal sample preparation and analysis .....	52
3.1.1 Petrographic, proximate and ultimate analysis of the coal macerals .....	53
3.2 Experimental apparatus and techniques .....	53
3.2.1 The 4kg laboratory-scale coke oven facility .....	53
3.2.2 Coking tests and plastic layer sample preparation .....	56
3.2.2.1 In-situ measurement of the temperature profiles and internal gas pressures .....	56
3.2.2.2 Sampling and treatment of plastic layers .....	57
3.3 Analytical techniques to analyse the plastic layer samples .....	59
3.3.1 Synchrotron Micro-CT imaging and image analysis .....	59
3.3.2 Micro-CT image analysis .....	59
3.3.3 ATR-FTIR .....	60
3.3.4 TG-FTIR .....	63
Chapter 4. In-situ studies of the characteristics of the plastic layers .....	65
4.1 Introduction .....	65
4.2 In-situ measurements during the coking process .....	67
4.2.1 Heat transfer and temperature profiles in the coke reactor .....	67

4.2.2 Cokes produced from the coking experiments .....	68
4.3 Changes in the thickness of the plastic layer .....	70
4.4 Changes in the IGP peaks and the characteristic temperatures with the passage of the plastic layer .....	73
4.5 Chapter summary .....	83
Chapter 5. The physical and chemical structure transitions in the plastic layers .....	84
5.1 Introduction .....	84
5.2 Morphological transition in the plastic layer .....	85
5.3 Correlations between the chemical structures and the coal properties .....	88
5.4 Transitions in the chemical and physical structures across the plastic layer .....	91
5.5. Chapter summary .....	98
Chapter 6. The characteristics of the plastic layers investigated using a thermo-gravimetric analyser coupled with a Fourier-transform infrared spectrometer .....	99
6.1 Introduction .....	99
6.2 TG analysis of the extracted plastic layer samples .....	101
6.3 TG-FTIR analysis of the extracted plastic layer samples .....	105
6.4 Discussion on pyrolysis behavior across the plastic layer and coal properties .....	110
6.5 Chapter summary .....	112
Chapter 7. Conclusions .....	113
Chapter 8. Recommendations .....	116
References .....	118
Publication .....	126
Research projects .....	127

## List of Figures

Figure 1.1. Process description of iron making and the roles of coke in a blast furnace [1].	1
Figure 1.2. The formation of the plastic layer in the coke oven [15].	4
Figure 2.1. Characterization of the thermoplasticity of coking coal [18].	8
Figure 2.2. Association of volatile matter contents and vitrinite reflectance on the production of poor, medium and good coking coals [23].	9
Figure 2.3. Flow Diagram of the coke making process [28].	10
Figure 2.4. Formation and migration of the plastic layer during coking in a coke oven [30].	12
Figure 2.5. Correlation between vitrinite reflectance and CSR [41].	16
Figure 2.6. Effect of mean maximum vitrinite reflectance and Gieseler maximum fluidity on coke strength [42].	16
Figure 2.7. Temperature distribution in the coke oven and its impacts on the formation of the plastic layer [14].	18
Figure 2.8. Generation of internal gas pressures at different locations in the coke oven [14].	19
Figure 2.9. Generation of oven wall pressures during the coking process [13, 47].	20
Figure 2.10. Fissure development in the BHP research coke oven (RCO) as a function of time [54].	23
Figure 2.11. The evolution of volatile matter species during pyrolysis [59].	25
Figure 2.12. The changes in the coal macromolecular structure during carbonization [64].	28
Figure 2.13. The effects of various heating rates on the characteristic temperatures measured by the Gieseler plastometer [14].	29
Figure 2.14. The reduction of swelling and thermoplastic property as a function of level of oxidation [14].	30
Figure 2.15. A change in Gieseler fluidity in the thermoplastic range [18, 78].	31
Figure 2.16. Characterization of the dilatation properties using an Audibert-Arnu Dilatometer [79].	32
Figure 2.17. Schematic of the formation of the plastic layer in a coke oven [25, 46].	33
Figure 2.18. Schematic diagram of the porosity changes in the plastic layer.	35
Figure 2.19. Permeability changes in the plastic layer estimated by a micro-CT imaging technique [48, 87].	36
Figure 2.20. Schematic diagram of a sole-heated oven (left) and a vertical cross-sectional image of $\mu$ -focus X-ray CT showing the plastic layer (right) [92].	39
Figure 2.21. Schematic of a sole-heated oven (left) and the partially-coked sample produced from the oven (right) [86].	39
Figure 2.22. Schematic of the top view of the experimental setup for the carbonization of coal with X-ray filming technique (left) and the X-ray picture of the heated charge of a coal sample (right) [93-96].	40
Figure 2.23. Changes of intralayer pressure-temperature relationship during the carbonisation of a coking coal [96].	41

Figure 2.24. Schematic of the thermogravimetric-plastometer-swelling pressure (TG-P-SP) apparatus [97].	42
Figure 2.25. Results from the synchronized measurements by using the TG-P-SP.	42
Figure 2.26. Schematic of the 4 kg double-heated wall coke oven to investigate the formation of the plastic layer [98, 99].	44
Figure 2.27. Schematic of the numerical modelling to predict internal gas pressure and the results [105].	45
Figure 2.28. Estimation of the molecular weight distributions of metaplast using the modified CPD modelling [26].	46
Figure 3.1. Schematic diagram of the 4 kg laboratory-scale double-heated wall coke oven [98, 99].	54
Figure 3.2. Photograph of the 4 kg laboratory-scale double-heated wall coke oven.	54
Figure 3.3. Schematic of the experimental set-up of the 4 kg coke oven for the in-situ measurements.	57
Figure 3.4. Schematics of (a) the sampling probe and (b) the coal sample in the sampling tube in which the plastic layer is formed during the heating of the coking coal [98, 99].	58
Figure 3.5. Micro-CT images of horizontal sections from different locations in the C2 plastic layer: (a) Initial softening layer; (b) Intermediate plastic layer; (c) Resolidifying layer [98].	59
Figure 3.6. Cross-sectional images of a C2 sample retrieved by the reconstruction of the slices (the grids were aligned with the locations at which the plastic layer samples were extracted).	60
Figure 3.7. Photograph (top) and schematic (bottom) of the Spectrum Two™ ATR system from PerkinElmer.	61
Figure 3.8. ATR-FTIR spectrums of C2 and samples extracted from different locations: raw coal, initial softening layer (56 mm), intermediate plastic layer (53 mm) and resolidifying layer (45 mm).	62
Figure 3.9. De-convolution of spectra for C2 parent coal in the region from 3200-2750 cm <sup>-1</sup> to obtain CH <sub>2</sub> /CH <sub>3</sub> . Black line: original spectra; short dotted red line: retrieved spectra; and double dotted blue line: de-convolution bands.	63
Figure 3.10. Photograph (top) and schematic (bottom) of the TG-FTIR analyser.	64
Figure 3.11. FTIR spectra of the volatile matters from a plastic layer sample during TGA heating [99].	64
Figure 4.1. Smoothed measurement results of the temperature profiles for the six coals measured in different locations within the coke reactor: (a): C0, (b): C1, (c): C2, (d): C3, (e): C4 and (f): C5.	68
Figure 4.2. Coke samples produced from the coking experiments in the 4 kg coke oven.	69
Figure 4.3. Smoothed measurement results of the temperature profiles for the six coals measured in different locations within the coke reactor: (a): C0, (b): C1, (c): C2, (d): C3, (e): C4 and (f): C5.	70
Figure 4.4. The methodology of data exploration for estimating the thicknesses of the plastic layers based on the isothermal planes between the initial softening temperature (IST) and the solidification temperature (ST).	71

Figure 4.5. Changes in the estimated thicknesses of the plastic layers of the six coals across the width of the coke reactor. ....	72
Figure 4.6. Correlations between the plastic ranges and thicknesses of the plastic layers at (a) 5-150 mm; and (b) the half thicknesses at 200 mm. ....	73
Figure 4.7. The IGP curves of the six coals measured at different locations in the coke reactor: (a): C0, (b): C1, (c): C2, (d): C3, (e): C4 and (f): C5. ....	74
Figure 4.8. Changes in the maximum IGPs measured across the width of the coke reactor. ....	75
Figure 4.9. Characteristic temperatures of the IGPs at the different locations where they: (a) started to rise, (b) reached a maximum and (c) disappeared. ....	77
Figure 4.10. Cross-sectional micro-CT images of the plastic layer samples for the six coals. ....	80
Figure 5.1. Changes in the porosities as a function of distance, estimated by the image analyses of the cross-sectional micro-CT images. ....	87
Figure 5.2. Correlations between the mean maximum vitrinite reflectance and the $A_{ar}/A_{al}$ values of the six coals, which was in good agreement with previous findings [70]. ....	89
Figure 5.3. Cross-sectional micro-CT images of the plastic layers and their adjacent layers (left column), aligned with changes in the $A_{ar}/A_{al}$ values and the normalized peak areas of aliphatic CH (right column). ....	93
Figure 5.4. Changes in the normalized peak areas of the CH <sub>2</sub> and CH <sub>3</sub> of the plastic layers (a-f: C0-C5). ....	94
Figure 6.1. Changes in the DTG curves of the raw coals and the plastic layer samples extracted from the borders of the characteristic regions: (a): C0, (b): C1, (c): C2, (d) C3 and (e): C4 The $I_{Cn}$ , $M_{Cn}$ and $R_{Cn}$ were indicated as red in Figure 5.5. ....	103
Figure 6.2. Changes in the maximum rates of the weight losses of the raw coals and the sub-samples extracted at the boundaries of the characteristic regions ( $R_{Cn}$ , $M_{Cn}$ and $I_{Cn}$ were indicated in red in Figure 5.5). ....	104
Figure 6.3. Total weight losses of the raw coals and the sub-samples extracted from the borders of the characteristic regions ( $R_{Cn}$ , $M_{Cn}$ and $I_{Cn}$ were indicated in red in ....	104
Figure 6.4. Changes in the evolution curves of the aliphatic CH for the raw coals and the plastic layer samples, as monitored by the FTIR: (a): C0, (b): C1, (c): C2, (d) C3 and (e): C4. ....	106
Figure 6.5. Changes in the intensity peaks of the aliphatic CH for the raw coals and the plastic layer samples. ....	106
Figure 6.6. Correlations between the Gieseler maximum fluidities and the changes in the DTG peaks and aliphatic intensity peaks between the parent coals and the sub-samples at $M_{Cn}$ . ...	107
Figure 6.7. Changes in the evolution curves of the aromatic CH for the raw coals and the plastic layer samples, as monitored by the FTIR: (a): C0, (b): C1, (c): C2, (d) C3 and (e): C4. ....	109
Figure 6.8. Changes in the intensity peaks of the aromatic CH for the raw coals and the plastic layer samples. ....	109

## List of Tables

<b>Table 2.1. Classification system for coking coals and non-coking coals based on their elemental compositions and volatile matter contents [20].</b> .....	9
<b>Table 2.2. Requirements for an acceptable coke quality grade in Australia [34].</b> .....	15
<b>Table 3.1. Properties of the six Australian coking coals used in this study.</b> .....	52
<b>Table 3.2. Test conditions for coking experiments.</b> .....	57
<b>Table 3.3. Band assignments of the FT-IR absorption peaks for spectral analysis [64].</b> .....	62
<b>Table 5.1. Structural parameters of the six coking coals obtained from the analyses of the ATR-FTIR measurements</b> .....	88

## Nomenclature

Symbol	Description	Units
IGP	Internal gas pressure	kPa
OWP	Oven wall pressure	kPa
IST	Initial softening temperature	°C
MFT	Maximum fluidity temperature	°C
ST	Solidification temperature	°C
$T_i$	Characteristic temperature where the IGP started to rise	°C
$T_{max}$	Characteristic temperature where the IGP reached a maximum	°C
$T_e$	Characteristic temperature where the IGP disappeared	°C
Romax	Mean maximum vitrinite reflectance	%
MMVR		
$A_{ar}$	Integrated area of aromatic C-H stretching band	$cm^{-1}$
$A_{al}$	Integrated area of aliphatic C-H stretching band	$cm^{-1}$
$A_{CH_2}$	Integrated area of $R_2CH_2$ stretching band	$cm^{-1}$
$A_{CH_3}$	Integrated area of $RCH_3$ stretching band	$cm^{-1}$
$Nor_{A_{al}}$	Normalized integrated area of aliphatic CH with reference to the aliphatic CH in raw coal	
$Nor_{A_{CH_2}}$	Normalized integrated area of $CH_2$ with reference to the $CH_2$ in raw coal	
$Nor_{A_{CH_3}}$	Normalized integrated area of $CH_3$ with reference to the $CH_3$ in raw coal	
$R_{max}$	Maximum rate of weight loss	%/min

## **Abstract**

The pyrolysis of coking coals in a temperature range of 350 to 550 °C involves not just chemical changes but also physical changes, which are referred to as thermoplasticity. With increasing temperature in the thermoplastic range, coking coals become softened and coalesce into a plastic mass and are then resolidified into a solid porous coke. These stages take place layer by layer in a coke oven due to the temperature gradients. A coal charge in an industrial coke oven undergoes a plastic transformation, which corresponds to the formation of a plastic layer. The plastic layer is a foam-like material consisting of molten vitrinite and liptinite, solid coal components (inertinite macerals) and the gases generated by the decomposition of the coal. It forms near the heating walls and migrates toward the centre of the oven. The migration is attributed to a decrease in the temperature gradient in the coke oven as the coal charge adjacent to the heating wall is heated rapidly and the heat is then transmitted to the rest of the coal charge. As the temperature exceeds the resolidification temperature, the plastic layer gradually converts into a layer of viscoelastic semi-coke, having a typical cellular coke structure. With a further temperature increase, the order and size of the aromatic layers of the semi-coke increase, followed by condensation reactions which correspond to the formation of the solid porous residue, coke. When the plastic layers merge in the centre of the oven and the centre temperature reaches a desirable temperature (900-1100 °C), followed by a period of soaking time, the whole coal charge is converted into coke. The coking process occurs over approximately 17-18 hours. After the venting of residual gases, the coke oven doors are opened in order for the coke to be pushed from the batteries. Once the coke has been quenched, it is crushed and screened to obtain the proper size for use in a blast furnace. The formation of the plastic layer is considered as a critical stage in the coking process as the pore structures, which are closely related to the coke quality, are mainly determined during this process. The generation of significant amounts of volatile matters (gases) in the thermoplastic phase builds up the internal gas pressure (IGP). The transmission of IGP to the coke oven walls causes coking pressure against the walls, which is referred to as the oven wall pressure (OWP). It is known that an excessive OWP causes serious oven wall damage, shortening the battery life and an increased pushing force when the coke is discharged. To prevent these problems, a maximum allowable OWP of 10 kPa is widely accepted.

The physical and chemical changes that occur in a thermoplastic temperature range have been widely investigated due to their impacts on the coal-coke transformation and the phenomenon attributed to the formation of the plastic layer. Pre-heated samples prepared in the thermoplastic range were analysed by a variety of analytical techniques, such as Fourier-transform infrared spectroscopy (FTIR), solid-state  $^{13}\text{C}$  nuclear magnetic resonance (SSNMR), X-ray powder diffraction (XRD). A two-stage solvent extraction was used to acquire the light and heavy extracts formed in the thermoplastic range. The extracts were analysed using laser desorption time-of-flight imaging mass spectrometry (LDI-TOF-IMS),  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrometry and gas chromatography-mass spectrometry (GC-MS). An in-situ FTIR was employed to measure the functional group changes while a single coking coal was heated in the thermoplastic range. These studies provide an understanding of the changes in the chemical structures that occur in the thermoplastic stage and proposes explanations for its mechanisms.

However, what happens in real coking conditions, in particular heating conditions, is far more complicated than in the above experimental conditions. Therefore, another way of studying the plastic layers is by direct observation of the process and in-situ measurement of the thermoplastic properties, while they are happening, although this is extremely difficult for coal heated in an oven. However, a few attempts have been made by different researchers who have used sole-heated ovens combined with micro-CT and X-ray filming techniques. These techniques were employed to observe the pore structures inside the plastic layer, which provided a better understanding of the transitions in the physical structures of coal to coke during the coking process. However, these techniques used rather small amounts of coal samples (several hundred grams scale) which were heated from one side. This means that the heat transfer conditions, including the temperature gradients, may vary greatly from those in a practical coke oven. Under such conditions, it is questionable whether the characteristics of the plastic layer would be equivalent to those in large-scale ovens. In addition, the previous research activities have largely focused on the changes in the physical structures of the plastic layer, rather than the changes in the chemical structures.

Therefore, the main objectives of this study are to investigate the changes in the chemical and physical structures inside the plastic layer, under practical heating conditions, in order

to provide insights into the underlying mechanisms of the plastic layer. In particular, this research is focused on the: (a) development of a 4 kg laboratory-scale coke oven which enables the sampling of plastic layer samples and the in-situ measurement of the temperature profiles and internal gas pressures at different locations under practical heating conditions; (b) characterization of the thermoplastic behaviours of six Australian coking coals with varying petrographic properties and Gieseler maximum fluidities using the 4 kg coke oven; (c) in-situ study of the formation of the plastic layers regarding the changes in the thicknesses of the plastic layers and the internal gas pressures during coking; (d) characterization of the changes in the physical and chemical structures inside the plastic layers formed from the six Australian coking coals through a combination of analytical techniques; and (e) identifying the effects of the petrographic properties and Gieseler maximum fluidities on the characteristics of the plastic layers.

To achieve these objectives, a 4 kg laboratory-scale double-heated coke oven was employed for the in-situ measurement of the temperature histories and internal gas pressures in different locations of the coal charge and the sampling of plastic layer samples. A noticeable geometric feature of the 4 kg coke oven is that the length of the laboratory coke oven (400 mm) is similar to the width of a practical coke oven. Additionally, insulation enveloped the surface of the coal charge, except for the heating wall sides, in order to simulate the one-dimensional heat transfer from the heating walls. Six Australian coking coals with different petrographic properties and Gieseler maximum fluidities were selected for the coking experiments. The crushed coals were charged in the coke reactor with a packing density of  $825\text{kg/m}^3$  and were placed in the coke oven for heating. The pressure probes, together with the thermocouples, were placed across the width of the coal charge to measure the temperature profiles and IGPs at multiple points throughout the coking cycle. For the plastic layer sampling, the sampling probe located in the coke reactor was used to acquire semi-coke samples that consisted of loose coal, thermoplastic regions and coke/semi-cokes. The pore structures of the semi-coke samples were analysed using the Synchrotron micro-CT in a non-destructive method before the extraction of the plastic layer samples. The plastic layer samples were then sectioned from the thermoplastic regions of the semi-coke samples and they were analysed using attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy and a thermogravimetric analyser coupled with a Fourier-transform infrared spectrometer (TG-

FTIR). The ATR-FTIR was used to analyse the chemical structures of the parent coals and the sectioned plastic layer samples regarding their structural parameters, such as  $A_{ar}/A_{al}$ ,  $CH_2/CH_3$ , aliphatic CH and its components ( $CH_2$  and  $CH_3$ ). The TG-FTIR was employed to investigate the pyrolysis behaviours of the sectioned plastic layer samples during the TGA heating, including their volatile matter yields and the changes in the aliphatic and aromatic CH structures of the volatile matter.

Based on the in-situ study of the formation of the plastic layers, the new findings of the present study are as follows: (a) the thicknesses of the plastic layers were estimated using a data exploration of the measured temperature profiles and the characteristic temperatures obtained from the Gieseler fluidity test. It was observed that the thicknesses of the plastic layers were consistent with the Gieseler thermoplastic temperature ranges of the parent coals; (b) the changes in the IGP termination temperatures measured in different locations of the coal charges indicated the different extents of the fissuring at the coke/semi-coke sides, which influenced the maximum IGPs. These results were attributed to the properties of the coals, such as their mean maximum vitrinite reflectance, maceral concentrates, Gieseler maximum fluidities and volatile matter contents.

The characterization of the physical and chemical changes inside the plastic layers using the analytical techniques provided the following insights: (a) there were correlations between the Gieseler maximum fluidities, the chemical structures analyzed by structural parameters and the petrographic properties (Mean maximum vitrinite reflectance and vitrinite contents). The selected coals with the lower mean maximum vitrinite reflectance and the higher vitrinite contents showed lower  $A_{ar}/A_{al}$  ratios, which indicated lower contents of the aliphatic CH in the coal structures. It seemed that this appeared to cause higher levels of decomposition in the thermoplastic ranges, resulting in the higher Gieseler maximum fluidities. These correlations impacted on the different physical and chemical characteristics of the plastic layers; (b) the ATR-FTIR results showed that the normalized aliphatic CH decreased in the initial softening regions. This was followed by a relatively constant stage, and finally a drastic decrease on the coke sides of the plastic layers. These changes were consistent with a loss of bonds throughout the devolatilization process, which were analysed by the TG-FTIR. However, the levels of response appeared to vary with the Gieseler maximum fluidities derived from the chemical structures of the

six coals; (c) the higher fluidity coals that appeared to have higher aliphatic CH contents showed a lower decrease in their aliphatic CH at the earlier stages of the thermoplastic regions due to the aliphatic hydrocarbons in the volatile matter. This may have potentially caused further depolymerization in the intermediate plastic regions, which corresponded to the higher fluid levels of the plastic layers. In this context, the higher fluidity coals showed higher maximum porosities in the thermoplastic regions due to the higher degrees of gas entrapment in the highly viscous plastic regions. This suggested that the aliphatic functionalities of a coal may play a significant role in the development of its plastic properties and the subsequent semi-coke formation during the coking process.