



## Full Length Article

# A study on the structural transition in the plastic layer during coking of Australian coking coals using Synchrotron micro-CT and ATR-FTIR

Soonho Lee<sup>a</sup>, Jianglong Yu<sup>a,b,\*</sup>, Merrick Mahoney<sup>a</sup>, Priscilla Tremain<sup>a</sup>, Behdad Moghtaderi<sup>a</sup>, Arash Tahmasebi<sup>a,b</sup>

<sup>a</sup> Chemical Engineering and International Collaborative Centre for Carbon Futures, University of Newcastle, Callaghan, NSW 2308, Australia

<sup>b</sup> Key Laboratory of Advanced Coal and Coking Technology of Liaoning Province, School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, China



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## ABSTRACT

The chemistry of the plastic layer in a coke oven plays a critical role in coke-making and has a great impact on coke quality. In this study, progressive changes of the plastic layer were investigated using a combination of analytical methods. Three Australian coking coals with different vitrinite contents were used to produce plastic layer samples using a 4 kg lab-scale coke oven. The plastic layer samples were analysed by means of Synchrotron micro-CT scanning and attenuated total reflectance-Fourier transform infrared (ATR-FTIR) analysis to delineate the characteristic regions of each layer. The peak separation and quantitative calculation of FTIR spectra allowed the analysis of changes in structural parameters and functional groups of each plastic layer. The results showed drastic changes in physical and chemical structures of the plastic layer samples for all coals tested and were also strongly influenced by coal type. For the high-vitrinite coals, it seems that relatively larger amounts of the plastic mass were developed due to the timely rupture of large number of the bridge bonds in the intermediate plastic regions and efficient hydrogen transfer to stabilize the radicals generated. This led to a more drastic growth of pores and larger maximized porosities in the intermediate plastic regions. Conversely, the low-vitrinite coal was assumed to form lower amount of the plastic mass in the intermediate plastic region due to less rupture of aliphatic bridge bonds and inefficient hydrogen transfer. This was attributed to a lower degree of the pore development and the lower porosity observed in the region.

## 1. Introduction

When coking coal is heated inside the coke ovens, it experiences a thermoplastic stage during which the coking coal softens, forming a plastic layer from which the coke is formed [1–3]. Due to the large temperature gradient in the coke ovens, a plastic layer forms early during heating near the heating wall and moves from the wall to the center of oven, leaving behind semicoke and ultimately coke product. The porosity and the pore wall structure, which significantly affect the coke formation and quality are mainly formed in the plastic layer [4–6]. In addition, various phenomena occurring in the plastic layer may influence the coke oven operation and related safety issues [7,8]. It is therefore important to investigate the chemistry of the plastic layer under realistic heating conditions and the subsequent impacts on coke quality.

The formation of thermoplasticity in coking coals has been described in the literature. Coal has three dimensional macromolecular

networks which are composed of aromatic sites, cross-linked by functional groups such as aliphatic bridge bonds and oxygen bridges [9]. In the thermoplastic range, weak bridges consisting of the functional groups are ruptured from the macromolecule. The rupture contributes to the generation of plastic mass with moderate molecular weight, possibly reflecting the formation of the fluid-like phase [10]. To support this well-known concept, it was suggested that the stabilization of radicals generated during the depolymerization is also required through hydrogen transfer from hydro-aromatic structures, in order to develop the plastic mass [11,12]. The lack of transferable hydrogen in the sequence of stabilizing the radicals is responsible for resolidification, when the plastic matter cross-links to form a char structure.

Several studies [13–17] have been performed to investigate the chemical mechanism of the thermoplasticity of coking coal. Previous studies [14,16] employing FTIR, indicated that there is a closer relationship between changes in aliphatic C–H of the coal and the thermoplasticity compared with other functional groups. It was found that

\* Corresponding author.

E-mail address: [jianglong.yu@newcastle.edu.au](mailto:jianglong.yu@newcastle.edu.au) (J. Yu).

the decomposition of the aliphatic C–H in the macromolecular structure occurs in the plastic range, resulting in an increase in the aromaticity. Nomura et al. [14] suggested that the reasons for the decrease in the aliphatic C–H are the evolution of aliphatic-rich low-molecular materials, rupture of aliphatic side chains attached to aromatic rings, and methylene bridges between structural units. Shin et al. [13] employed an in-situ FTIR to investigate the decomposition trend in the thermoplastic range, where real time changes of aromatic and aliphatic C–H were obtained. It was suggested that early breakage of aliphatic C–H before entering the thermoplastic range leads to early cross-linking and stabilization of radicals, exhibiting low-fluidity. Recently, ATR-FTIR was used to investigate the chemical changes of coal structure during heating [18,19]. Odeh [15] studied the decomposition of bituminous coals during the carbonization using the ATR-FTIR. The increase in aromaticity of the coal structures occurred as the macro-structure became more structurally ordered, due to the growth of aromatic lamella. However, studies on small samples do not reflect the temperature gradients present across the plastic layer in a coke oven and as such may not capture the progressive transformation and possible interactions between different sections of the plastic layer in a coke oven.

There were several attempts to investigate progressive changes of the plastic layer by using various analytical techniques. Laser desorption time of flight imaging mass spectrometry (LDI-TOF-IMS) was employed to analyze the changes in the molecular size of the plastic layer. This study showed that a mid-ranged (500–1000 Da) structure increased while 4000 Da structures dropped at the beginning of the visible plastic layer. The increase in the mid ranged structure was consistent with the generation of fluid like material with an increase in fluidity due to the decomposition of the coal structure in the thermoplastic range [17]. Zubkova [20] used X-ray to investigate plastic layers formed from coals with different caking capacity, which was confirmed by images obtained during scanning electron microscopy analysis. Synchrotron micro-CT was performed to study the physical mechanism of coke formation with high resolution in a non-destructive way [21–23]. The features allowed evaluation of the micro-structure of both the plastic layer and the coke. Despite these studies, the underlying mechanism of the plastic layer formation has not been fully understood due to the difficulties of in-situ sampling of the plastic layer under realistic coke oven conditions.

Aiming at a better understanding of the plastic layer formation, this study investigated the physical and chemical transitions across the plastic layer. A 4 kg double-heated wall coke oven (4kg coke oven) equipped with in-situ plastic layer sampling probe was developed to collect plastic layer samples under simulated coke oven heating which were studied using several advanced analytical techniques. Three Australian coking coals with different vitrinite contents and similar rank were chosen to produce plastic layers in the 4 kg coke oven. Characteristic regions in each plastic layer were delineated by Synchrotron micro-CT. ATR-FTIR was then used to investigate the changes in functional groups across the plastic layer in the extracted samples. This was matched with cross-sectioned micro-CT images. The combination of analytical processes enabled the investigation of the effect of different vitrinite contents on the progressive structural changes in the plastic layer.

## 2. Experimental

### 2.1. Coal samples and sample preparation

The properties of the three Australian coals used for the preparation of the plastic layer samples are shown in Table 1. The mean maximum vitrinite reflectance of the coals corresponding to coal rank was in the narrow range of 1.27–1.39 but they showed a wide range of vitrinite contents. The sample selection made it possible to see the impact of the vitrinite contents on the nature of the plastic layer by reducing the

**Table 1**

Properties of Australian coking coals used in this study.

Coal samples	C1	C2	C3
<i>Proximate Analysis (ad)</i>			
Inherent Moisture (%)	1.2	0.9	1.5
Ash (%)	8.7	7.8	9.5
Volatile Matter (%)	19.5	21.7	22.1
Fixed Carbon (%)	70.6	69.6	66.9
<i>Gieseler Fluidity</i>			
Initial Softening Temperature (°C)	435	415	417
Max Fluidity Temperature (°C)	465	460	461
Solidification Temperature (°C)	490	495	495
Plastic Range (°C)	55	80	78
Max Fluidity (Log 10)	1.11	2.28	2.54
<i>Petrographic analysis</i>			
Mean Maximum Vitrinite Reflectance (%)	1.39	1.32	1.27
Vitrinite (% , mmf)	39.6	61.7	71.6
Liptinite (% , mmf)	/	0.4	0.2
Inertinite (% , mmf)	60.4	37.9	28.2

effect of coal rank. In addition, it was assumed that the characteristic temperatures (Table 1) measured by a Gieseler plastometer would contribute to the formational characteristics of the plastic layer such as its location and thickness.

### 2.2. Coking experiments in the 4 kg lab-scale coke oven

A 4 kg lab-scale coke oven experimental rig was built and used to produce plastic layer samples under conditions similar to the practical coke ovens. As shown in Fig. 1, a noticeable geometric feature of the 4 kg coke oven was that the length of the lab coke oven (400 mm) was similar to the width of the practical coke oven and the coal sample was heated from the two walls at the ends of the oven. This created a one-dimensional heat transfer condition and enabled investigation of the behaviour of the plastic layer formed under conditions relevant to the large-scale coke ovens. Under the simulated conditions, the fast sampling of the plastic layer was done through a sampling probe located at the left side of the coke reactor. In addition, the temperature profile development and the internal gas pressure at multiple points was obtained from the in-situ measurements.

The first stage of the experimental preparation was to crush the coal samples to a top size of 3 mm. For the coking tests, coal was packed in a quartz tube with a charging density of 825 kg/m<sup>3</sup>. The prepared sample was placed into the sampling probe, then placed into the left side of the reactor as shown in Figs. 1 and 2(a). The remaining space in the coke reactor was charged with the same coal sample and with the same packing density of 825 kg/m<sup>3</sup>. The coal charges in the sampling tube and in the rest of the chamber were surrounded by the insulation to simulate one-directional heat transfer from both heating walls as shown in Fig. 1. The insulation reduced the heat transfer from the boundaries of the coal charges, except for the heating wall sides.

### 2.3. Sampling of plastic layer during coking

Plastic layer samples were obtained during the coking tests by using the sampling probe shown in Fig. 2. The sampling probe consisted of an insulating brick and a cylindrical quartz tube (ID: 40 mm, length: 100 mm) in which a coal charge was placed. The insulating brick was used to achieve a one-dimensional heat transfer condition from the heating wall. The quartz tube in the sampling probe was heated as the temperature of the oven wall was raised from room temperature to 1000 °C at a rate of 10 °C/min. The thermocouples at the middle and the periphery of the quartz tube (50 mm and 100 mm from the heating wall) indicated that the middle was heated from 100 °C to 500 °C at a rate of 8 °C/min while the temperature at the tube periphery increased from ambient temperature to 100 °C and dwelled. These data were used

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