

**A Mechanistic Study Of The Structural
Transformations In Australian Coking Coals
And Blends Across The Plastic Layer During
Coking**

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Abbreviations

Abbr.	Definition
IGP	Internal Gas Pressure
Micro-CT	Micro Computed Tomography
SMCT	Synchrotron micro-CT
IR	Infrared Spectroscopy
^{13}C NMR	Solid-state ^{13}C carbon Nuclear Magnetic Resonance spectroscopy
XRD	X-ray Diffraction
SEM	Scanning Electron Microscope
ATR	Attenuated total reflectance
FTIR	Fourier transform Infrared Spectroscopy
TGA	Thermogravimetric analysis
LDI-TOF-IMS	laser desorption time of flight imaging mass spectrometry
CSR	Coke strength after reaction with carbon dioxide
CRI	coke reactivity index
F/Macroporosity	Void fraction
F_t	Void fraction of total macropores
F_i	Void fraction of isolated macropores
D_n	Density of the macropore number
D_{nt}	Density of the total voids number
D_{ni}	Density of the isolated voids number
$V_{f49.25\mu\text{m}}$	Volumetric fraction of diameter (39.40 μm - 59.10 μm) voids

Md	The mean diameter of the voids
$A_{\text{ar-H}}$	The integrated area under aromatic bonded hydrogen peaks
$A_{\text{al-H}}$	The integrated area under aliphatic bonded hydrogen peaks
A_{HC2}	The integrated area under methylene peaks
A_{HC3}	The integrated area under methyl peaks
CH_3	Methyl carbon
CH_2	Methylene, methyne carbon
Al-O	Oxygen-bonded aliphatic carbon
Ar-H	Protonated aromatic carbon
Ar-C	Carbon-bonded aromatic carbon
Ar-O	Oxygen-bonded aromatic carbon
PL	Plastic layer
IS layer	Initial softening layer
IM layer	Intermediate plastic layer
RS layer	Resolidified layer
IST	Initial softening temperature
MFT	Maximum fluidity temperature
ST	Solidification temperature
δ_{b+1}	The average number of bridges and loops per cluster
δ_b	The average number of aliphatic bonded methylene per cluster
δ_l	The average number of aromatic bonded methylene per cluster
σ_0	The average number of side chains per cluster
σ_{+1}	The average number of aliphatic bonded methyl per cluster
σ_{-1}	The average number of aromatic bonded methyl per cluster

ω_p	The average number of protonated aromatic carbons per cluster
ω_c	The average number of carbon-bonded aromatic carbons per cluster
ω_{ta}	The average number of total aromatic carbons per cluster
f_{ar}	The fraction of aromatic carbon in the skeletal structures per cluster

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Abstract

The quality of coke is virtually determined by the chemistry in the plastic layers that form during the coking process. Much of the previous research in the open literature on the underlying chemistry of the thermoplastic behaviours of single coals and blends have been carried out under impractical coking conditions, in terms of the sample sizes, the dimensions of the coal beds and the heating conditions in particular. When a single coal or coal blend is heated inside a coking oven, they undergo complex chemical and physical changes during the pyrolysis process. A plastic layer is formed during the coking process when the temperature of the coal bed is increased to 350 °C. The plastic layer is a foam-like thermoplastic material which consists of molten vitrinite and liptinite and solid coal components (inertinite macerals). However, volatile matters are generated by the decomposition of the coal during the coking process. The plastic layers initially form near the oven walls and migrate towards the centre of the oven. The formation of the cross-linking structures in the thermoplastic range is crucially associated with the quality of the coke produced. Due to the limited resources of premium coking coals in the world, coal blending has become a common practice in the coke making industries. The quality of a coke product is influenced by the interactions between individual coals in the blends during the coking process. Therefore, an understanding of the changes in the chemical and physical structures that take place during the formation of the plastic layers of coking coals and their blends is a core part of what determines a coke oven's operations and the quality of the cokes that it produces.

Therefore, one of the main objectives of this study is to investigate the changes in the physicochemical structures of the selected Australian coking coals and their blends during the formation of their plastic layers. This research is primarily focused on: (a) studying

the behaviours of the Australian coking coals and their blends during the coking process in a 4 kg laboratory-scale coke oven, i.e., the changes in the thicknesses of the plastic layers and the transformations in the internal gas pressures; (b) characterising the changes in the physical structures, i.e., the transformations in the macropores and the coalescence of the macropores in the thermoplastic range during the coking of the coal blends; (c) representing the changes in the chemical structures of coal blends during the formation of their plastic layers, e.g., bridge bonds, looped structures, side chains, protonated aromatic carbons, carbon bonded aromatic carbons and the sizes of the aromatic clusters; (d) elucidating the correlations between the physical structures and the chemical structures in the plastic layers during heating.

To achieve these objectives, a 4 kg laboratory-scale dual-wall-heated coke oven testing rig at the Newcastle Institute for Energy and Resources (NIER) site at the University of Newcastle was employed for the in-situ measurements (temperature histories and internal gas pressures in different locations in the coal charges) and the plastic layer sampling. Three Australian coking coals with similar ranks but with different vitrinite contents and Gieseler fluidities were blended with different blending compositions. The plastic layer samples were analysed using several quantitative analytical techniques, including Synchrotron micro-CT (SMCT), 3D image analysis software (GeoDict), Synchrotron infrared spectrometer (Synchrotron IR), solid-state ¹³carbon nuclear magnetic resonance (¹³C NMR) spectroscopy and micro gas chromatography (micro-GC), in order to understand the transformations in the physicochemical structures of the Australian coking coals and their blends.

The results from the in-situ measurements during the coking process, i.e., the changes in the thicknesses of the plastic layers and the internal gas pressures, has shown that: (a) the

addition of a coking coal with a high vitrinite content and high Gieseler fluidity to the coal blends seemed to significantly influence the thicknesses of the plastic layers; (b) the addition of a coking coal with a high vitrinite content and high Gieseler fluidity to the coal blends appeared to improve the maximum internal gas pressure (IGP) in the centre of the coke oven. These results essentially meant that the impacts of the characteristics of the coal blends are critical in determining their coking behaviours in a coke oven.

A comprehensive study of the transformations in the physicochemical structures of coals and blends in their plastic layers is valuable in order to determine a coke oven's operations and the quality of the coke it can produce. Firstly, the transformations in the physical structures of the Australian coking coals and their blends in the thermoplastic range were analysed using various 3D structural parameters, such as the total void fraction, the numbers of total and isolated voids, and the pore size distributions. Based on the analysis of the 3D images, the coalescence of the pores in the thermoplastic region during the coking process has been clarified. It was also clearly shown that the blending of high vitrinite coals in blends creates more large pores and closed pores during the plastic layer stage. This increased the chances of producing coalesced pore structures and more significant total porosities. With an increase in the proportion of the high vitrinite coking coal in the blend, more channel-like pore structures and large-sized pores were formed during the plastic layers. The analysis of the 3D images also enabled the characterisation of the pore connectivity that was not possible using 2D image analysis.

The changes in the chemical structures during the formation of the plastic layer are then elucidated through a combination of Synchrotron IR, ^{13}C NMR spectroscopy and micro-GC. It was evident that there are dramatic changes in the chemical structures during the plastic layer stage due to the cross-linking reactions, side chain elimination and release

of volatile matters. Both the ^{13}C NMR and Synchrotron IR analyses showed that the total aromaticity increased consistently in the plastic layers for all of the coals tested, while the amounts of the side chains decreased significantly in the plastic layer. There was a clear trend showing that the total number of bridge bonds and looped structures increased, indicating that the degree of cross-linking would increase throughout the plastic layer after certain stages of the coking process. It was found that the changes in the cross-linking structures in the plastic layers were strongly dependent on the properties of the parent coking coals. It appears that the plastic layer samples from the coals with low fluidities exhibited cross-linking structures with a high degree of branching and aromaticity, while the coals with high fluidities formed cross-linking structures with a relatively low degree of aromaticity and branching, but with a large number of bridge bonds and looped structures. The analysis of the gases using micro-GC verified the cross-linking reactions and side chain elimination that had been reflected in the Synchrotron IR and ^{13}C NMR results. It is likely that the transferable methyl carbons, methylene carbons and hydrogen were strongly correlated to the cross-linking reactions and side chain elimination in the thermoplastic region, which was reflected in the release profiles of the methane and hydrogen gases during the plastic layer stage. It was also found that the addition of coals with a high vitrinite content and high Gieseler fluidity in a blend with a coal with a low vitrinite content and low Gieseler fluidity seemed to significantly impact on the nature of the parent coal.

Finally, in order to correlate the physical structures with the chemical structures in the plastic layer stage, the parameters of the macropore structures, i.e., the macroporosity and number of macropores, were analysed as a function of the parameters of the chemical structures in the plastic layer, i.e., the average number of methyl carbons per cluster, the average number of methylene carbons per cluster, and the average number of total

aromatic carbons per cluster. It was noted that there was an overall increase in the macroporosity, which was accompanied by dramatic changes in the chemical structures during the formation of the plastic layer, i.e., a strong increase in the methylene carbons, a decrease in the methyl carbons and a decrease in the total aromatic carbons. The decrease in the number of macropores was also accompanied by a decrease in the aromatic structures during the formation of the plastic layer. However, the changes in the number of macropores are not strongly correlated with the transformations in the methylene carbons, methyl carbons and the degree of aromaticity in the thermoplastic range, suggesting that the transformations in the macropores are dramatically impacted by the changes in the cross-linking structures and the release of the volatile matters, i.e., methane and tar, during the formation of the plastic layer.