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Linking thermoplastic development and swelling with molecular weight changes of a coking coal and its pyrolysis products

Quang Anh Tran*\(^a\), Rohan Stanger\(^a\), Wei Xie\(^a\), Nathan Smith\(^b\), John Lucas\(^a\), Terry Wall\(^a\)

\(^a\)Chemical Engineering, the University of Newcastle, Callaghan, NSW 2308, Australia
\(^b\)Analytical & Biomolecular Research Facility, the University of Newcastle, Callaghan, NSW 2308, Australia

* Corresponding author. Email: quanganh.tran@uon.edu.au

Abstract

The thermoplastic development of an Australian coking coal was investigated by linking thermal swelling with changes in molecular weight of its pyrolysis products. Coal thermal swelling was investigated together with volatiles evolution and characterisation of generated volatiles (including volatile tar and light gases). The molecular weight distributions of coal and its solvent extracts were measured by using Laser Desorption/Ionization Time of Flight Mass Spectroscopy (LDI-TOF-MS). Solvent extraction (by acetone and tetrahydrofuran (THF)) was initially used on the raw coal to aid interpretation of thermo-swelling by volumetric expansion measurements. The removal of ~2% solvent soluble matter from the raw coal (the mobile phase) reduced its swelling extent during heating by up to 22% (from 86% down to 68% and 64% for acetone- and THF- residues, respectively). Volatile release after solvent treatment remained unaffected. This suggested that the majority of the coal’s swelling behaviour could be attributed to the formation of heat-generated liquid matter (the metaplast) during pyrolysis.
Broad molecular weight changes were found in the solvent extractable component (metaplastic material extracted by acetone and THF) of the semi-coke. Prior to softening (350°C), the extractable components were composed of molecules mainly <500 Da. The upper limit in molecular weight distribution of solvent extracts increased significantly to 1800 Da at the onset of swelling (400-450°C) and decreased back to ~500 Da at the end of swelling (500°C). The spectra showed that the volatile tar and acetone extract (the light solvent extract) consisted of similar repeating structures separated 12-14 Da apart. As the treatment temperature increased, the molecular weight distribution of volatile tar increased in molecular mass approaching that of the acetone extract distribution (~600 Da). THF extract molecular weight distribution was a mixture of 12-14 Da and 24 Da repeating units which only became apparent at molecular weight above 600 Da.

The LDI-TOF-MS analysis of the solid coal showed that it contained a distribution of molecular structures centred at 2000 Da and spanning between 500 and 7000 Da. This raw coal spectrum also contained multiple repeating mass lines every 24 Da apart. Overall, these results suggested that the coal consisted of complicated structures which subsequently degraded into smaller fragments capable of forming a complex intermediate liquid phase and a distribution of lighter volatile tar species.

Keywords: Coal thermoplasticity; Solvent extraction; Metaplast

1 Introduction

1.1 Coal thermoplasticity

The transformation of coal to coke during coking is governed by the coal’s thermoplastic behaviour. During heating, the thermoplastic process includes softening, bubble formation, swelling, and eventually
resolidification at higher temperatures.\textsuperscript{1} The result of this process is that discrete coal particles are transformed into coke, a solid porous carbon residue that can act as a fuel, a chemical reducing agent, and a high-strength permeable support during blast furnace operation.\textsuperscript{2, 3} The most common tests that can be used to determine coal plastic properties include Gieseler plastometer and Arnu dilatometer.\textsuperscript{1} Although these two tests can be used to provide standardised information for empirical coal plasticity evaluation, they do not provide an understanding of the underlying chemical changes that lead to bulk physical transformation, nor do they adequately describe the actual thermoplastic behaviour in a coke oven.

1.2 Coal chemical structure and its devolatilisation models

In general, coal is envisaged to have a macromolecular network structure which consists of chains of aromatic and hydro-aromatic structures cross-linked with aliphatic and ether bridges.\textsuperscript{4-10} The coal network is highly porous and contains low molecular weight organic molecules known as the mobile phase\textsuperscript{11} that can be extracted by organic solvents.\textsuperscript{12, 13} To explain and predict product compositions generated during pyrolysis, different coal network models have been developed. These network models include the FLASHCHAIN model;\textsuperscript{14} the functional group – depolymerisation, vaporization and cross-linking (FG – DVC) model;\textsuperscript{15} the chemical percolation devolatilisation (CPD) model.\textsuperscript{16} All three models include network modelling, coal structure characterisation, depolymerisation reactions, cross-linking reactions, and non-condensable gas, tar, and char formation. The differences among these models lie in their chemical assumptions for devolatilisation mechanisms and mathematical approaches.\textsuperscript{17} These network models have been developed with the intention of supporting coal behaviour prediction during combustion processes which involves rapid devolatilisation of coal particles. However, coking coal pyrolysis occurs at a slow and uniform heating rate, approximately 3-5°C/min in a coke oven.\textsuperscript{18} Therefore, modifications are needed for the prediction of coking coal behaviour and coke strength development. A more fundamental understanding of thermoplasticity phenomena, including both chemical and physical changes, is needed to optimise these coking coals for commercial utilisation,\textsuperscript{19} in particular blend design in coke ovens which is currently still empirically based.
1.3 Coal metaplast

There are a number of hypotheses and theories that have been proposed to chemically explain coal thermoplasticity.\textsuperscript{20} Among them, the most noticeable theories are: the $\gamma$-fraction theory\textsuperscript{21} and the metaplast theory\textsuperscript{6, 22, 23}. The difference between the two theories is that the former assumes softening material is present in the raw coal, while the latter assumes that it is thermally generated. Based on the metaplast theory, the metaplast refers to the fraction that does not immediately evaporate either to the particle surface or into bubbles dispersed throughout the molten coal during pyrolysis.\textsuperscript{23, 24} The extent of metaplast formation is determined by competition between volatilisation of the lighter material, thermolysis rates of the coal macromolecular structure, and retrogressive rates that lead to solid formation.\textsuperscript{25} The metaplast is thought to be thermally unstable and it can decompose to form volatiles and/or be transformed into coke.\textsuperscript{22} During coking coal pyrolysis, the amount of metaplast increases at first and subsequently decreases. The metaplast can be isolated by rapidly cooling the coal after heating and treating it with a solvent.\textsuperscript{1} In practice, the choice of solvent will determine the largest structures removed during this extraction process. Molecular weights up to 1,000,000 Da have been observed in solvent extracts from semi-cokes using CS$_2$/NMP.\textsuperscript{26} However, by using tetralin (a well-known hydrogen donor) in a high-temperature solvent extraction (350°C), the metaplast was judged to correspond to the compounds of <800 Da in molecular weight.\textsuperscript{27} The amount of solvent-soluble constituents increased greatly at the fluidity stage and then decreased towards resolidification stage, which suggested that solvent-soluble constituents were related to fluidity behaviour.\textsuperscript{28} Recently, Takanohashi et al.\textsuperscript{26} stated that the fluidity of coking coal was determined by both the components that present in raw coal ($\gamma$-fraction) and the components that were generated during heating (metaplast). Based on this study on solvent extraction of heat-treated coals, they proposed a “continuous self-dissolution model” in which the lighter molecular weight components (such as $\gamma$-component, chloroform-soluble) should act as a solvent that can dissolve heavier molecular weight components during heating. Such continuous dissolution is needed for coal softening and fluidity during
carbonisation. Both physical and chemical changes during coal pyrolysis contributed to its fluidity property, however, the nature of these changes and their effect on fluidity are not well understood.

This present work focuses on linking thermal swelling extent and volatiles evolution with changes in molecular weight distribution of coal and its solvent extracts at different points during pyrolysis. The swelling extent was analysed by Computer Aided Thermal Analysis (CATA), a novel technique that can measure coal thermal and swelling behaviour simultaneously. In addition to total volatiles evolution recorded by Thermogravimetric Analysis (TGA), Dynamic Elemental Thermal Analysis (DETA) was utilised to quantify volatile tar and light gases evolution based on elemental carbon content. Solvent extraction was undertaken on the semi-cokes prepared at different final pyrolysis temperatures between 350 and 600°C. The molecular weight distribution of coal and the solvent extracts was obtained by using Laser Desorption Ionization- Time of Flight- Mass Spectrometry (LDI-TOF-MS) technique.

2 Experiments

2.1 Coal sample

An Australian coking coal was wet-sieved to 100-210 μm prior to testing. Coal petrographic analysis on the single coal size fraction was performed using standard ISO 7404/5. Petrography results with proximate and ultimate analyses are given in Table 1.

<table>
<thead>
<tr>
<th>Analytical techniques</th>
<th>Components</th>
<th>Proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate analysis</td>
<td>Ash</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>(wt%, db)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Volatile matter</td>
<td>23.7</td>
</tr>
</tbody>
</table>

Table 1: Properties of the investigated coal
<table>
<thead>
<tr>
<th><strong>Fixed Carbon</strong></th>
<th>66.5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C</strong></td>
<td>89.13</td>
</tr>
<tr>
<td><strong>H</strong></td>
<td>4.24</td>
</tr>
<tr>
<td><strong>N</strong></td>
<td>1.95</td>
</tr>
<tr>
<td><strong>O+S</strong></td>
<td>4.68</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Petrographic analysis</th>
<th>R_{\text{Max}} *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitrinite</td>
<td>55.6</td>
</tr>
<tr>
<td>Inertinite</td>
<td>44.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Maceral components</th>
<th>Telovitrinite</th>
<th>Detrovitrinite</th>
<th>Semifusinite</th>
<th>Fusinite</th>
<th>Inertodetrinite</th>
<th>Mineral matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td>50.7</td>
<td>2.7</td>
<td>40</td>
<td>1.3</td>
<td>1.3</td>
<td>4</td>
</tr>
</tbody>
</table>

* Mean Maximum Reflectance

### 2.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on the coking coal and its Soxhlet extraction residues using thermogravimetric analyser Q50 manufactured by TA instrument. To analyse sample mass loss during pyrolysis, about 10 mg sample was heated from room temperature to 100°C using 20°C/min heating rate and held at this temperature for 10 minutes to remove excess solvents and moisture. The sample was then heated to 1000°C with 5°C/min increment under nitrogen atmosphere (50 ml/min flow rate). When the sample temperature reached 1000°C, 50 ml/min air flow was supplied into the heating chamber to oxidise the remaining coke for 30 minutes. Ash yield collected at the end of TGA experiments were used for the calculation of extraction yield via ash tracer method.\(^{30}\)
\[ W = \frac{10^4 (A_1 - A_0)}{A_1 (100 - A_0)} \]  

(1)

where \( W \) is the extraction yield (\%, dry basis), \( A_0 \) is the ash content of the raw coal (\%, dry basis), and \( A_1 \) is the ash content of the solvent residue (\%, dry basis).

2.3 Computer Aided Thermal Analysis

Computer Aided Thermal Analysis (CATA) was employed to examine coal swelling behaviour during pyrolysis. Approximately 2 g of coal was packed into 11.07 mm ID quartz tube at a density of ~950 kg/m\(^3\). The swelling ratio was determined by transient change in the length of the coal pellet which was measured by a linear variable differential transformer (LVDT) during pyrolysis:

\[ \text{Swelling ratio} = \frac{\Delta L}{L_o} \times 100\% \]  

(2)

Where \( \Delta L \) is the transient change measured by the LVDT, \( L_o \) is the length of the packed coal pellet (~20 mm). In CATA experiments, duplicate runs were conducted with the weight variation was controlled to be <0.1 g and acceptable deviation in maximum swelling extent was <3%. For swelling comparison between raw coal and its solvent residues in this work, the difference in utilised weight was recorded at ~0.05 g while ~0.02 g was the weight difference recorded between two residues. In addition to thermal swelling, thermal swelling rate was also calculated to gain insight into phenomenon occurred during plastic range. To achieve this goal, the swelling rate was obtained as the first derivative of thermal swelling profile.

During CATA experiments, 30 ml/min argon flow was supplied into the heating chamber to carry generated volatiles out of the coal pellet. As coal was heated at 5°C/min rate, the upstream inlet gas pressure was also measured. The inlet gas pressure has been shown previously to correspond with changes in bed permeability during coal softening. The difference in pressure between the front-end and
back-end of the coal pellet was assigned as the pressure drop (ΔP). The significant increase in pressure drop value (ΔP >2 kPa) was taken as the swelling onset point. Details of the CATA technique can be found elsewhere.31-33

2.4 Dynamic Elemental Thermal Analysis

Dynamic Elemental Thermal Analysis (DETA) was utilised to investigate the evolution of total volatiles, dynamic tar, and light gases during coal pyrolysis. Samples were heated from room temperature to 800°C using 5°C/min heating rate under inert atmosphere generated by argon flow. The volatiles were combusted using a custom heated O₂ lance downstream of the coal sample with combustion products (CO₂/CO, H₂O, H₂, NOₓ, SOₓ, and O₂) measured at the furnace exit after cooling. These measurements enable the calculation of elemental composition of the volatiles during pyrolysis and are referred to as Total-Volatiles mode. Light-Gases operation mode operated with the O₂ lance placed in a second chamber. An iced tar condenser was placed between the heating furnace and the second combustion chamber. The “tar by difference” was calculated by subtracting light gases from total volatiles measurement. Solid residue (coke) was combusted after pyrolysis by supplying an additional flow of oxygen into the system when the sample temperature reached 800°C. The working principal of this technique is outline elsewhere.34-36

2.5 Solvent extraction

Acetone and tetrahydrofuran (THF) were used for solvent extraction studies. Between these two solvents, acetone was considered to be weaker than THF since the difference between acetone electron donor number (DN=17) and its electron acceptor number (AN=12.5) was +4.5, lower than that in THF which was reported to be +12 (DN=20, AN=8).37 The choice of THF as the “heavier” solvent to study metaplast is derived from previous researchers’ opinions on the formation of “colloidal dispersions” which could bias the molecular weight measurements.38 This phenomenon has been observed in asphaltenes.39 Two types of solvent extraction were used in this study: conventional Soxhlet extraction and multi-stage solvent extraction.
Soxhlet extraction was conducted on raw coal to inspect the change in coal swelling behaviour after it had been exhaustively extracted by organic solvents. The second type of extraction was multi-stage solvent extraction performed under room temperature to investigate the variation in molecular weight distribution (MWD) of solvent extracts obtained from raw coal and preheated semi-coke samples.

**Soxhlet extraction**

About 5g coal was put in a quartz thimble which was then inserted in the Soxhlet extraction apparatus. Heating power was adjusted so that a 20 min/cycle reflux was applied to both acetone- and THF-extraction in 24 h. In both cases, the refluxed solvent became colourless before this 24-hour mark was achieved. Solvent extraction residues were removed from the quartz thimble, dried under vacuum for 24 h, before being subjected to swelling behaviour (CATA) and volatiles release (TGA) investigation.

**Multi-stage solvent extraction**

Multi-stage batch extraction was conducted in the first stage by extracting coal and semi-coke (heated coal sample) with ~200 mL acetone. After 72 h with regular stirring, the solid residue was removed and added ~200 mL distilled THF for second stage extraction. This process was performed sequentially at room temperature rather than using Soxhlet extraction technique to avoid any possible impacts of boiling solvent on the thermally unstable extracts (the metaplast). Acetone-soluble fraction (Acetone extract) and THF-soluble fraction (THF extract) were products of this approach and were used to obtain information on the changes of their molecular weight distributions (MWD) at different pyrolysis temperatures. Since the aim of this work was to observe changes in MWD of pyrolysis products, solvent extraction yield was not acquired.40
2.5.1 Preparation of heat treated semi-cokes prior to solvent extraction

About 500 mg coal was heated in a Sinku Riko infrared gold image furnace to temperatures between 350°C and 600°C using 5°C/min heating rate. Products of the heat-treatment process were divided into two components: semi-coke, the remained solid component; and volatiles, the gaseous component vaporised during pyrolysis.

Generated volatiles were driven towards a downstream tar condenser by supplying 30 ml/min argon flow into the heating chamber. The tar condenser was surrounded by ice in an insulation bucket. By doing so, volatiles were further divided into volatile tar (condensable fraction); and light gases (non-condensable fraction). Volatile tar was collected for further investigations by washing the condensable fraction with acetone. Semi-cokes obtained from different pyrolysis temperatures were subjected to a multi-stage solvent extraction process to generate solvent extracts which were then analysed by mass spectrometry.

2.5.2 Laser Desorption Ionization- Time of Flight- Mass Spectrometry

The extractable material (from raw coal and heat-treated samples) and the collected tar were analysed using Laser Desorption Ionization- Time of Flight- Mass Spectrometry technique (LDI-TOF-MS). In addition to solvent-soluble components, LDI-TOF-MS was also utilised to characterise MWD of solid coal (solid state LDI-TOF-MS). The experimental scheme showing the derivation of generated LDI-TOF-MS samples is outlined in Figure 1.
The LDI-TOF-MS experiments were conducted on Bruker Daltonics UltrafleXtreme MALDI TOF/TOF Mass Spectrometer for both dissolved liquid extracts and solid samples. For liquid extract samples, a volume of 0.8 μL was deposited, matrix-free, onto a Ground Steel target plate and the solvent (acetone or THF) was allowed to evaporate at ambient temperature. For solid coal analysis, coal was ground for approximately 2 minutes prior to embedding the sample on the target plate. The solid coal sample was
deposited on 3M™ double sided electrical tape. Excess particles were removed from the targeting plate by nitrogen flow and only particles held by the tape were subjected to solid LDI-TOF-MS analysis.

Samples were analysed using a smartbeam II laser (Nd:YAG, 335 nm) in positive, reflectron mode. A total of 2000 laser shots were accumulated for each sample at 500 shot intervals from random positions in the sample slot. Laser power was kept at 60% energy level for liquid sample and at 80% energy level for solid coal sample. The detected mass was set from 20 to 7980 Da, the limitation of detector in reflectron mode. The obtained spectra were presented for ions with molecular weight higher than 200 Da since lower molecular weight compounds were generally considered as fragmentation of larger molecules during ionisation. As a result, no further investigations were conducted on these lower molecular weight materials. This LDI-TOF-MS operational mode and sampling scheme (except solid state analysis) have been used to observe changes in solvent extracted material from heated coal in our previous work.  

3 Results

3.1 Thermal swelling behaviour

The influence of solvent extraction prior to heating on coal thermoplasticity was evaluated for both acetone and THF. Thermal swelling behaviour of raw coal and Soxhlet solid extraction residues was obtained by CATA technique and is illustrated in Figure 2. Calculated coal swelling rate and pressure drop profile of gas passing through raw coal on heating within the plastic range (400-600°C) are given in Figure 3. Table 2 presents selective data obtained from CATA experiment on raw coal.
Figure 2: Thermal swelling behaviour of raw coal and Soxhlet solid extraction residues.

Figure 3: Thermal swelling rate and pressure drop of raw coal within the plastic range (400-600°C)
Table 2: Summary data from CATA experiments on raw coal

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Swelling rate (%/min)</th>
<th>Pressure drop (ΔP, kPa)</th>
<th>Phenomena</th>
</tr>
</thead>
<tbody>
<tr>
<td>433</td>
<td>-</td>
<td>&gt;2</td>
<td>Swelling onset</td>
</tr>
<tr>
<td>450</td>
<td>&gt;1</td>
<td>-</td>
<td>Swelling acceleration</td>
</tr>
<tr>
<td>457</td>
<td>-</td>
<td>74</td>
<td>Maximum in pressure drop</td>
</tr>
<tr>
<td>464</td>
<td>26</td>
<td>-</td>
<td>Maximum in swelling rate</td>
</tr>
<tr>
<td>482</td>
<td>&lt;1</td>
<td>-</td>
<td>Swelling stopped</td>
</tr>
<tr>
<td>538</td>
<td>-</td>
<td>&lt;2</td>
<td>No resistance on carrier gas</td>
</tr>
<tr>
<td>675</td>
<td>-</td>
<td>-</td>
<td>Contraction started, swelling percentage dropped from 83% to 82%</td>
</tr>
</tbody>
</table>

Raw coal thermal swelling behaviour

As the coal sample was heated, the packed coal pellet underwent dramatic changes in length (and therefore volume). Changes in length of the packed pellet were first observed at 450°C (defined by swelling rate exceeding 1%/min). The rate of swelling then increased significantly, reaching its first peak of 21%/min at 455°C which coincided with the significant rise in pressure drop profile. The second peak, maximum thermal swelling rate (26%/min), was detected at 464°C. After this temperature, the rate of sample volumetric expansion decreased dramatically with a shoulder peak recorded at 472°C. At 482°C, swelling stopped and thermal swelling extent at this point was 83% compared to its initial packing length.
at room temperature. This swelling rate profile was coal-specific and was expected to be influenced by sample particle size.

The increase in pressure drop ($\Delta P > 2$ kPa) across the packed pellet, indicating softening onset, started at about $430^\circ$C and was earlier than the detectable change in volumetric measurement at $450^\circ$C. The maximum in pressure drop was measured at $457^\circ$C, slightly lower than the temperature at maximum swelling rate ($464^\circ$C).

Changes in pressure drop through the coal pellet occurred over a wider temperature range compared to swelling rate. Specifically, the temperature at which the pressure drop value reduced back to smaller than 2 kPa after swelling was $538^\circ$C, while swelling had already stopped at $482^\circ$C. It is unclear at this point why pressure drop and the end of swelling do not coincide. However, the pressure drop measurement may be more sensitive to the beginning of high temperature contraction.

**Impact of coal extractable removal on thermal swelling behaviour**

A decrease in maximum swelling was observed in both Soxhlet extraction residues as shown in Figure 2. While raw coal possessed a maximum swelling of 83%, this value was only 68% and 64% for acetone and THF-residue, respectively. The fall in maximum swelling demonstrated the impact of a solvent treatment step on its residues. Acetone, the weaker solvent, reduced 15% of coal maximum swelling while this decrease in maximum swelling was 19% when THF, the stronger solvent, was used. Thus, removing the soluble portion of the initial mobile phase in this coal can reduce the subsequent thermo-swelling by up to ~22%.

Although the coal had been exhaustively extracted by two different organic solvents, it is clear that the removal of acetone- and THF-extracts from raw coal were not entirely responsible for the swelling behaviour. This suggested that either the “mobile phase” was not entirely removed during solvent extraction because it remained trapped in the coal network, $^{41, 42}$ or that it is the heat-generated components (the metaplast) that contributed the most towards coking coal swelling behaviour.
3.2 Volatiles characterisation

Total volatiles evolution from coal and its solvent residues

Raw coal and its Soxhlet extraction residues were analysed by TGA. Their devolatilisation profiles (DTG, Derivative Thermogravimetric Analysis) are shown in Figure 4 with summary data presented in Table 3.

![Figure 4: DTG profiles of raw coal and its Soxhlet extraction residues](image)

Table 3: Summary data obtained from raw coal and Soxhlet extraction residues

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volatile matter (wt%, dry)</th>
<th>Coke yield (wt%, dry)</th>
<th>Ash yield (wt%, dry)</th>
<th>Extraction yield* (wt%, db)</th>
<th>R_max (wt%/min)</th>
<th>T_max °C</th>
<th>Weight loss up to 300°C (wt%, daf)</th>
</tr>
</thead>
</table>
The DTG profile of raw coal shown in Figure 4 has been broadly divided into three different regions: pre-plastic region (<300°C), plastic region (300-600°C), and post plastic region (>600°C). Although the sample was held at 100°C for 10 minutes prior to being heated to 1000°C to remove excess solvents and moisture, it is clear that light compounds still vaporised in the pre-plastic region. These materials accounted for approx. 1% of weight loss during raw coal pyrolysis on dry-ash-free basis. Primary devolatilisation occurred in the plastic region with maximum rate of weight loss (R_{Max}) recorded at 479°C (T_{Max}). This temperature, interestingly, was close to the temperature at which coal swelling stopped (482°C, Table 2). In post-plastic region, coal continued to lose weight to the end of TGA experiment with a shoulder peak in DTG profile detected at around 750°C.

In the Soxhlet extraction residues, a similar decomposition trend was observed in both residues in all three regions. The decomposition of acetone residue ended at about 250°C, while THF residue continued to lose weight towards higher temperatures, leading to an overlap between its pre-plastic decomposition and primary devolatilisation in plastic region. For further investigation, weight loss up to 300°C of solvent residues was obtained. This comparison revealed that between 100 and 300°C, solvent residues decomposed more than raw coal. While raw coal lost only 1% weight loss in this region, this value in acetone- and THF-residues was 1.8 and 2.2%.

<table>
<thead>
<tr>
<th></th>
<th>Raw coal</th>
<th>Acetone residue</th>
<th>THF residue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20.4</td>
<td>70.4</td>
<td>21.9</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>9.16</td>
<td>68.7</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>2.09</td>
<td>9.34</td>
</tr>
<tr>
<td></td>
<td>0.708</td>
<td>0.713</td>
<td>0.695</td>
</tr>
<tr>
<td></td>
<td>479</td>
<td>481</td>
<td>482</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>

* Calculated via as tracer method

** Maximum rate of weight loss

*** Temperature at maximum rate of weight loss
Extraction yield calculated by the ash tracer method (Eq. (1)) showed that both solvents only removed about 2% of the initial mass on dry basis. Despite the removal of only 2% of the coal mass through solvent extraction, it is noted that this removal had a significantly higher impact on swelling. However, the maximum swelling of residues was still considerable (68% and 64% for acetone- and THF-residues, respectively), it is clear that the extractable components alone was not responsible for the bulk of thermal swelling extent.

*Characterisation of volatiles evolved during raw coal pyrolysis*

Further characterisation of volatiles generated during raw coal pyrolysis was conducted by using Dynamic Elemental Thermal Analysis (DETA), a novel technique that can differentiate dynamic tar and light gases from total volatiles evolution. Dynamic changes are presented as the evolution of elemental carbon and linked with key phenomena occurring in coal swelling profile as shown in Figure 5. Key temperatures in DETA experiments are presented in Table 4. Results of DETA analysis in both total volatiles and light gases mode are summarised in Table 5.
Figure 5: Dynamic carbon evolution during coal pyrolysis.

Table 4: Key temperatures in DETA analysis

<table>
<thead>
<tr>
<th>Carbon evolution</th>
<th>Carbon evolution</th>
<th>Carbon evolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>start (^a) (°C)</td>
<td>peak (°C)</td>
<td>completion (^b) (°C)</td>
</tr>
<tr>
<td>Total volatiles</td>
<td>334</td>
<td>469</td>
</tr>
<tr>
<td>Dynamic Tar</td>
<td>330</td>
<td>463</td>
</tr>
<tr>
<td>Light gases</td>
<td>437</td>
<td>494</td>
</tr>
</tbody>
</table>

\(^a\) 1% of total carbon evolution between 300-800°C

\(^b\) 99% of total carbon evolution between 300-800°C

Table 5: Summary of coal DETA analysis
By integrating the volatile tar carbon evolution shown in Figure 5, it was found that the temperature which corresponded to 1% of dynamic tar carbon evolution between 300-800°C was 330°C (Table 4). This point was considered to be the start of tar evolution and was ~100°C earlier than the swelling onset of coal pellet (433°C, Table 2). Tar evolution peaked at 463°C, just before the coal pellet reached its maximum in swelling rate (at 464°C). The end point of tar evolution was found to be 536°C (Table 4) and was just before the point at which no resistance exerted on carrier gas as presented in Table 2.

The onset evolution of light gases began at 437°C and was close to swelling onset (Table 2). Light gases evolution rate peaked at 494°C (Table 5). As a result, the maximum evolution of total volatiles at 469°C could be mainly attributed to tar evolution. The evolution of tar completed at 536°C while light gases continued to evolve out of the sample towards the end of DETA experiment. Combined with the pressure drop profile in Figure 3, the sudden drop in ∆P between 520-530°C could be linked with the end of tar evolution. In addition, as shown in Table 5, the amount of volatile tar evolved out of the coal was about four times more than that of light gases within the swelling range (between 433 and 482°C). This

---

### Fractional split of volatiles released between 433-482°C (% volatile carbon)

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total volatiles</td>
<td>12.84</td>
<td>4.09</td>
<td>0.27</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>Dynamic Tar&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.39</td>
<td>2.71</td>
<td>0.23</td>
<td>0.00</td>
<td>83.5</td>
</tr>
<tr>
<td>Light gases</td>
<td>5.45</td>
<td>1.37</td>
<td>0.04</td>
<td>0.00</td>
<td>16.5</td>
</tr>
<tr>
<td>Coke</td>
<td>76.80</td>
<td>0.80</td>
<td>0.30</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>89.64</td>
<td>4.89</td>
<td>0.57</td>
<td>0.03</td>
<td>4.87&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> by difference
observation, once again, emphasised the important role of tar evolution and the build-up of its precursor (the metaplast) on coal swelling behaviour.

3.3 Molecular weight distribution of coal and its pyrolysis products

The LDI-TOF-MS technique was employed to analyse changes in molecular weight distribution (MWD) of coal and its pyrolysis products. The pyrolysis products include vaporised component (volatile tar), and extractable components (acetone- and THF-extract) from semi-coke.

3.3.1 Raw coal extracts

Multi-stage extraction was conducted on raw coal (no thermal treatment) to receive information on MWD of coal extractable at room temperature (~20°C). Results are presented in relative intensity and shown in Figure 6.

Figure 6: Molecular weight distribution of coal solvent extracts at room temperature
Acetone and THF-extract from coal both contained >200 Da materials. The upper limit in acetone extract MWD was ~600 Da while this value in MWD of THF extract extended to ~1000 Da. The difference in this upper limit is attributed to the difference in solvent strength. The 200-600 Da components were also presented in THF extract after it had been previously extracted by acetone. This is likely due to the limited solubilities of heavier compounds in acetone.

3.3.2 Pyrolysis products

Volatile tar

Volatile tars were collected during coal heat-treatment process. Their selected MWDs are illustrated in Figure 7 at 350, 400, and 500°C. At 350°C, the volatile tar does not form any particular shape of distribution and appears to contain a relatively small number of significant peaks. In addition, its low intensity (maximum intensity: 95) coupled with the DETA results suggested that the amount of volatile material formed at this temperature was low. As the pre-treatment temperature was increased from 350 to 500°C, there was a consistent increase in volatile tar molecular weight. At 400°C, the upper limit of volatile tar MWD was about 400 Da. This value then increased up to about 600 Da as treatment temperature reached 500°C.
Figure 7: Changes in volatile tar molecular weight distribution as a function of treatment temperature

*Semi-coke extracts*

Selected spectra of acetone and THF extracts from pre-treated semi-cokes are presented in Figure 8 and Figure 9, respectively. The acetone extracts showed relatively consistent molecular structures up to 500 Da were maintained in the coal during heating. These molecular structures are of similar range to the volatile tar results and are consistent with previous work. \(^{40}\)
The THF extracts from the semi-coke displayed a significant sensitivity to temperature, changing from an initial upper limit of 500 Da to up to 1800 Da and then back. The THF extract at 350°C (Figure 9) possessed a MWD similar to THF extract from raw coal (Figure 6) with molecular class of compounds in the range of 200-1000 Da. Such similarity did not exist between acetone extracts obtained at room temperature and at 350°C. With increasing heat treatment temperature, there was an increase followed by a subsequent decrease in MWD of acetone and THF extracts. Specifically, the upper limit in acetone extracts at 400°C extended to about 500 Da. In comparison, THF extracts showed a significant expansion in MWD at 400°C, and the inclusion of additional class of compounds that became apparent between 600 and 1800 Da with repeating peaks separated every 24 Da. The upper limit of these compounds decreased from 1800 Da to about 600 Da at 500°C with the disappearance of the 600-1800 Da compounds. Interestingly, THF extract MWD at 500°C was similar to spectrum of volatile tar collected also at this temperature (spanning between 200 and 600 Da, Figure 7).
Figure 8: Changes in molecular weight distribution of acetone extracts from heated coal
Figure 9: Changes in molecular weight distribution of THF extracts from heated coal
3.3.3 Solid state LDI-TOF-MS on coal

In addition to the investigation of pyrolysis products dissolved in organic solvents, LDI-TOF-MS was also utilised to conduct studies on solid coal particles. The obtained spectrum from this solid state LDI-TOF-MS experiment is presented in Figure 10.

The solid coal spectrum displayed a right-skewed distribution with molecular weight spanning from 500 to beyond 7000 Da peaking between 1500 and 2000 Da. Because LDI-TOF-MS solid state analysis used in this study was in Reflectron mode, it is clear that the obtained spectrum did not represent the entire coal molecular structure, and that coal possessed a much more complex structure compared to its generated pyrolysis products of which highest molecular weight only reached ~1800 Da. For further investigations, bulk molecular weight distributions of coal and its pyrolysis products are viewed in detail in the next section.

3.4 Interpretation of molecular weight spectra

Previous sections provided an overview on solid coal particles and on changes in MWD of pyrolysis products as a function of temperature. However, each obtained spectrum by itself contained information that can only be analysed if the data is viewed at narrower MW scale. This incremental analysis was conducted on both solid coal and its pyrolysis products and is presented in Figure 11 and Figure 12.
3.4.1 Pyrolysis products

At narrower scales (e.g., between 325 and 375 Da), MWD of both volatile tar and acetone extract contained repeating structures every 12-14 Da between peaks with each local peak group consisting of satellite lines in a distribution on either side. Such behaviour was commonly observed by Herod et al., Rodgers and Marshall, Nomura et al., and Stanger et al., and considered to be representative of homologous series adding additional methyl groups (i.e., -CH3) to a base aromatic unit. Figure 11 shows an example for the THF extract prepared at 450°C.

The 12-14 Da repeating structure recorded in tar and acetone extract, though aligned to the same molecular weight, was less pronounced in THF extract spectrum (Figure 11a) and could only be observed in THF extract up to 600 Da. Individual peaks in volatile tar, acetone and THF extracts spectra at MW <600 Da aligned to the same molecular weights, suggesting that the same chemical structures existed in these pyrolytic products. Above 600 Da (Figure 11b), an additional group of peaks characterised by repeating every 24 Da apart from each other emerged in THF spectrum.
3.4.2 Solid coal

Incremental analysis on solid state LDI-TOF-MS is shown in Figure 12a-d in enhanced views at ~1000, ~1500, ~2000, and ~4000 Da regions. For clarity, the spectral lines were presented as a continuous curve instead of discrete vertical lines.

Figure 11: Incremental analysis on THF extract obtained at 450°C
The enhanced views presented from Figure 12a to Figure 12d shows that the bulk MWD of solid coal consisted of different peak groups which were separated by 24 Da increments. However, the shape of each 24 Da repeating peak comprised of a number of substantial sub-peaks which exhibited complex behaviour at higher molecular weight. Specifically, at about 1000 Da, a peak group could be considered to consist of three significant sub-peaks with a dominant second peak each separated by a 4 Da increment. At 1500 Da, the second and third sub-peaks had similar prominence. At 2000 Da the peak broadening became apparent with significant overlap between peaks, and eventually no distinguished peak could be observed at beyond 4000 Da. This was due to the decrease in resolving power of high mass compounds, a feature of LDI-TOF-MS instrument.
To perform incremental analysis throughout the coal spectrum, a peak group consisted of three local peaks: peak 1, 2, and 3 (at 1034, 1038, and 1042 Da, respectively) were chosen from Figure 12a. The corresponding MW of their peak family at higher molecular weight was obtained by adding these initial values to multiples of 24 Da. These repeating multiples were 16, 46, and 128 to reach the molecular weights in Figure 12b, c, and d, respectively. The calculated peak family at ~1500 Da (Figure 12b) aligned well with the calculated peak positions. At ~2000 Da, none of the calculated peaks using repeating number of 46 aligned with the obtained peak. In each case, the sub-peaks appeared to shift +2 Da away from the calculated values. At 4000 Da this shift increased to about +8 Da. Clearly, this observed phenomenon in the coal’s structure is complex and further work is required to understand its molecular importance.

4 Discussion

4.1 The role of volatiles in driving swelling

Volatile evolution was measured with the DETA technique as a mixture of volatile tars and light gases. When combined with the thermo-physical measurements from the CATA technique, it was found that tar evolution was closely associated with coal swelling behaviour. This was evident in the dominance of generated volatile tar over light gases evolution within the swelling range (Table 5) and the similar temperatures of peak tar release with maximum swelling rate (Table 2 and Table 4). However, tar evolution was shown to occur over a much wider temperature range than the thermoplastic region. This clearly suggests a more complex relationship exists between volatiles driving swelling and overall thermoplastic behaviour.

The onset of light gas evolution was found to occur at similar temperature to swelling onset. Light gases have previously been linked with cross-linking mechanisms and are commonly included together in pyrolysis models such as FLASHCHAIN, FG – DVC, and CPD. A plausible explanation for this complex process may be that the tar evolution is indicative of semi-volatile materials that are capable of...
adding to the fluid forming material during the plastic phase and that the light gases can act as the driver for swelling. In the thermoplastic range (430-482°C), tar evolution accounted for 84% of the total volatiles release (in terms of mass of carbon), compared to just ~16% in the case of light gases. However, the condensable tars measured a peak molecular weight at ~250-350 Da which extended up to 500 Da. Such a molecular size is consistent with 5-7 ringed aromatics with much higher boiling temperatures such as benzo(a)pyrene (5 rings, 252 Da, boiling point 495°C) or coronene (7 rings, 300 Da, boiling point 525°C). The outcome of these combined measurements suggests that actual volumetric flow of volatile tars is low despite the mass flow rate being greater than light gases. As an estimate, the volumetric contribution of tars (as coronene 300 Da) and light gas (as CH₄) to swelling was calculated as 18% and 82%, respectively. This difference in volumetric flow supports the delay between the measured softening (from ΔP) and swelling, in that the release of tars after softening provides insufficient driving force without the evolution of light gas.

4.2 Molecular changes in pyrolysis products during coking

Pyrolysis products, both vaporised and solvent-extractable components from the semi-coke, were obtained through pre-heating coal to a suite of temperatures that covered the plastic range. The volatile component had the lowest molecular range, with an upper limit of 400-600 Da. This upper-limit of 600 Da was small compared to previous work which reported up to ~1000 Da molecular sizes under rapid heating conditions (~1000°C/s). The explanation for this might simply be that different coals were used in two studies, or that the slow heating rate in this study may have allowed a certain retention time of volatile tar inside the coal particle, which can lead to greater extent of secondary reactions between escaping tar and the solid residue.

With respect to solvent soluble components, this work has shown that the molecular weight distribution of the raw coal extractable materials is similar to that of extracts up to 350°C, while further increases in temperature results in significant structural changes that coincide with a “bulk” thermoplastic response (i.e., softening and swelling). This thermoplastic behaviour corresponded to an observed increase in
molecular size of the solvent-soluble components, particularly in the range of 500-1800 Da, which subsequently disappeared on resolidification. This change in molecular character of the solvent extracts along with the consistent increase in MWD of volatile tar clearly suggests depolymerisation of coal structure to form smaller fragments, consistent with the pyrolysis mechanisms described in FLASHCHAIN, \textsuperscript{14} FG-DVC, \textsuperscript{15} and CPD\textsuperscript{16} models.

Detailed incremental analysis on the pyrolysis products obtained at 450°C showed that there was a repetition of peak series separated by 12-14 Da on volatile and solvent extracts, particularly at MW <600 Da. These results agree well with previous works on tar conducted by Herod et al.\textsuperscript{41} and Nomura et al.\textsuperscript{43}, or on solvent extraction of semi-coke performed by Stanger et al.\textsuperscript{40}. In addition, it was found that position of peaks in this particular MW range appeared to align well between vaporised (volatile tar) and <600 Da components in acetone and THF extracts. This alignment indicates a similarity in their chemical structure consistent with a tar vaporisation mechanism as explained by Unger and Suuberg\textsuperscript{46} (as opposed to a tar cracking mechanism). Under this scenario, tar species could be formed during pyrolysis and yet remain within the coal structure prior to vaporising. This tar retention would lead to a build-up of semi-volatile material that could contribute towards fluid development.

For compounds with MW higher than 600 Da, there appeared an additional 24 Da repeating structure in THF extract spectrum. This 24-Da repeating unit (e.g., an ethylene structure -C≡C-) has been implicated in soot formation,\textsuperscript{47} and has been suggested as a key decomposition pathway in coal pyrolysis\textsuperscript{48}. Further heating led to the disappearance of these compounds. At 500°C, THF extract spectrum possessed a similar MWD compared to the collected volatile tar. This suggests that the 500-1800 Da molecular structures are a key intermediate in the formation of a thermoplastic phase, and that material <500 Da are not able to independently form this phase alone. This temperature, interestingly, was close to the peak in light gas evolution (at 494°C). Such observation in light gases production between 400-500°C fits with moderate-temperature cross-linking mechanism that occurs after tar evolution reaches its maxima, as described by Deshpande et al.\textsuperscript{49} and Solomon et al.\textsuperscript{50, 51}. 
4.3 Solid state LDI-TOF-MS

Solid state LDI-TOF-MS has been applied to solid coal particles by several researchers including the Argonne Premium Coal Suite,\textsuperscript{52} maceral rich coals,\textsuperscript{53} and as a form of image analysis\textsuperscript{54}. This work has measured comparable molecular range to that of Herod et al.\textsuperscript{52} and Stanger et al.\textsuperscript{54} for similar reflectance coals. Further incremental analysis was conducted on different regions in coal MW spectrum to gain better understanding of coal chemical structure rather than just focusing on determining the largest molecular size in coal (as in Herod et al.\textsuperscript{52}). The coal spectrum contained a series of peak groups separated by 24 Da spacing, similar to >600 Da region recorded in THF extract spectrum. Importantly, the observed 12-14 Da repeating structure in MW spectra of volatile tar, acetone extract, and THF extract at MW <600 Da region was not apparent in the raw coal, indicating the importance of the pyrolysis process in producing these fractions and the complexities involved in the structure of coal.

5 Conclusions

A number of analytical techniques (CATA, TGA, DETA, and LDI-TOF-MS) were utilised to study thermoplastic properties of one Australian coking coal. Bulk changes were measured via its thermal volumetric expansion and volatiles release (including tar and light gases evolution). Molecular changes were measured in condensed volatile tar and solvent extracts from heated semi-cokes and compared to that of the solid coal. Results of this present work are:

- Both the mobile phase (solvent extractable materials in raw coal) and the metaplast (heat-generated materials) contributed to coking coal swelling property. Although the removal of the mobile phase led to a dramatic reduction in thermal swelling capacity, the metaplast was found to be mainly responsible for coal swelling behaviour.
The majority of volatile release within the thermo-swelling range was measured as tar evolution. However, the commencement of swelling phenomenon was found to be closer to the onset of light gases release.

The observed thermo-physical changes within the plastic range were found to be reflected in the changes in molecular structures of the pyrolysis products. In particular, the appearance and subsequent disappearance of 500-1800 Da material with 24 Da repeating structure closely followed the development of the thermoplastic process.

The molecular weight distribution of raw coal extended beyond 7000 Da and was much broader compared to its tar and solvent extracts. The spectrum was found to consist of multiple repeating peak groups separated by 24 Da, similar to the reoccurring pattern found in solvent extract at MW higher than 600 Da.

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References


