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Study of chemical structure transition in the plastic layers sampled from a pilot-scale coke oven using a thermogravimetric analyzer coupled with Fourier transform infrared spectrometer

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Abstract

The aim of this study was to characterize the pyrolysis behavior of the plastic layer formed during the coking process in a 4kg laboratory-scale facility. The 4 kg coke oven was used to produce semi-coked coal samples including the plastic region. The semi-coked samples were scanned by Synchrotron micro-CT to characterize the physical structure changes and identify the sampling locations. Samples corresponding to notional points of softening, maximum fluidity, and resolidification of the plastic layer were obtained for five coking coals of varying thermoplastic properties. Pyrolysis behavior and structural changes of the plastic layer samples were analyzed by a thermogravimetric analyzer coupled with a Fourier transform infrared spectroscopy (TG-FTIR) and an attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). The TG-FTIR analysis allowed the characterization of the changing nature of volatile matter, in which aliphatic and aromatic C-H bonds were observed to undergo the greatest reduction during the plastic layer formation. This was in a line with the ATR-FTIR results which also showed structural changes across the plastic layer. The results suggest that the

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aliphatic CH bonds of the five coals underwent the greatest reduction with the progression of the plastic layer in the coal charge. One particular observation of interest was that the decomposition trends of the aliphatic CH across the plastic region varied with the thermoplastic properties of the coal samples, implying that the aliphatic structures may play a significant role in the development of plastic properties during the formation of the plastic layer.

***Keywords*:** Coking coals; Plastic layer; Pyrolysis; TG-FTIR; Chemical structure change.

1. Introduction

Coking coals undergo chemical and physical structure changes during the pyrolysis process inside the coke oven. Thermoplasticity is known as the chemical and physical changes of coking coals in a temperature range of 350-500 °C. As a result of the thermoplasticity, coking coal charge in undergoes a plastic transformation in the coke oven, leading to the formation of a thin plastic layer [1]. The plastic layer consists of the molten vitrinite, non-softened coal components, and tarry products, which are formed during the decomposition of the coal in the thermoplastic range. A further temperature increase causes the cross-linking reactions and thus recodification of the plastic layer to form semi-coke. Taking the process into account, a change in the temperature gradient contributes to the migration of the plastic layer from the heating wall to the center of the coke oven, leaving behind a solid porous residue, i.e. coke. The plastic stage is critical in the coking process as the porosity and the pore wall structure, which significantly affect the coke formation and quality, are mainly determined during this stage [2-4]. Gas entrapment in the plastic layer leads to the generation of the internal gas pressure (IGP), the transmission of which to the oven walls may result in the generation of oven wall pressure (OWP). It is known that high OWPs may cause operational problems, such as serious oven wall damage, the shortening of the battery life time, and increase in the pushing force during coke discharge [5, 6]. For this reason, the pyrolysis coking coals have been extensively studied to predict the behavior inside coke ovens.

Generally, coal structure consists of three-dimensional macromolecular networks composed of aromatic sites with grouped aromatic carbons (2-6 rings of average size) [7]. The aromatic sites are cross-linked by aliphatic bridge bonds and oxygen bridges. In the temperature range of 200-400 °C (pre-plastic stage), hydrogen bonds and carboxylic acid decompose, releasing gaseous species such as CO_2 and H_2O. In the plastic range (350-550 °C), weak bridge bonds consisting of the functional groups (i.e., methylene) are ruptured from the macromolecular structure of coal, accompanied by the dealkylation of side chains. This decomposition contributes to the generation of unstable aromatic fragments. The stabilization of generated radicals by hydrogen transfer reactions lead to the production of plastic mass, which has a moderate molecular weight to avoid vaporization [8, 9]. This process is responsible for the exhibition of the fluid-like property in the plastic layer [10]. Several studies suggested that the diameter of the aromatic clusters decreases and the layer spacing increases in the plastic stage due to the disorientation of the aromatic sheets [11, 12]. Some of the aromatic fragments, which are small enough to vaporize are emitted as tars in the plastic layer. Niksa reported that both the plastic mass and the tar are in the molecular weight range of 100-3000 Da [13]. Two kinds of tars can be seen based on the different pyrolysis temperatures [14]. During low-temperature pyrolysis, aromatic and low molecular weight hydrocarbon compounds are mainly present in coal tars. High-temperature coal tars consist of cyclic aromatic hydrocarbon (single ring benzene and alkyl benzene) and aromatic clusters with 20 or more rings [15]. An earlier study suggested that the generated tars pose an influence on the inter-dissolution between non-softened char and plastic mass at the initial softening stage [5]. This leads to an increase in the fluidity of the plastic layer by several orders of magnitude. During the primary pyrolysis, the main gases emitted are CO_2, light aliphatic gases, CH_4, and H_2O [16].

As the temperature increases above the thermoplastic range (post-plastic stage), the lack of transferable hydrogen in the sequence of stabilizing the radicals causes the plastic mass to cross-link and form char structures. This process is known as the resolidification of the plastic layer [9]. Subsequently, the char structures undergo aromatization and condensation of the aromatic clusters

with forming polycyclic compounds. This corresponds to the evolution of CH_4 due to the removal of methyl groups from the periphery of the massive char structures. Lastly, further ring condensation gives rise to the evolution of H_2. This post plastic stage involves the rearrangement to the ordered aromatic structures, which increases the size of the aromatic clusters and decreases the layer spacing [11].

The migration of the volatile matter generated in the plastic layer has been investigated extensively. It is known that most of the volatile matter (~ 90 %) generated in the plastic layer, escape from the semi-coke side [17, 18]. Among the volatile matter released, the primary tars traverse the coke to the oven wall via the fissures formed in the coke in a temperature range of 600-700 °C. Once the tars reach the oven wall, they travel upwards to space above the coal charge. In the residence time of 20-40 s in the coke and 5 s in the free space, the tar molecules are cracked into light hydrocarbons, hydrogen, and polycondensed aromatic residues at around 800 °C [5]. The rest of the volatile matter generated from the plastic layer (10 %) is released to the cooler side of the plastic layer, i.e. coal side [17, 18]. As previously reported [5], the primary tars in the volatile matter are mainly composed of constituents with high boiling points. When released to the cooler side of the plastic layer, the tar condenses on the surface of the coal particles. The repetition of this process with the migration of the plastic layer causes the heavier fractions of the tars to move toward the center of the coke oven. This increases the fluidity and gradually reduces the softening temperature of the loose coal region ahead of the plastic layer [5].

The drawbacks of previous studies in analyzing the pyrolysis behavior in the thermoplastic range are the experimental conditions (i.e., heating conditions and sample size), which may differ from practical coking conditions. This makes it difficult to gain an understanding of the plastic behavior under practical coking conditions. Additionally, the investigations of the migration of the volatile matter have failed to provide detailed chemical structure changes in the plastic layer as it migrates from the oven wall to the center of the coal charge. In this context, it seems that the structural

transformation during the formation of the plastic layer is not yet fundamentally understood and requires further investigation.

In this study, TG-FTIR analysis was used to measure the changes in the volatiles release as well as the evolution of the aromatic and aliphatic hydrocarbons in the plastic layer. A 4 kg lab scale double-heated wall coke oven, which simulates the one-directional heating conditions inside industrial coke ovens was used to produce semi-coked samples using five Australian coking coals varying with petrographic and thermoplastic properties. The samples consisted of coke/semi-coke, a plastic layer, and loose coal. The plastic region was scanned by Synchrotron micro-CT to show its physical structure transition. Then, sub-samples were extracted from the various locations of the plastic layer, delineated by the micro CT images. TG-FTIR analysis was used to investigate the changes in the rate of mass loss and evolution of the volatile matter components of aromatic and aliphatic hydrocarbons in the sub-samples. When combined with the ATR-FTIR results and cross section micro-CT images, the information obtained in this study allowed a realistic investigation of the changes taking place during the plastic later formation, and thus providing the very much data needed to understand the transition from coal to semi-coke inside the coke oven. This study also identified the parameters of the five coals affecting the pyrolysis behavior of the coal during the plastic layer formation.

2. Experimental

2.1 Coal samples preparation and characterization

The properties of five Australian coking coals used in this study are shown in Table 1. The mean maximum vitrinite reflectance of the coals was in a narrow range of 1.27-1.32, except for the C1 (1.39). The vitrinite contents were in a wider range between 39.6-71.6 %. The ATR-FTIR was employed to analyze the chemical structures of the coals by using structural parameters such as A_{ar}/A_{al} and CH_2/CH_3 by following previous studies [19]. The A_{ar}/A_{al} ratio was obtained by integration of characteristic bands of aliphatic and aromatic CH (3000-2800 cm^{-1} and 3100-3000 cm^{-1}). The aliphatic CH band was de-convoluted to obtain the peak areas of CH_2 and CH_3 bands (2920 cm^{-1} and 2950 cm^{-1}) and to calculate

the ratio CH_2/CH_3. Previous finding has suggested that a correlation exists between the structural parameters and chemical structure of coal [20-22]. The A_{ar}/A_{al} ratio presents the degree of condensation of the coal structure, which is referred to as the degree of aromaticity, and the CH_2/CH_3 ratio corresponds to the length or branching degree of aliphatic chains.

Table 1. Sample properties and structural parameters (A_{ar}/A_{al} and CH_2/CH_3) of the five Australian coking coals used to produce the plastic layer samples

Coal samples	C0	C1	C2	C3	C4
Proximate Analysis (ad)					
Inherent Moisture (%)	1.3	1.2	0.9	1.5	2.3
Ash (%)	7.2	8.7	7.8	9.5	7.6
Volatile Matter (%)	22.4	19.5	21.7	22.1	21.2
Fixed Carbon (%)	69.1	70.6	69.6	66.9	68.9
Ultimate Analysis (daf)					
Carbon (%)	88.7	89.9	88.1	88.7	89.2
Hydrogen (%)	5	4.8	5	5	4.8
Nitrogen (%)	2.1	1.7	2.1	2	1.9
Total Sulphur (%)	0.4	0.4	0.6	0.55	0.39
Oxygen (%)	3.8	3.2	4.2	3.8	3.7
Gieseler Fluidity					
Initial Softening Temperature (ST) (°C)	430	435	415	417	428
Max Fluidity Temperature (MFT) (°C)	455	465	460	461	461
Solidification Temperature (RT) (°C)	480	490	495	495	494
Plastic Range (°C)	50	55	80	78	66
Max Fluidity (dd/min)	5	13	189	345	46
Max Fluidity (Log 10)	0.7	1.11	2.28	2.54	1.66
Petrographic analysis					
Mean Maximum Reflectance (%)	1.29	1.39	1.32	1.27	1.31
Vitrinite %	58.9	39.6	61.7	71.6	66
Liptinite %	0.8	\	0.4	0.2	\
Inertinite %	40.3	60.4	37.9	28.2	34
Structural parameters (ATR-FTIR)					
A_{ar}/A_{al}	0.15	0.17	0.13	0.11	0.14
CH_2/CH_3	3.72	3.87	3.19	3.24	3.73

127 *2.2 Sampling of plastic layer samples during coking*

128 A 4kg lab-scale coke oven was used to acquire semi-coked coal samples containing the plastic
129 layers under practical heating conditions. As previously reported [19], the key feature of this apparatus
130 was the length of 4 kg coke oven (400 mm) which was similar to that of practical coke ovens.
131 Additionally, insulation enveloped the surface of the coal charge except for the heating wall sides to
132 simulate the one-directional heat transfer from the heating walls (Fig 1(a)). The sampling probe (left
133 side of Fig. 1 (a)) enabled the acquisition of plastic layer samples formed in the practical conditions
134 with the in-situ measurement of temperature profiles at 50 and 100 mm from the heating wall. For
135 sampling plastic layer samples, the received coals were crushed to top 3 mm. Then, the coals were
136 carefully packed in a quartz tube (L: 100 mm, ID: 40 mm) with a controlled charging density of 825
137 kg/m³ as illustrated in Fig. 1 (b). During the packing, a thermocouple was embedded into the coal bed,
138 placed at 50 mm of the quartz tube. The prepared quartz tube is placed into the sampling probe, then
139 inserted into the coke reactor as shown in Fig. 1 (a). The remaining space in the coke reactor was then
140 charged with the same packing density of 825 kg/m³. The heating walls were heated from ambient
141 temperature to 1000 °C at a rate of 10 °C/min. When the temperature at 50 mm reached 500 °C, the
142 sampling probe was removed from the reactor and placed into a cooling chamber purged with nitrogen.
143 The temperature at 50 mm had increased from ambient temperature to 500 °C at a rate of 8 °C/min
144 while the temperature at 100 mm had increased from ambient temperature to 100 °C and dwelled. The
145 semi-coked samples were scanned by Synchrotron micro-CT imaging in a non-destructive way. Then,
146 the incremental extraction as a function of distance from the heating wall was carried out to obtain
147 sub-samples by the method as previously reported [19]. The sub-samples extracted were ground to
148 <62 μm size for the TG-FTIR and ATR-FTIR analyses.

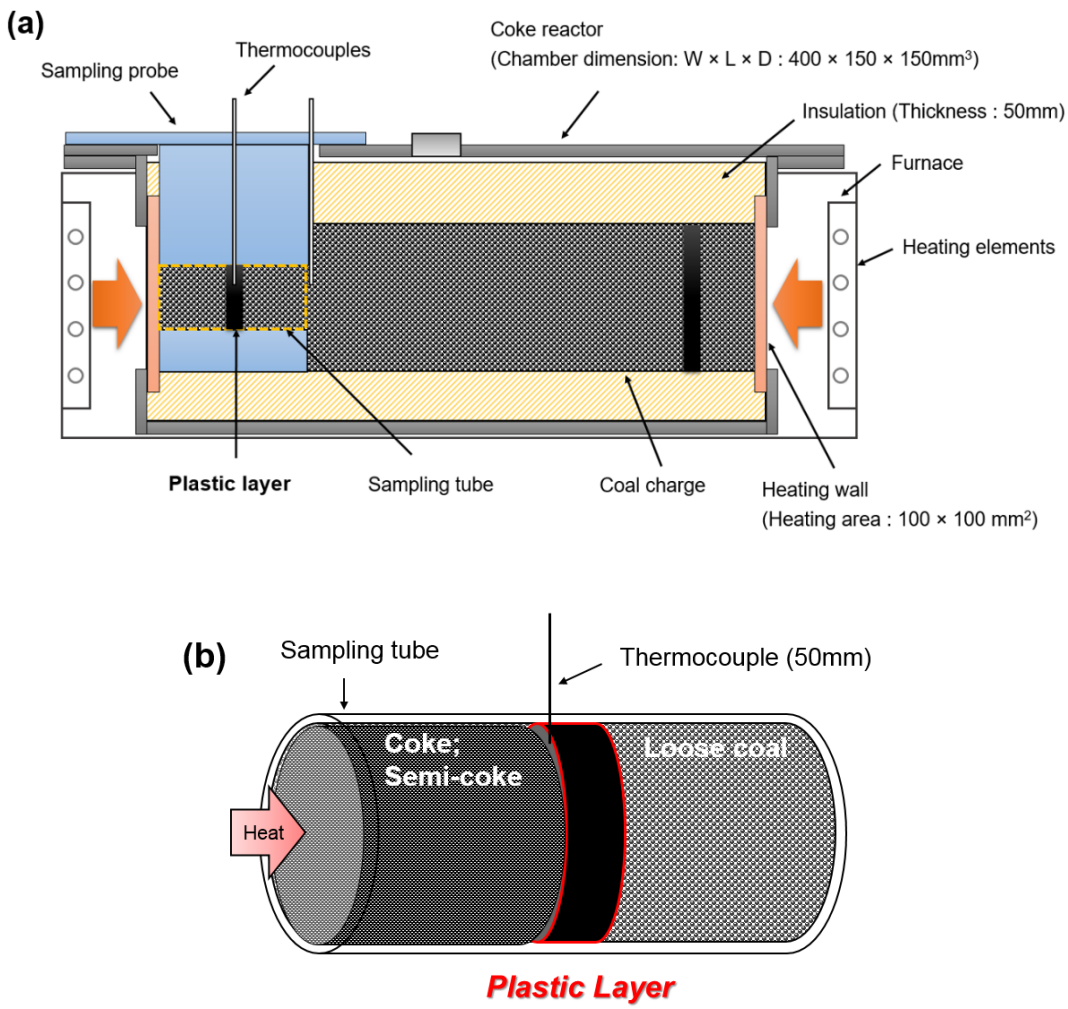


Fig. 1. The schematic diagram of the 4kg lab-scale coke oven (a) and the sampling tube containing the plastic layer (b) [19].

2.3 Synchrotron Micro-CT analysis

The plastic regions in the semi-coked samples were scanned by micro-CT imaging at the Imaging and Medical Beamline at the Australian Synchrotron, following the previous method [19]. A Ruby Detector was used, configuring the resolution of each image as 9.81 µm per pixel. The data collection was performed at an X-ray energy of approximately 30 keV, while the quartz tube containing the plastic region was rotated over 180 degrees. 6300 vertically stacked slices were acquired to retrieve the 60 mm height of each plastic region. The retrieval of cross-section images was carried out by stitching the slices together, using CSIRO's X-TRACT software from the MASSIVE cluster.

2.4 TG-FTIR analysis of plastic layer samples

Fig. 2 in the supplementary materials shows that the cross-section images of the semi-coked samples were gridded at 2 mm intervals based on the accurate measurements using Image J software [23]. The red marks (S_{Cn}, M_{Cn} and R_{Cn}) pointed out the approximate locations at which plastic layer samples were extracted, corresponding to notional positions of softening, maximum fluidity and resolidification identified by changes in porosity. The regions right adjacent to S_{Cn} with presenting pore nucleation in the coarse particles were referred to as initial softening layers. The regions between S_{Cn} and M_{Cn} with displaying the initiation of bubble growth were the beginning of intermediate plastic layers. There was dramatic bubble growth between M_{Cn} and R_{Cn} with presenting highest porosity, referred to as intermediate plastic regions. The TG-FTIR was employed to analyze the pyrolysis behavior of the plastic layer samples extracted from S_{Cn}, M_{Cn} and R_{Cn}. The results enabled the investigation of the progressive pyrolysis characteristics inside the plastic layers. About 5 mg of the plastic layer sample was placed in a crucible, then heated to 950 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. FT-IR spectra were recorded by the accumulation of 32 scans with a spectral resolution 4 cm^{-1} for a scan range of 500–4000 cm^{-1} as presented in Fig. 3. Online mass loss was measured by the TGA. The evolution of gaseous products, such as aliphatic and aromatic hydrocarbons were monitored by FTIR. The spectral analysis was done by integrating areas under spectral curves of the gaseous products based on the wavenumber assignments (aromatic hydrocarbons: 3025 – 3200 cm^{-1}, and aliphatic hydrocarbons: 2800 – 3024 cm^{-1}) [22].

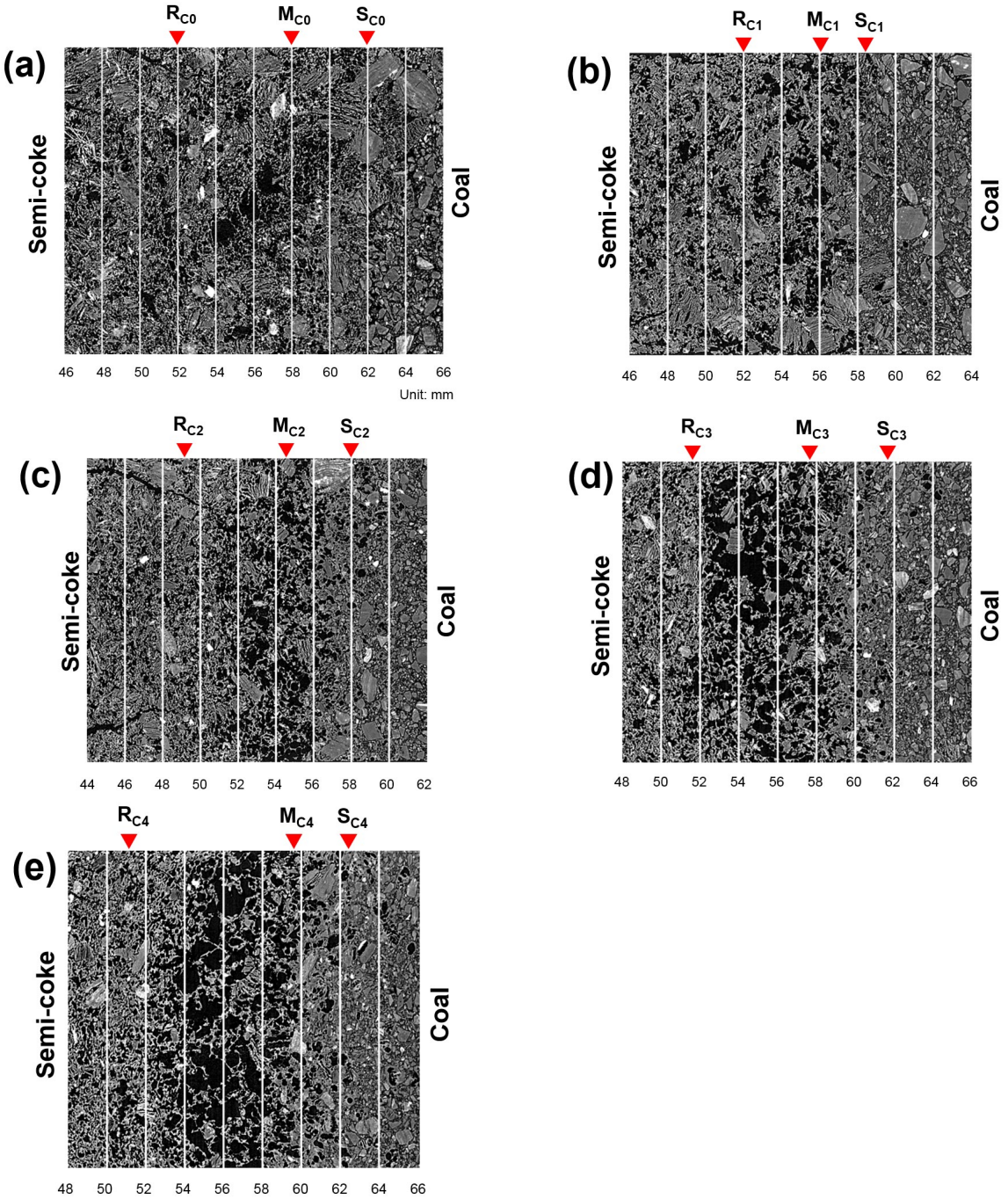


Fig. 2. Cross section images of the plastic regions with delineating locations of sampling the plastic layer samples for TG-FTIR analysis ((a): C0, (b): C1, (c): C2, (d) C3 and (e): C4). The red marks (S_{Cn}, M_{Cn} and R_{Cn}) point to the approximate locations at which plastic layer samples were extracted and correspond to notional positions of softening, maximum fluidity and resolidification identified by changes in porosity.

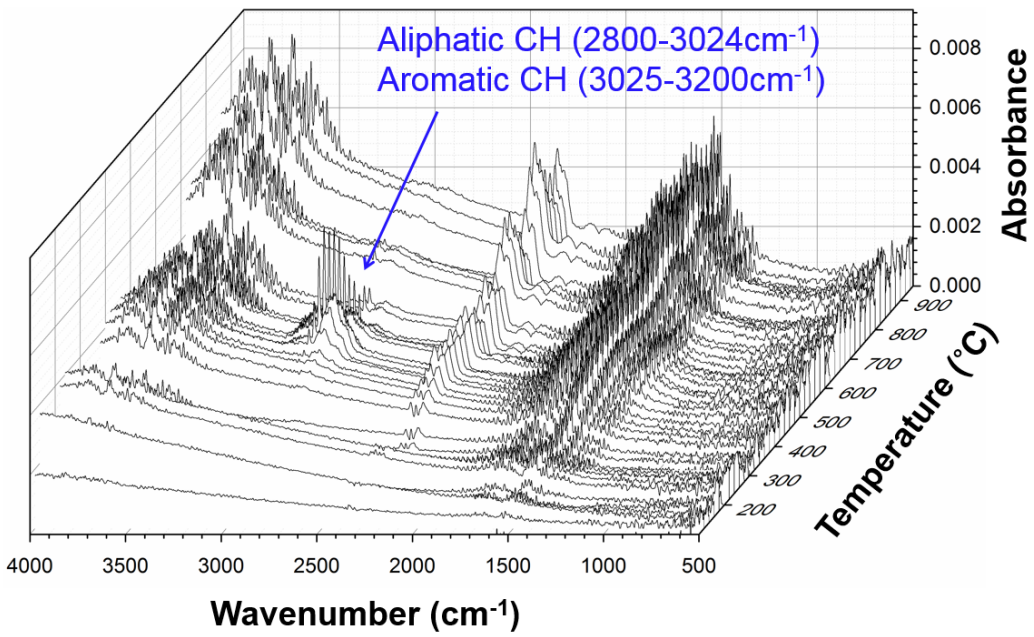


Fig. 3. FTIR spectra of the volatile matter for the parent coal of C0 during TGA heating.

3. Results and discussion

3.1 Thermogravimetric analysis of plastic layer

The differential thermogravimetric (DTG) curves of the raw coals and the plastic layer samples are illustrated in Fig. 4. The DTG curves of the raw coals showed that the degree of weight loss varied with temperature, showing a single major peak at about 500 °C. Based on the DTG curves, the pyrolysis process of the raw coals can be divided into several stages. The slight mass loss at temperatures below 200 °C, was attributed to the evolution of adsorbed moisture. With a further temperature increase from 200 °C to 400 °C, a gradual increase in the weight loss rate was evident. As reported earlier [24, 25], this can be attributed to the release of CH_4 and CO_2 due to the rupture of the weaker bonded aliphatic bridges, as well as thermal decomposition of carboxyl groups. The major DTG curve was observed in a temperature range of 400-600 °C. The sharp DTG peaks, which were referred to as the maximum rates of the weight loss (R_{max}), were observed in the temperature range between the maximum fluidity temperatures (MFT) and the resolidification temperatures (ST) (Table 1). These results were consistent with previous findings [26]. The primary devolatilization in this

temperature range involved the evolution of volatile tar, CH_4, and other light hydrocarbons [27-29]. This pyrolysis process involving the devolatilization was consistent with the evolution of aliphatic and aromatic hydrocarbons in the temperate range of 400-700 °C, as detected by the FTIR.

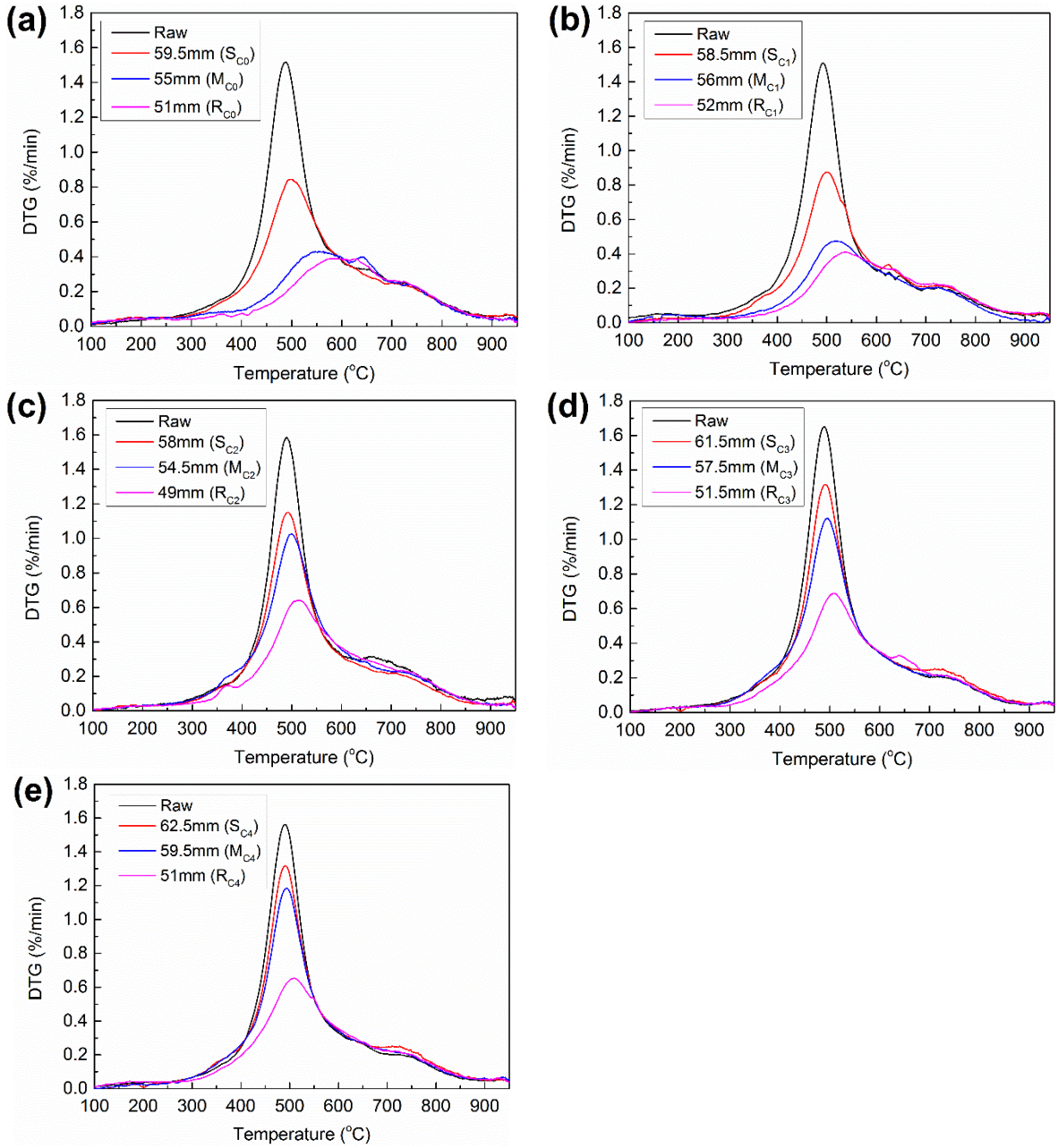


Fig. 4. Changes in the DTG curves of the raw coals and the sub-samples: (a): C0; (b): C1; (c): C2; (d) C3; and (e): C4.

It is interesting to note that the changes in the intensity of the DTG curves of parent coals and the corresponding plastic layer samples depended strongly on the fluidity of the coals, as shown in Fig. 4. Fig. 4 (a) and (b) show that for C0 and C1 coal with lower Gieseler fluidities (Table 1), a more dramatic decrease in the peak intensities was observed from the initial softening layers (~S_{C0} and ~S_{C1}) to the beginning of the intermediate plastic regions (M_{C0} and M_{C1}). In contrast, for the C2, C3, and C4 coals with a relatively higher Gieseler fluidity (Table 1), the major changes in the peak intensities were generally detected in the intermediate plastic regions (i.e. M_{C2}-R_{C2}, M_{C3}-R_{C3}, and M_{C4}-R_{C4}). These changes in the intensity of peaks are shown as the changes in the R_{max}s and the total weight losses in Figs. 5 and 6.

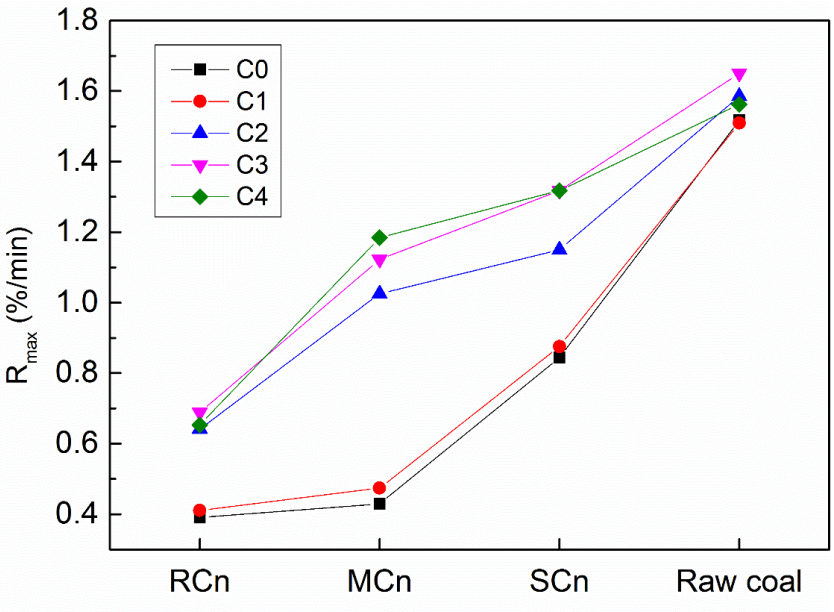


Fig. 5. Changes in the maximum rates of the weight losses of the raw coals and the sub-samples extracted at the boundaries of the characteristic regions (R_{Cn}, M_{Cn} and S_{Cn} were indicated as red in Fig. 2).

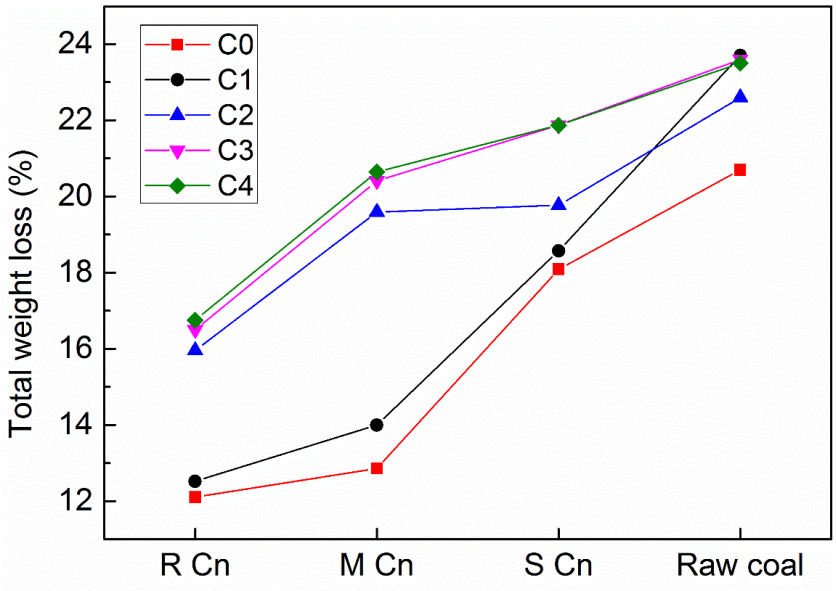


Fig. 6. The total weight losses of the raw coals and the sub-samples extracted from the borders of the characteristic regions (R_{Cn}, M_{Cn}, and S_{Cn} were indicated as red in Fig. 2).

3.2 FTIR results of the volatile matter from the pyrolysis of the plastic layer samples

Figs. 7 and 9 present the evolution curves of aromatic and aliphatic hydrocarbons in the parent coals as well as the corresponding plastic layer samples. Table. 1 shows that the changes in the chemical structure of the plastic layer estimated by the structural parameters of A_{ar}/A_{al} and CH_2/CH_3 correlated well with the fluidity properties of parent coals. As shown in Table 1, the C0 and C1 coals (with low fluidities) contain lower vitrinite contents and the higher rank only for C1. These coals had a higher A_{ar}/A_{al} and CH_2/CH_3 ratios (Table 1), suggesting the presence of highly condensed aromatic structures with longer aliphatic chains or lower branching degree of the aliphatic structures [20-22]. The C2 and C3 coals (with higher fluidities) were of similar rank with higher vitrinite contents, leading to a lower A_{ar}/A_{al} and CH_2/CH_3 ratios. This implies that the macromolecular structures of C2 and C3 were composed of less condensed aromatic clusters with shorter aliphatic chains or high branching degree of aliphatic structures.

236 Fig. 7 shows the evolution of aliphatic hydrocarbons during the TG-FTIR heating of parent coals
237 as well as the sub-samples. The changes in the peak intensity of the evolution curves provide valuable
238 information on the amount of aliphatic hydrocarbon that was released from different characteristic
239 regions such as the initial softening layers and intermediate plastic regions. Figs. 5, 6 and 8 show that
240 the decreasing trends of the peak intensities of the aliphatic hydrocarbons with the progression of the
241 plastic layer were consistent with the decreases in $R_{max}s$ and the total weight loss, implying that the
242 mass loss of the coal and plastic layer samples were predominantly due to the release of the aliphatic
243 hydrocarbons during the coking process.

244 Fig. 9 shows that the decreasing trends of the peak values of aliphatic hydrocarbons and the DTG
245 curves in the plastic regions varied with the Gieseler maximum fluidity of the parent coals. In case of
246 C0 and C1 coals with the lower Gieseler maximum fluidities, a large decrease in the peak values of
247 the aliphatic hydrocarbons to M_{C0} and M_{C1} were observed, showing a different trend with the higher
248 fluidity coals. These results implied that larger amounts of the aliphatic hydrocarbons were evolved
249 prior to the intermediate plastic layers of the lower fluidity coals. Xiang et al. [20] suggested that coals
250 with higher A_{ar}/A_{al} and CH_2/CH_3 release a larger volume of volatile matters with less amounts of plastic
251 mass produced during the overall pyrolysis process. In this regard, the relatively higher A_{ar}/A_{al} and
252 CH_2/CH_3 of C0 and C1 coals (Table 1) may explain the larger evolution of the aliphatic hydrocarbons
253 at the earlier stages of plastic layer formation. It has been reported that aliphatic components within
254 the coal macromolecule play an important role in stabilizing the radicals generated during the thermal
255 decomposition of coal in a thermoplastic range producing moderate molecular weights, referred to as
256 plastic mass [30, 31]. In this context, it is possible that the earlier removal of the aliphatic components
257 ahead of the intermediate plastic layer formation led to the lack of donable hydrogen in the intermediate
258 plastic regions, thus generating less amount of the plastic mass. Such lower fluid-like properties lead
259 to less entrapment of gases in the plastic region, resulting in lower porosities as reported in the previous
260 study by the authors on the image analysis of the micro-CT images (Fig. 2) [19].

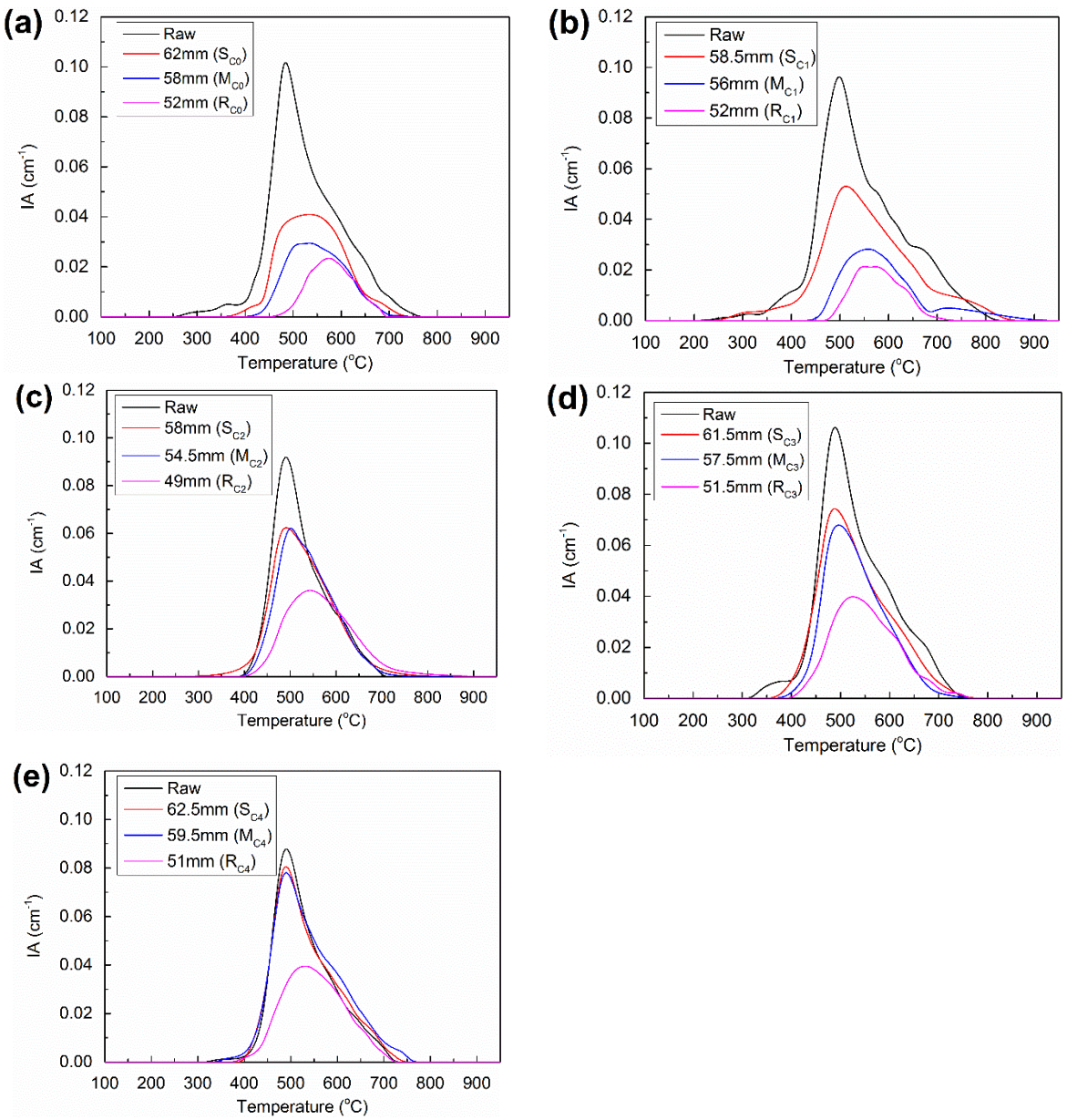


Fig. 7. Changes in the evolution of the aliphatic hydrocarbons for the raw coals and the sub-samples, monitored by the FTIR ((a): C0, (b): C1, (c): C2, (d) C3 and (e): C4).

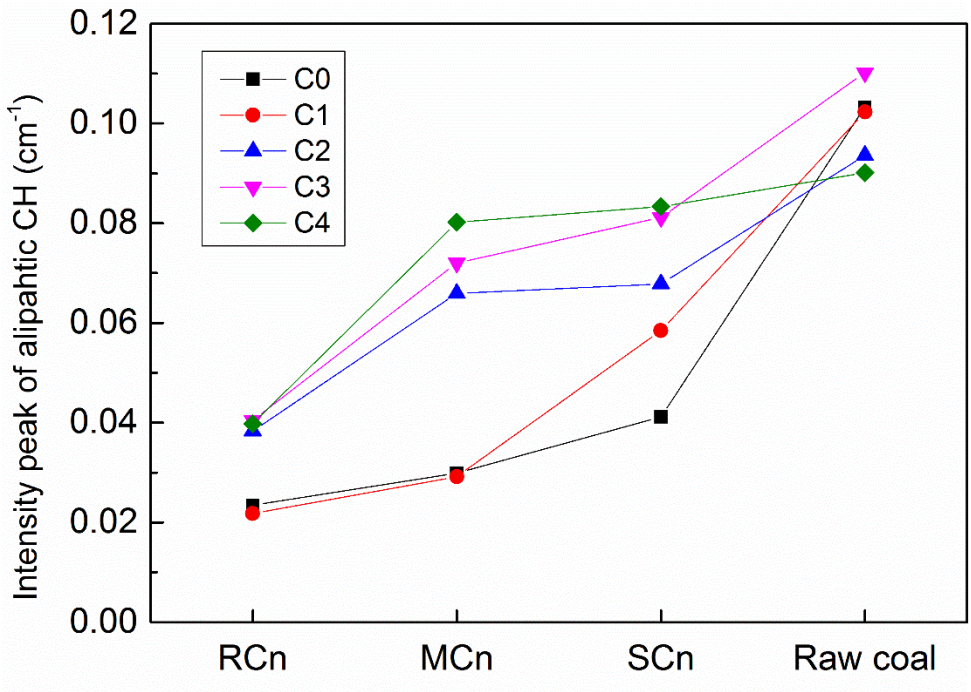


Fig. 8. Changes in the intensity peaks of the aliphatic hydrocarbons for the raw coals and the sub-samples.

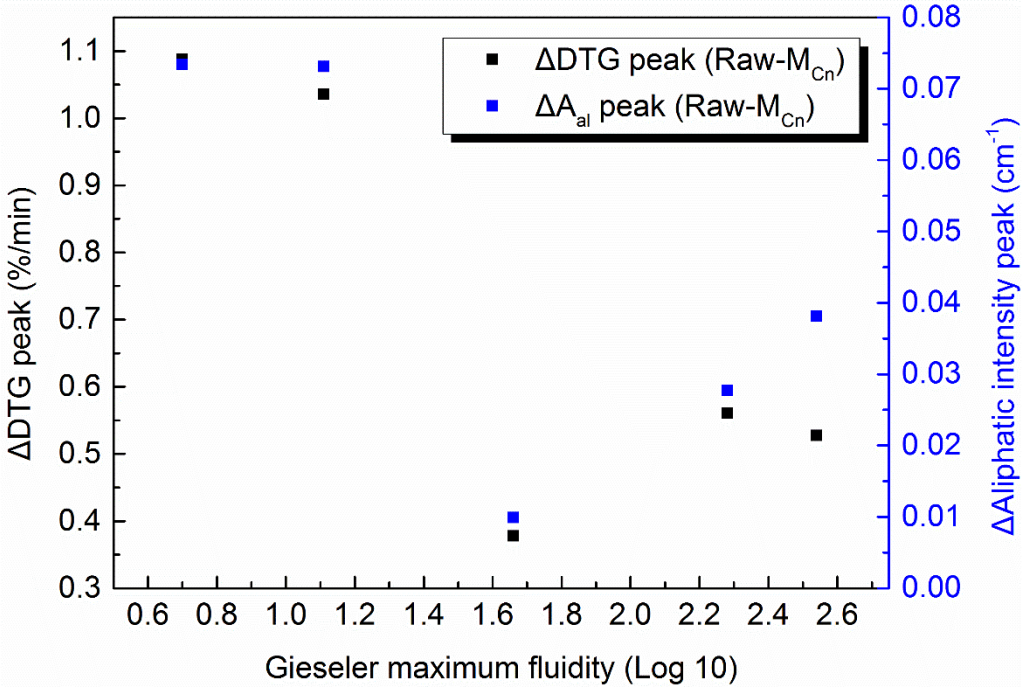


Fig. 9. Correlation between the Gieseler maximum fluidities and changes in the DTG peaks and the aliphatic intensity peaks between the parent coals and the sub-samples at M_{Cn}.

Fig. 10 presents the changes in the evolution of aromatic hydrocarbons from the raw coals and the plastic layer samples. The evolved aromatic hydrocarbons are considered as major tar components. As previously suggested, tars consist of aromatic hydrocarbons with alkyl-substituents [32]. Fig. 11 shows that the intensities of the aromatic CH peak gradually decreased across the plastic layer, but show little variations between different coals (except C1 which appeared lower for all samples).

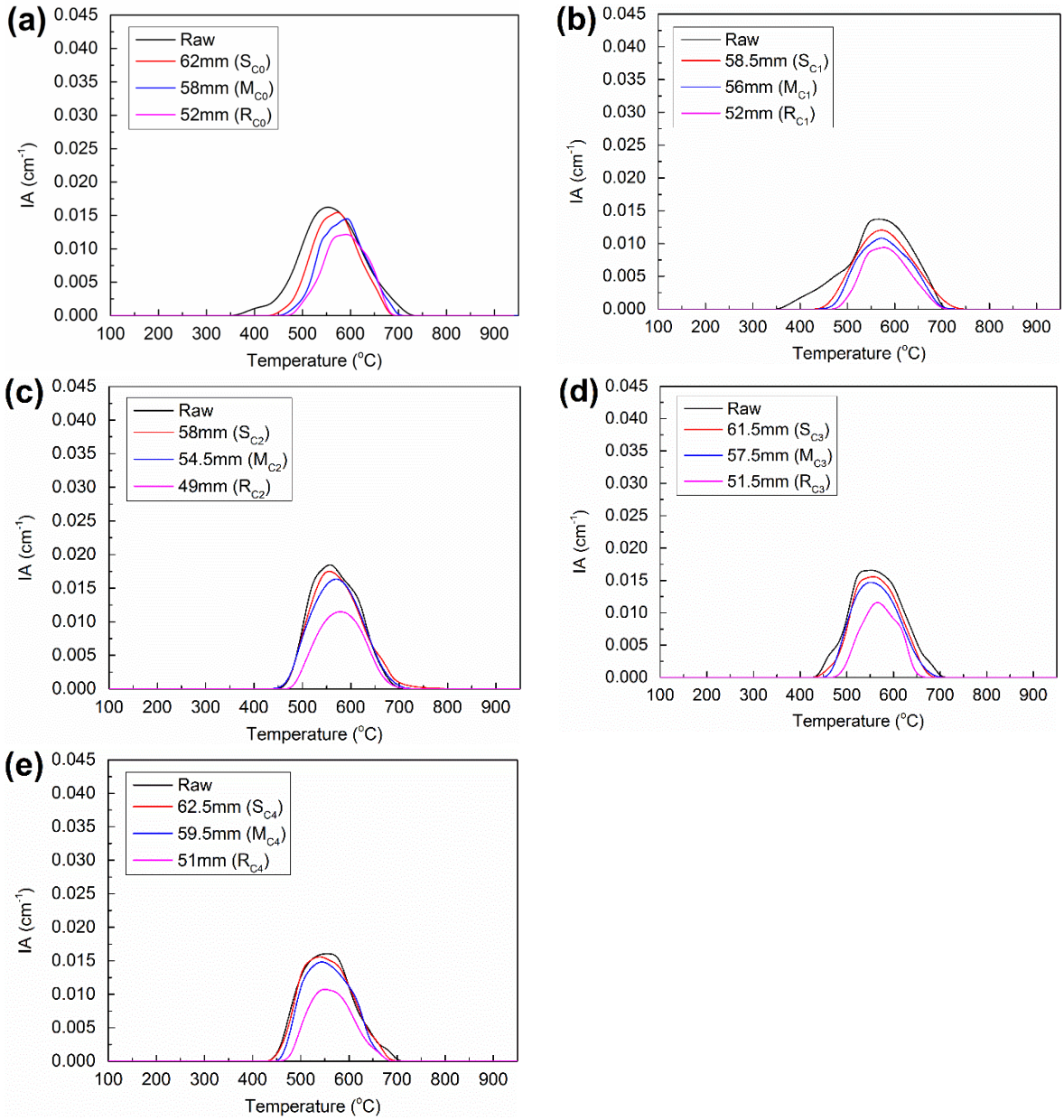


Fig. 10. Changes in the evolution of the aromatic hydrocarbons for the raw coals and plastic layer samples as measured by the FTIR: (a): C0; (b): C1; (c): C2; (d) C3; and (e): C4.

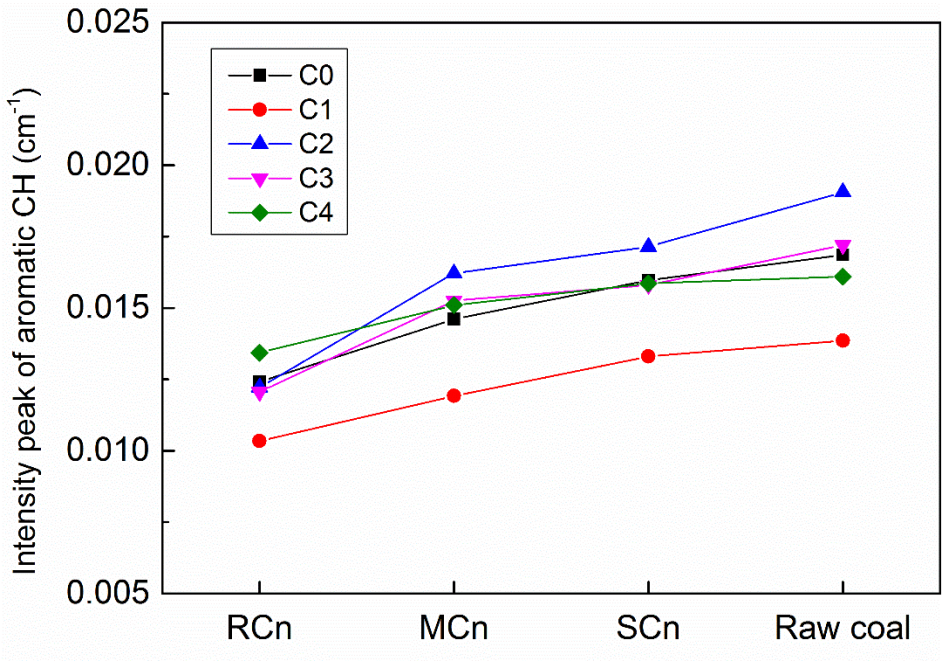
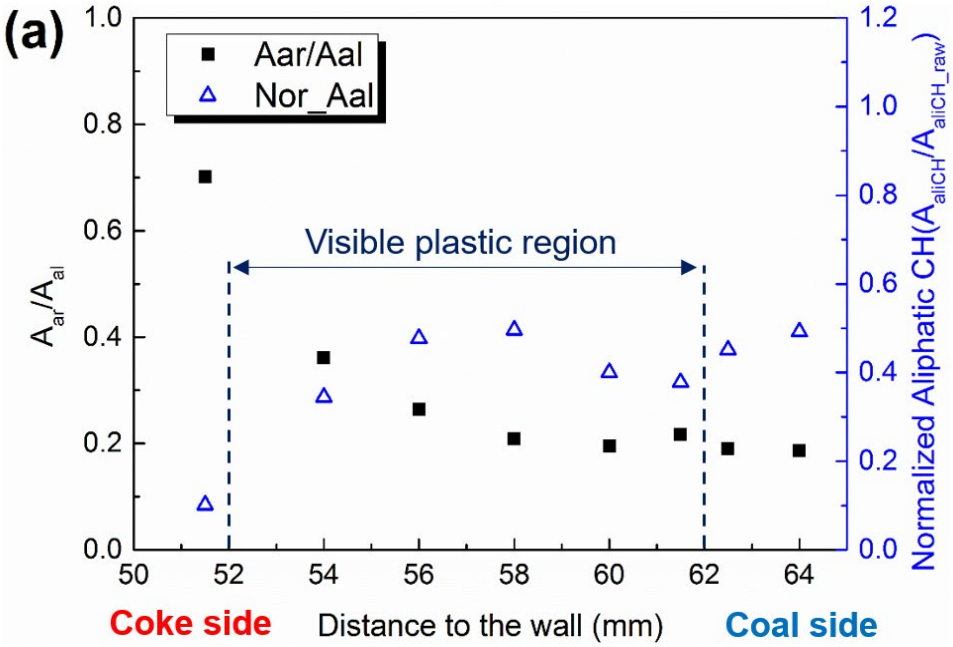


Fig. 11. Changes in the intensity peaks of the aromatic hydrocarbons for the raw coals and the sub-samples.

3.3 ATR-FTIR analysis of the chemical structure changes across the plastic layer

The ATR-FTIR analysis results showed that in C0 and C4 coals the pyrolysis behavior in the initial softening layers was in a good agreement with the structural transformation inside the plastic layers (Fig. 12). The ATR-FTIR results for samples C1, C2, and C3 were presented in our previous study [19]. The ATR-FTIR results for the C0 and C4 coals in Fig. 12 are calculated based on the ratio of aromatic CH to aliphatic CH signal intensities in plastic layer samples (A_{ar}/A_{al}) as well as the ratio of the aliphatic CH in the plastic layer samples to the aliphatic CH in the raw coal (Nor A_{al}). As seen in Fig. 12, the A_{ar}/A_{al} ratio showed an overall increasing trend across the visible plastic layer from the coal side to the coke side for both C0 and C4 coals. The normalized aliphatic CH was decreased at the coal sides of the visible plastic regions. This was followed by a relatively constant stage and finally a drastic decrease on the coke side of the plastic layer. These changes were consistent with a loss of bonds throughout the devolatilization process and increasing aromatization of the semi-coke structure. However, the level of response appears to vary with fluidity level of the parent coal. Fig. 12 shows that the lowest fluidity C0 coal underwent a larger change in the concentration of aliphatic CH groups

on the coal side of the plastic region during the devolatilization (see Fig. 7 (a)), compared to the higher fluidity C4 coal (see Fig. 7 (e)). The A_{ar}/A_{al} value the lowest fluidity C0 coal increased drastically from 0.2 to 0.7 across the plastic layer, while in case of the higher fluidity C4 coal only a slight change from 0.15 to 0.3 was observed. The ATR-FITR analysis results for the C1 (low fluidity), C2, and C3 (higher fluidity) coals in our previous study [19] showed that the changes in the A_{ar}/A_{al} ratio and the aliphatic CH were also dependent on the fluidity of the parent coal. These results suggested that the higher fluidity coals (C2, C3, and C4) contain higher levels of aliphatic CH structures, which may in turn potentially cause further depolymerization in the plastic regions.



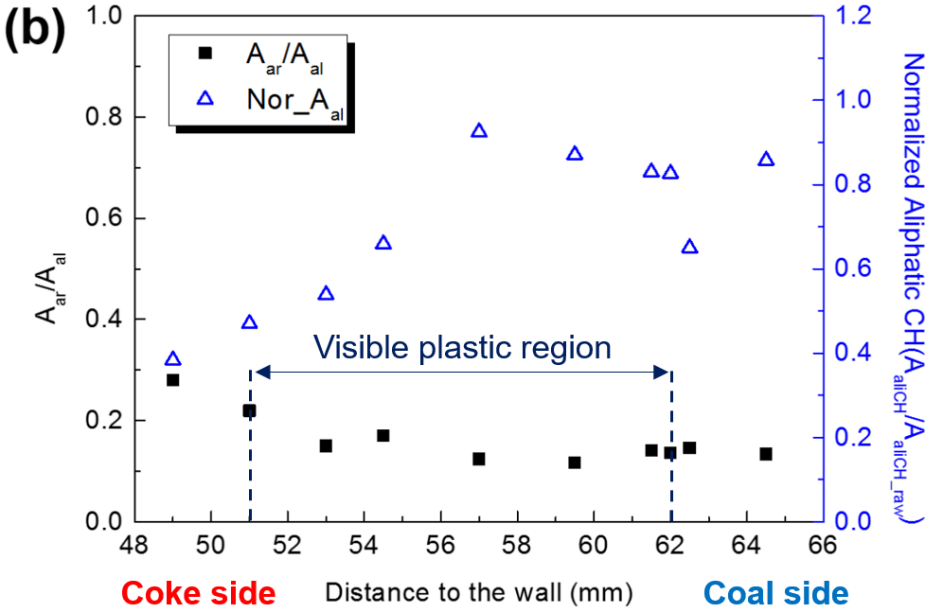


Fig. 12. ATR-FTIR analysis of the changes in the structural parameters (A_{ar}/A_{al} and normalized aliphatic CH) across the plastic layers: (a): C0; and (b): C4. Visible plastic region refers to higher porosity region identified by Synchrotron micro-CT scans, noting that the hot side of the coke oven is closest to the wall and that lower temperatures are encountered with increasing distance from the wall.

3.4 Discussion on behavior across the plastic layer and coal properties

This work has detailed a novel methodology to obtain the representative plastic layer samples formed under the practical heating conditions in the 4kg laboratory scale system. The plastic layer samples were analyzed by the combination of analytical techniques such as TG-FTIR, ATR-FTIR and micro-CT scanning. This provides the opportunity to characterize pyrolysis behavior of coking coals, in particular the chemical structure changes across the plastic layer formed during the coking process. It was shown that the level of volatile matter was reduced in the plastic layer samples corresponding to the notional points of softening, maximum fluidity, and resolidification which took place during the coking of five coking coals of varying thermoplastic properties.

Of particular interest was the changing of the nature of volatile matter as characterized by FTIR, which showed that the aliphatic C-H structures were underwent the greatest reduction across the plastic layer. The aromatic C-H structures appeared to be relatively unchanged with only minor reduction across the plastic layer. These results suggested that the aliphatic functionalities in coal may play a significant role in the development of plastic properties and subsequent semi-coke formation inside the coke oven. It is not yet clear whether this observed change in aliphatic bonding is caused by the aliphatic species or tar species with aliphatic side chains. However, the structural changes observed in the solid samples in the lead up to the resolidification appeared to support the notion of increasing aromatisation at the expense of aliphatic content (reporting to the volatiles).

The pyrolysis concepts governing this process are well known, but difficult to translate to the performance of individual coals undergoing one-dimensional heat transfer in a coke oven. This work has attempted to link the changes in the bulk thermoplastic properties to the chemical structure in both solid and volatile phases. There is a consensus that the physical structure of the coke is determined to a large extent during the plastic layer formation and migration to the centre of the coal charge. This has direct implications on the quality of the resultant coke in terms of reactivity and strength. Despite the critical role of plastic layer in shaping the final quality of the coke, the exact mechanism of the changes in the chemical structure of coal as it transitions from coal to semi-coke during the plastic later formation is not well understood and therefore was the major subject of this study. The findings of this study sheds light on the chemical structure transition inside the plastic layer from that of coal to semi-coke. The major finding was that the formation of the plastic layer is closely associated with the removal of aliphatic CH from coal structure. Further research is required for linking such chemical change to the finer features of coke structure to better understand the impact of chemical structure changes during the plastic layer formation to the strength and reactivity of the final coke product.

4. Conclusions

- This study has characterized the pyrolysis behavior of the plastic layer formed in a 4kg coke oven which simulated practical heating conditions. The TG-FTIR and ATR-FTIR were used to anaylze the plastic layer samples of five coking coals of varying thermoplastic properties.
- The TG-FTIR results implied that the level of aliphatic hydrocarbons in the volatile phase was generally reduced in the plastic layer samples corresponding to the notional points of softening, maximum fluidity and resolidification. Meanwhile, Aromatic C-H structures appeared to remain relatively unchanged across the plastic layer. This was in a good agreement with the structural changes of the solid samples, as analyzed by ATR-FTIR.
- Comparing the decomposition trends of the aliphatic structures in the five coals tested, it was observed that the higher fluidity coals showed a smaller reduction in the aliphatic CH structures at the beginning of the plastic regions via the evolution of aliphatic hydrocarbons. Subsequently, the aliphatic CH bonds were largely decreased in the intermediate plastic region. In contrast, the low fluidity coals presented the larger decreases in aliphatic CH bonds to the beginning of the plastic regions via the release of aliphatic hydrocarbons. This suggests that the different decomposition trends of the aliphatic structures may pose a strong impact on the development of plastic properties during the formation of the plastic layers.

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