Dynamic measurement of coal thermal properties and elemental composition of volatile matter during coal pyrolysis

Rohan Stanger*, Wei Xie, Terry Wall, John Lucas, Merrick Mahoney

Department of Chemical Engineering, University of Newcastle, Callaghan, Australia

Abstract

A new technique that allows dynamic measurement of thermal properties, expansion and the elemental chemistry of the volatile matter being evolved as coal is pyrolysed is described. The thermal and other properties are measured dynamically as a function of temperature of the coal without the need for equilibration at temperature. In particular, the technique allows for continuous elemental characterisation of tars as they are evolved during pyrolysis and afterwards as a function of boiling point. The technique is demonstrated by measuring the properties of maceral concentrates from a coal. The variation in heats of reaction, thermal conductivity and expansion as a function of maceral composition is described. Combined with the elemental analysis, the results aid in the interpretation of the chemical processes contributing to the physical and thermal behaviour of the coal during pyrolysis. Potential applications in cokemaking studies are discussed.

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1. Introduction

The current standard methods of coal analysis are designed as indicators of general coking behaviour, principally as a means of comparing coals against one another, rather than providing a prediction of behaviour in a coke oven. Indices such as fluidity, dilatation, reflective index and vitrinite content are typically used to prepare a coal blend to target final coke strength. Such relationships are empirical in nature and based on large scale testing and/or historical performance at commercial scale. One obvious problem with such a methodology is that the introduction of coals outside of the testing envelope presents a significant risk to operations. From a coal supplier’s perspective, selling new coals or existing coals with changing properties must be accompanied with a significant amount of costly large scale testing which may not encompass the entirety of blend parameters. Coking performance of a single coal within a blend is difficult to predict, particularly when it may interact during its metaplastic transition. Current methods of analysis are not well suited to deriving fundamental understanding of the coal to coke transformation, mainly because each test is performed under different conditions. This paper describes two new thermal analysis techniques...
designed to capture a range of on-line measurements, both thermo-physical and thermo-chemical, which enable a more complete picture of the coking process.

2. Materials and methods

2.1. Thermo-physical analysis

The experimental apparatus can be used in two main configurations. The first method determines thermo-physical properties (apparent volumetric specific heat, thermal conductivity, thermal diffusivity, volumetric swelling and bed permeability) continuously during pyrolysis. The second method determines thermo-chemical changes by characterising the volatile evolution (separately as tar and light gas) as continuous elemental streams of carbon, hydrogen, nitrogen, oxygen and sulphur (CHNOS). Fig. 1 shows the apparatus set-up for the thermo-physical measurements which are taken from a custom built heating chamber consisting of an outer and inner quartz tube and a graphite sheath (over the inner quartz tube used for furnace control and heat flux determination). The heating chamber was set in a Gold Image Infrared Rapid Heating Furnace (RHF). The apparent volumetric specific heat, thermal conductivity and thermal diffusivity are determined using a numerical technique Computer Aided Thermal Analysis (CATA [1–4]) which uses a calibrated heat flux and measured surface and centre temperatures across a packed bed of coal to inversely solve the heat equation for the thermal properties (shown in Eq. (1)).

\[
\rho C_p \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r k \frac{\partial T}{\partial r} \right)
\]

where \( \rho \) – density (kg m\(^{-3}\)), \( C_p \) – specific heat (J kg\(^{-1}\) K\(^{-1}\)), \( k \) – thermal conductivity (W m\(^{-1}\) K\(^{-1}\)), \( T \) – temperature (K), \( t \) – time, \( r \) – radius (m), \( T_{r,t} \) is the temperature expressed in K of the node \( r \) for the time \( t \) (s).

The heat flux is calibrated using the apparent thermal resistance of a graphite sheath surrounding the central quartz tube, which is determined beforehand with a copper cylinder of known dimensions. The physical swelling and permeability are determined by using a linear variable differential transducer (LVDT) and a pressure transducer. The coal is packed against a fixed alumina rod set on the gas inlet side and allowed to expand against a moving alumina rod connected to the spring loaded LVDT magnetic core. The spring constant is calibrated for force measurements; however, these are not presented here. Swelling results are presented as a percentage of original bed length, which is typically between 20 and 30 mm depending on maceral content (some maceral fractions having expanded to 400%). The bed permeability (Eq. (2)) is determined by measuring the pressure of the carrier gas on the inlet of the furnace and assuming the exiting pressure is atmospheric.

\[
\frac{\Delta P}{L} = \frac{1}{k} \mu U
\]

\( \Delta P \) is the pressure drop across the bed expressed in Pa (up to 400 kPa), \( \mu \) is the viscosity of the carrier gas argon expressed in Pa s, \( U \) is the carrier gas velocity in m/s, \( L \) is the length of the packed bed.

2.2. Thermo-chemical analysis

The thermo-chemical analysis is based on the concept of converting the volatile matter into combustion products as they are evolved using a custom built O\(_2\) lance. By analysing the combustion products the results can be used to back-calculate the elemental streams CHNOS as they are evolved from the coking material. This technique is known as Dynamic Elemental Thermal Analysis (DETA [5,6]). The lance is placed downstream of the evolving volatile matter and separately heated to 950 °C. Fig. 2 shows the lance and flue gas analysis equipment added to the back end of the furnace and heating chamber. By using this in situ method of conversion the tars are prevented from condensing downstream and can be included in the on-line analysis. The combustion products are analysed using a LiCor A CO\(_2\)/H\(_2\)O infrared analyser and a Testo 350XL flue gas analyser (O\(_2\), CO, H\(_2\), NO, NO\(_2\), SO\(_2\), hydrocarbons). Infrared analysis of H\(_2\)O was found to be important over more conventional (and cheaper) relative humidity or dew point probes because such probes do not allow moisture determinations at low concentrations in the time scales measured. There are 4 modes of operating the DETA apparatus. The first mode combusts all of the volatiles (tars + light gases, i.e., Total Volatiles) and is the same configuration shown in Fig. 2. The second mode, Char Combustion, adds a second stream of O\(_2\) to the front end of the furnace to combust the residual coke/char and weighs back the ash after cooling. Mode 3, Gas Only combustion, uses a second sample of coal and introduces a condenser for the tars and a secondary combustion tube for the light gases. By comparing the Total Volatiles combustion with the Gas Only combustion the Dynamic Tar evolution (i.e., the material condensed out) may be mathematically derived. The condensed tar (and water) was collected using an acetone wash and added back to the quartz crucible by evaporating the acetone. Mode 4, Tar Only, analyses the collected material by vaporising it from the crucible and combustion it using the same lance configuration as the mode 1 Total Volatile. The mode 4 test provides a method of characterising the tars in terms of elemental distribution and boiling point.

2.3. Sample

The samples used in this work are maceral concentrates derived using a water based technique developed by Galvin et al. [7,8] known as the reflux classifier. Briefly, the separation occurs via a series of inclined plates stacked in parallel. The parent coal particles are mixed as a slurry and fluidised into the plates such that the lightest particles (with the lowest settling velocity) are removed at the top as overflow and the heavier particles settle onto the bottom of the channel and slide back down to re-mix with the original slurry (i.e., refluxed). The parent coal was first sized and fed into the reflux classifier in a single fraction of 106–212 µm. The maceral concentrates were successively removed from the slurry by increasing the water flow rate after several hours at each setting. Here the results of three maceral concentrates (vitrinite rich, medium vitrinite and inertinite rich) are selected
Fig. 1 – Extended CATA apparatus for measurement of solid properties (Cp, k, swelling, permeability) set in a Gold Image Rapid Heating Furnace (RHF).

Fig. 2 – DETA apparatus for measurement of volatile properties (CHNOS of tar and gas) during evolution.

<table>
<thead>
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<th>Table 1 – Parent coal properties.</th>
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<tr>
<td><strong>Proximate analysis</strong></td>
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<td>Inherent moisture</td>
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<td>Ash</td>
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<td>Volatile matter</td>
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<td>Fixed carbon</td>
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<td>Total sulfur</td>
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<tr>
<td>Phos in coal</td>
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<td>CSN</td>
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<td>Maximum dilatation</td>
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<th>Table 2 – Maceral concentrate properties.</th>
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<td>Property</td>
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<tr>
<td>Ash</td>
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<tr>
<td>Density</td>
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<tr>
<td>Total vitrinite</td>
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<tr>
<td>Total inertinite</td>
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based on the amount of vitrinite and inertinite. The parent coal properties are given in Table 1 and the maceral concentrate properties are given in Table 2.

3. Results and discussion

3.1. Thermo-physical properties

The three maceral concentrates were heated at 10 °C/min from room temperature to 1000 °C in either a packed bed for the thermo-physical measurements or packed into a crucible for the thermo-chemical analysis. Fig. 3 shows the apparent volumetric specific heat and thermal conductivity of three maceral concentrates. The apparent volumetric specific heat curves include changes in density and heats of reaction. Of the three maceral concentrates, the vitrinite rich fraction (86.4% V) shows a significant exothermic reaction during primary pyrolysis with a peak occurring at 505 °C. This process begins at 380 °C where the vitrinite concentrate begins to rise in an initial endothermic reaction which peaks at 417 °C and follows into the larger exothermic reaction. By comparison, the inertinite rich concentrate (32.4% V) begins the initial endothermic reaction at a similar temperature to the vitrinite concentrate but extends this behaviour across a broad temperature interval until approximately 600 °C. Several smaller endothermic peaks appear within this region, the dominant peak occurring at 550 °C. This small endothermic peak also appears to a smaller extent in the vitrinite rich concentrate. Also these changes for the medium vitrinite concentrate are between the vitrinite rich concentrate and inertinite rich concentrate. At higher temperatures, the three maceral concentrates undergo an inflexion between 725 and 800 °C. Also in Fig. 3 is the apparent thermal conductivity of the three maceral concentrates. All fractions show no features other than a slight rise in conductivity up to around 460–470 °C when the thermal conductivity begins to vary considerably between maceral fractions. The vitrinite undergoes a minor reduction followed by a sharp rise in conductivity from 0.2 to 0.75 W/mK, coinciding with the large exothermic trough in specific heat. The inertinite fraction undergoes a broader reduction in conductivity from 470 to 550 °C. After this transition, all maceral concentrates show a dramatic incline which corresponds to the high temperature exotherm. It is believed that this high temperature increase in thermal conductivity is a numerical result of exothermic graphitisation coupled with the relatively non-conductive nature of the semi-coke.

The physical swelling of the material is an important property which is typically measured using a dilatometer. However, there is an inherent benefit of measuring multiple parameters during a single experiment, reducing the overall testing time and allowing direct comparison of each variable. Fig. 4 shows the comparison of thermo-swelling behaviour in the three maceral concentrates. The extent of swelling behaviour
between these maceral fractions was significant, with the inertinite displaying a small linear increase in bed length from 25 to 900 °C (consistent with thermal expansion of typical materials) and the vitrinite rapidly swelling to 400% of its original packed length (of 20 mm). The vitrinite rich concentrate swelling occurred over a short temperature range between 440 and 505 °C consistent with the exothermic behaviour and sharp increase in thermal conductivity. The rapid swelling occurs at 464 °C. The medium vitrinite concentrate initiated swelling at a higher temperature with a lower extent compared to the vitrinite rich concentrate, which corresponds to its smaller changes in apparent specific heat and thermal conductivity between 440 and 505 °C. At higher temperatures, all maceral fractions underwent high temperature contractions in bed length. In the vitrinite rich fraction, this began at 675 °C, while this began after 900 °C for the inertinite concentrate and 720 °C for the medium vitrinite concentrate.

The final measurement taken during this experiment was pressure drop. As the vitrinite rich concentrates are responsible for swelling and exothermic reactions, the vitrinite permeability was determined. Fig. 4 gives the pressure drop and the calculated bed permeability for the vitrinite rich concentrate (86.4% V). This pressure was measured on the gas inlet with the outlet pressure assumed to be atmospheric. The pressure rises linearly up to around 400 °C. This minor thermal increase is thought to arise from the effect of temperature in expanding the carrier gas flowing through the packed bed.

Above this temperature exists two distinct peaks, the smaller at 464 °C and the larger at 505 °C. These temperatures coincide with the rapid swelling and the end of swelling. The pressure drop begins to subside after peak devolatilisation and is reduced to zero as the resolidified bed begins to contract at 675 °C allowing gas to flow around the outside of the bed rather than through it. The bed permeability accounts for changes in bed length (considerable) along with smaller effects such as the temperature and pressure on gas flow rate (and thus velocity). An attempt at accounting for volatile evolution was made using both TGA and DETA results; however, this was found to be relatively small and subject to assumptions. The calculated bed permeability shows that the minimum permeability occurs during the first pressure peak and thus rapid swelling. After which the expansion of the bed keeps the permeability relatively stable until swelling is finished, resulting in a significant increase in permeability. Due to the lack of thermo-plastic behaviour, the inertinite permeability was not determined.

### 3.2 Thermo-chemical properties

The DETA thermo-chemical analysis provides a large suite of data which can be used as a characterisation method for dynamic behaviour and for calculating total yields of tars and gases (through integration of results). DETA results of carbon and hydrogen evolution are given in Figs. 5 and 6.
for the vitrinite rich (86.4\% V) and inertinite rich (32.4\% V) maceral concentrates, respectively. These results are given in three curves corresponding to Total Volatiles, Gas Only and the mathematically derived Dynamic Tar. The units for these curves are ppm/g coal which relates back to the combustion gas species from which they are calculated; CO₂ and CO for carbon evolution and H₂O and H₂ for hydrogen evolution. Overall, the two maceral concentrates exhibit significantly different evolution curves though the initiation and peak temperatures are similar. The vitrinite rich concentrate shows sharp peak evolution for all three volatile streams, approximately double the size of volatile peaks in the inertinite concentrate which also appear to have broader shapes. It can be observed that the initial volatile evolution consists of predominantly condensable tar species beginning at around 300 °C, with light gas production beginning at 400 °C. Peaks tar evolution occur at 495 °C and 510 °C for vitrinite rich concentrate (86.4\% V) and inertinite rich concentrate (32.4\% V), respectively, while light gas peaks appear at 505 °C for vitrinite rich concentrate and 520 °C for inertinite rich concentrate. Rapid tar evolution for carbon was complete at 545 °C for vitrinite rich concentrate (86.4\% V) and 585 °C for inertinite rich concentrate (32.4\% V). Rapid tar evolution for hydrogen is complicated by the formation of pyrolytic H₂O which occurs in a clearly separate stage for the vitrinite rich concentrate (560–775 °C) and appears overlapped with the end of tar evolution for the inertinite rich concentrate (ending ~865 °C). Above 600 °C, the light gas evolution appears dominated by the evolution of hydrogen, which must be predominantly in the form of H₂ (and some H₂O). This forms a significant secondary peak at 750 °C and corresponds with the maximum contraction rate in the vitrinite rich concentrate.

3.3. Tar analysis – total condensed phase

After the condensation step in the mode 3 Gas Only experiment, the tars were washed out of the apparatus and dissolved in acetone. A portion of the dissolved tars were re-loaded into the quartz crucible and allowed to sit until the acetone had evaporated. In this way the tars were re-concentrated and placed back into the furnace for analysis. Fig. 7 shows the mode 4 maceral tar characterisation as they are re-vaporised and combusted to form a carbon and hydrogen distribution against boiling point. For this analysis the concentrations of combustion products represent the amount of tar re-loaded into the furnace rather than being indicative of the total amount of tar. Fig. 7 shows that there are two significant tar groups that form peaks at 209 °C and 355 °C for the vitrinite rich concentrate (86.4\% V) tar and 192 °C and 328 °C for the inertinite rich concentrate (32.4\% V) tar. The first group tars from the vitrinite rich concentrate had H/C~1 while tars from the inertinite rich concentrate had H/C>1. This could be that tars from the inertinite rich concentrate are more aliphatic than tars from the vitrinite rich concentrate. The second group tars with boiling point up to 400 °C for both coal maceral concentrates were similar and they showed H/C<1. One possible explanation for such bi-modal distribution of boiling points may be related to the aromatic ring size of the tars, with the first tar peak being based around 2 ringed naphthalene structures and the second peak being based on 3 ringed anthracene structures. Naphthalene and anthracene have boiling points of 218 °C and 340 °C, respectively, and a distribution of boiling points around these bases could potentially be indicative of the type of alkyl side chains they contain. Further work is needed to justify this theory. Of particular interest is the lack of higher molecular weight materials with boiling points within the range of thermoplastic behaviour (440–500 °C for the parent coal). This temperature range is marked in grey in Fig. 7. The material that is re-vaporised within this range appears to have a H/C>1 and it is not clear at what temperature the collected tars shift from vaporising pure tar species towards coking (producing lighter hydrocarbons and a carbon residue). However, there is a small yet significant amount of material that is removed above 500 °C up to 1000 °C, consisting predominantly of hydrogen. To a certain extent this is expected to be a result of coking occurring within the tars as the larger molecules decompose below their boiling point and releasing either H₂ or H₂O.

3.4. Discussion

Combining the thermo-physical and thermo-chemical analysis provides significant insight into the complex mechanisms occurring during coking. The most dramatic differences
between different coal maceral concentrates are observed in the thermo-swelling results. Clearly this behaviour is fundamentally related to the exothermic trough measured using the CATA technique. However, the swelling occurred over a relatively small temperature range within this exothermic region and therefore must occur as a consequence of a greater mechanism. The other thermo-physical measurements (thermal conductivity and permeability) also show a similar sharp trend to the swelling. The DETA results show that this region is also fundamentally related to the evolution of tar and gas-peak swelling/pressure drop occurring at the same temperature as peak gas carbon and hydrogen evolution. However, it is not yet clear why such sharp physical behaviour occurs over such a short temperature range within a larger thermal region. The inertinite displays no exothermic behaviour during primary devolatisation and consequently shows no thermo-physical phenomena, yet it also has similar volatile evolution curves albeit at a lower rate. Thus the question is raised: what mechanism produces exothermic thermo-plastic phenomena? It clearly occurs only in the vitrinite portion of the coal and yet the collected tars from each maceral concentrate display relatively similar types of tar “groups”. Further work into other maceral sub-groups, such as fusible inertinites, may help determine if such exothermic behaviour is limited to vitrinites or is common to other thermo-plastic materials.

4. Conclusions

Two thermal analysis methods have been developed to evaluate the dynamic changes occurring during coking. These techniques allow a direct comparison between thermo-physical and thermo-chemical phenomena and have been used on different maceral concentrates from the same coal to demonstrate the thermal behaviour occurring within a single coal. The thermo-physical and thermo-chemical measurements were observed between three coal maceral concentrates which showed that:

- Exothermic activity during primary devolatisation appears to be associated with plastic phenomena in the vitrinite fraction.
- Volatile evolution was significantly higher in the vitrinite fraction, with sharper peaks in both tar and gas phases compared to inertinite fraction. Peaks tar and gas evolution occurred at lower temperature for vitrinite rich concentrate compared to inertinite rich concentrate, the same trend for the completeness of peaks tar and gas evolution was also observed.
- Peak gas temperature also corresponded to peak swelling & pressure drop development temperature in the thermo-physical analysis.
- Volatile analysis of the collected tars showed similar distribution of components between maceral fractions with carbon evolution peaks around 200 and 340 °C. A relatively small fraction of the collected tars were re-vapourised in temperatures within the plastic temperature region above 440 °C.

Conflicts of Interest

The authors declare no conflicts of interest.

REFERENCES