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

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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.

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

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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)).

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

where ρ – 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.

$$\frac{\Delta P}{L} = \frac{1}{k} \mu U$$ (2)

ΔP is the pressure drop across the bed expressed in Pa (up to 400 kPa), μ 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_2O infrared analyser and a Testo 350XL flue gas analyser (O$_2$, CO, H$_2$, NO, NO$_2$, SO$_2$, hydrocarbons). Infrared analysis of H_2O 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 combusting 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