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Associations of physical, chemical with thermal changes during coking as coal heats – Experiments on coal maceral concentrates

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HIGHLIGHTS

- Physical, chemical and thermal events of heating coal macerals were synchronized.
- Thermo-expansion of coal used up to 21% of the volatiles to drive bubble growth.
- Vitrinite content affected the swelling temperature region and gas diffusion.
- Onset of tar evolution was identified as the lowest temperature event as coking.
- Condensable tars from high vitrinite have a higher overall H/C ratio.

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ABSTRACT

Dynamic measurements of physical, chemical and thermal changes in the transformation of coal maceral concentrates were made during heating at a rate of 10 °C/min to 1000 °C. The endothermic and exothermic processes were identified by measurements of apparent specific heat while the fluidity was indicated by the estimated thermal conductivity. Measurements of swelling and bed permeability were made, with continuous quantitative elemental analysis of gases and tars as they evolved. Data for two coal concentrates of high and moderate vitrinite indicate that the same reactions and events are occurring for the two samples, but to a greater extent for the high vitrinite sample. The research has noted the significance of evolved tars in the early events, being the lowest temperature event identified, with rapid tar evolution prior to the onset of swelling associated with permeability change. Further tar release and gas evolution is associated with a rapid swelling event, this event being substantially greater for the high vitrinite sample. The data has also quantified contraction at higher temperatures following swelling which is associated with the release of hydrogen containing gases. Evolved tars from the high vitrinite sample showed elevated H/C ratio indicating that vitrinite tars appear to be more aliphatic than those evolved from inertinite. A comparison of measured swelling with estimated volumetric flow rate of the volatiles has indicated that thermo-expansion of coal utilised up to 21% of the volatiles to drive bubble growth. This utilisation rate varied significantly across the plastic temperature range.

1. Introduction

Coke is commercially produced in coke oven batteries by carbonization of coal from room temperature (25 °C) to 1000 °C in atmosphere with no oxygen present. During cokemaking, coal undergoes softening, fusion and resolidification accompanied by swelling and contraction with temperature relating to successive endo- and exothermic reactions with the release of gas and tar [1,2]. Coal is generally described as consisting mainly of hydroaromatic and aromatic clusters linked by aliphatic bridges [3,4] besides the mineral compositions. Microscopically, these organic components of coal are made up of complex maceral constituents classified mainly as three groups, i.e., liptinite (exinite), vitrinite and inertinite [5,6]. The physical, chemical and thermal changes of heating coal are directly related to the coal maceral components [1,5,7]. Van Krevelen et al. [1] suggested that liptinite becomes extremely fluid when heating; the inertinite shows no fluidity, whereas vitrinite takes an intermediate position. Kidena et al. [8] and Xie et al. [9] found that the contents of aromatic clusters and aliphatic substituents vary from vitrinite to inertinite concentrates, which may affect the development of fluidity and swelling of heating coal.

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A number of techniques have been previously employed to investigate individual events involved in the physical, chemical and thermal changes as coal heats, for instance, Gieseler Plastometer [10,11] and Proton Magnetic Resonance Thermal Analysis (PMRTA) [12,13] for measuring fusibility and Rheometry [14–16] for viscosity; crucible swelling [10] and Audibert-Arnu dilatometer [10,11] for evaluating swelling; Thermogravimetric Analysis (TGA), Gas Chromatography (GC), Mass Spectrometry (MS), Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR) [9,17–22] for analysing chemical changes; and Differential Scanning Calorimetry (DSC) [23–25] and Differential Thermal Analysis (DTA) [26] for estimating thermal changes.

Two novel methods have recently been used to study the fundamental changes occurring during pyrolysis of coal maceral concentrates [27–29]. Of particular interest was the effect of vitrinite content on thermo-swelling as this has practical application in coking. Previous work has shown that macerals can be concentrated using water based separation methods [27]. It was observed that higher vitrinite fractions exhibit both higher swelling and larger exothermic heat generation during the thermoplastic phase [27,28]. In other work, the volatile release was found to be higher in vitrinite concentrates compared to inertinite concentrates [29]. The present study is focussed on physical and chemical changes as maceral concentrates are pyrolysed. Here, new techniques including Computer Aided Thermal Analysis (CATA) and Dynamic Elemental Thermal Analysis (DETA) were employed to synchronously evaluate the physical, chemical and thermal changes of heating coal. Computer Aided Thermal Analysis (CATA) for evaluating apparently specific heat, thermal conductivity and swelling of the heating coals has been recently introduced by Xie et al. [27]. The Dynamic Elemental Thermal Analysis (DETA) technique has been developed to quantify volatile release in terms of elemental composition (notably carbon and hydrogen) [29]. Using these two techniques, this work aims to associate the changes of these fundamental measurements during cokemaking for two coal maceral concentrates with different vitrinite contents separated from the same coal.

2. Samples

Coal maceral concentrates were separated using a water-based reflux classifier without the use of chemical media; details for this technique in separating coal maceral concentrates based on density are given in our previous paper [27]. For the purpose of removing the effect of particle size on the separation, particles were sized at 106–212 μm prior to density separation. The parent coal had a maceral component of 73.6% vitrinite and 26.4% inertinite (mmf). Vitrinite contents of separated coal maceral concentrates with particle size 106–212 μm varied from 26.1% to 91.2%. Based on the experimental results, two maceral concentrates with vitrinite contents 86.4% and 64.4% were used to clarify the associations of physical, chemical and thermal changes. The purity of the concentrates was determined by the separation apparatus and, while being different, they may be considered to be high vitrinite and moderate vitrinite samples.

Properties of these two maceral concentrates are presented in Table 1. Proximate and Ultimate analyses were based on Australia Standards 1038.1, 1038.3 and 1038.6. Standard petrographic analysis (ISO7404) was carried out to determine the coal maceral compositions. Relative density measurements of separated maceral concentrates were based on Australian Standards (AS 1141.6.2-1996). Gieseler Plastometer was determined by AS 1038.12.4.1.

Table 1
Coal maceral concentrates properties.

Sample	High vitrinite	Moderate vitrinite
Proximate analysis,% (ad)		
Air dried moisture	1.4	1.4
Ash	2.1	9.5
Volatile matter	20.9	18.7
Fixed carbon	75.7	70.3
Ultimate analysis,% (daf)		
Carbon	89.3	88.9
Hydrogen	4.88	4.68
Nitrogen	2.25	2.13
Sulphur	0.49	0.56
Oxygen (by difference)	3.0	3.7
Petrographic analysis		
Vitrinite (% mmf)	86.4	64.4
Inertinite (% mmf)	13.6	35.6
R_{vMax} (%)	1.47	1.51
Relative density (g/ml)	1.31	1.38
Gieseler Plastometer		
Initial softening temperature (°C)	425	435
Maximum fluidity temperature (°C)	470	475
Resolidification temperature (°C)	500	495
Plastic range (°C)	75	60
Maximum fluidity (ddpm)	90	10

3. Methodology

The experimental apparatus has two configurations. The first technique evaluates thermo-physical properties during coking, which includes apparent volumetric specific heat, thermal conductivity, volumetric swelling and bed permeability. The second technique determines thermo-chemical changes by characterising the volatile evolution (separately as tar and light gas) as continuous elemental streams of CHNOS. The detailed descriptions for these two techniques were given in our previous papers [27,29].

3.1. Apparent specific heat and thermal conductivity

The first experimental set-up uses the principle of the Computer Aided Thermal Analysis (CATA) technique which has been used in literature [30] and specifically modified in this work to measure volumetric swelling in the sample [27] and pressure drop of gas flowing through coal pellet along with the temperature profile. The heating chamber is shown in Fig. 1. The sample, approximately 2 g by mass was packed in a quartz tube to the length of 20 mm with a diameter of 11.80 mm. The pyrolytic experiments were conducted from room temperature to 1000 °C at a heating rate of 10 °C/min under an inert atmosphere with argon flowing of 30 ml/min. The temperatures of the graphite heating element, surface and centre of the sample were measured for estimating the apparent specific heat and thermal conductivity based on one dimensional heat conduction (Eq. (1)), which uses a calibrated heat flux. The heat flux to the sample surface 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. Details for how to estimate the apparent volumetric specific heat and thermal conductivity can be seen in our previous work [27].

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

In Eq. (1), where ρ is the density of the sample (kg/m^3), C_p is the specific heat (J/kg K), k is the thermal conductivity (W/m K), T is the temperature (K), t is the time, and r is the radius (m).

3.2. Swelling and permeability to gas flowing

In Fig. 1, the coal bed was restrained on one side by the alumina rod and allowed to expand on the other side through a Linear Variable Differential Transducer (LVDT). The LVDT readings as well as