Full Length Article

The effect of densification with NaOH on brown coal thermal oxidation behaviour and structure

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ABSTRACT

The thermal behaviour and chemical structure of densified products of two Victorian brown coals prepared with NaOH addition were analysed by differential gravimetric analysis/differential thermal analysis (DGA/DTA) and Fourier transform infrared spectroscopy (FTIR).

Acid washing of coal led to lower tendency to spontaneous combustion through a decrease in the total enthalpy change and a shift of the main mass loss stages to higher temperatures due to strengthening coal hydrogen bonding network.

The addition of a small amount of NaOH (such that pH < 7.5) shifted the main stages of the DTG/DTA curves to lower temperatures and had a catalytic effect on spontaneous combustion by disrupting the hydrogen bonds network and suppressing cross-linking reactions. The products densified with higher amount of NaOH (such that pH ≥ 7.5) showed lower proportions of mass loss at lower temperatures stages of the DGA/DTA curves during oxidation with air. The ion exchange of Na ions for hydrogen in acid functional groups, increases the polarity and strength of bonds leading to a more rigid coal structure, reduces the surface area and decreases the coal's tendency to react with oxygen and consequently delays the onset of combustion.

FTIR results showed that the order of thermal vulnerability of brown coal's functional groups toward decomposition/oxidation was as follows: aliphatic groups > carboxylic groups > carboxylate and aromatic groups > substituted aromatic groups ≈ polymerized ethers and ketones.

1. Introduction

Victorian brown coal has high moisture content (65–70 wt% db) and this critically impacts on virtually every facet of its utilisation. It is desirable to reduce the moisture content so as to minimise transportation costs (in the case of export) and improve the thermal efficiency of combustion. Unfortunately, drying also tends to increase its susceptibility to the undesirable phenomenon of spontaneous combustion [1–3].

Spontaneous combustion has long been a problem in the mining, storage, and transport of coal, presenting serious issues for coal producers [4]. This phenomenon can occur when the accumulation of the heat released in low temperature reactions is faster than its dissipation, leading to an increase in temperature of coal particles. The increase of temperature within coal particles accelerates the oxidation reactions and results in thermal runaway and combustion [4,5].

In previous work by the authors [6], the densification process, where brown coal is kneaded, extruded and then allowed to dry slowly to form a product known as 'densified coal', was applied to reduce the

brown coal's moisture content and spontaneous combustion tendency simultaneously. The results showed that the densification process reduced the brown coal moisture content by about 80%, and when NaOH was used as an additive, the spontaneous combustion propensity decreased significantly.

It has also been shown that the densification of Victorian brown coal with the addition of NaOH modifies its physical properties such as equilibrium moisture content, hardness and surface morphology. In addition, a clear correlation between coal surface area and pore volume versus spontaneous combustion tendency was established.

However, further study is required to provide detailed information on changes in the chemical structure and thermal behaviour that occur in products densified with NaOH to improve our understanding of their tendency to spontaneous combustion.

Thermogravimetry analysis (TGA) techniques, including differential thermogravimetry (DTG) and differential thermal analysis (DTA), have been widely used – to study the coal thermal behaviour and oxidation [7–10]. For example, Ma et al., [8] studied the reactivity of various Victorian brown coal lithotypes, through determining a set of

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parameters, such as $T_{i.g.}$ (ignition temperature of volatile matter), T_m (the temperature at which this maximum combustion rate take places) and R_m (the maximum combustion rate), from their combustion TG and DTA profiles. They suggested this method to predict coals combustion performance in industrial furnaces.

In addition, Fourier transform infrared spectroscopy (FTIR) has been used to characterise the chemical structure of low rank coals, especially in relation to the oxygen functional groups which are important to the conversion and utilization of lower rank coals [11–13]. Generally, the overlapping IR bands have been separated by deconvolution/curve-fitting methods to facilitate semi-quantitative comparison between samples [12,14–16].

In the present work DTG/DTA deconvolution, for the first time in this field, and FTIR were used to investigate and compare the self-heating/combustion behaviours and chemical structures of raw, acid washed and densified brown coal products, with NaOH as additive, and to relate this to information to their spontaneous combustion behaviour.

2. Experimental

Two Victorian brown coals, Morwell (MW) and Loy Yang (LY), originated from the Latrobe Valley, Victoria, were used in this study. To prepare densified coal product, 100 g of brown coal with – 35 ml of water or NaOH solutions (0.5, 1.0 and 1.5 M) was mechanically kneaded and, without any loss of material, the prepared dough was extruded in order to produce pellets of the desired shape and size. The wet pellets were allowed to dry slowly in air (ambient conditions), forming a dried and hard product [17–19].

The tendency of samples to spontaneous combustion was evaluated by the wire basket method. Details of the wire basket test, which was carried out to determine the critical ignition temperature (T_{cr}), the ambient temperature at which thermal runaway occurs, have been previously presented [17]. Standard methods used for characterization of the samples (such as CO_2 surface area, mercury porosimetry and inorganic matter measurements) and the acid washing method have been previously reported [17]. The results of ultimate and proximate analysis and major inorganic matter measurements of raw and acid washed coal are given in Table 1.

Temperature-programed oxidation experiments were carried out using a Setaram thermogravimetric analyser. For each test, 30 ± 0.1 mg of ground and sieved sample, < 0.018 mm, was loaded into a TGA cup and heated from 25 to 850 °C, with a linear heating rate of 1 °C/min, in a flow of air (30 cm³/min). The use of a low heating rate helped to improve the resolution of the DTG/DTA curves. The amounts of heat released from the samples (total enthalpy change) during temperature-programed oxidation were calculated from the total area under the DTA curve.

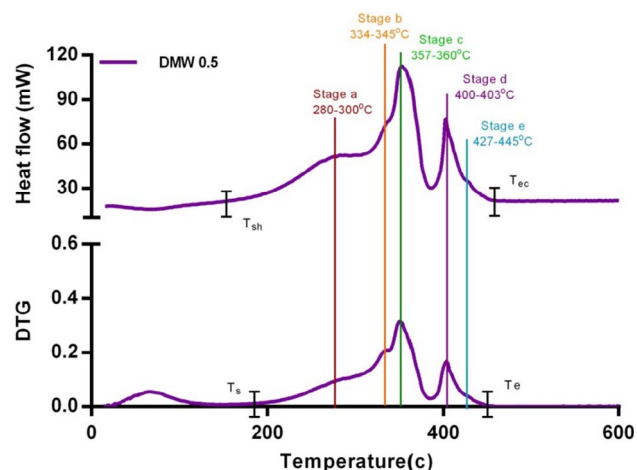Fig. 1 presents typical DTG/DTA curves illustrating the distinctive

Fig. 1. The typical DTG/DTA thermogram with exothermic stages and characteristic parameters.

exothermic stages. In Fig. 1, each exothermic stage is defined and labelled with a maximum peak temperature range. It should be noted that the number of exothermic stages and the maximum peak temperature of each stage vary between different samples. Characterisation parameters including the starting (T_s) and ending points (T_e) of the mass loss (DTG) curve are also labelled. Similarly, the points in the DTA curve marking the beginning (T_{sh}) and ending (T_{ec}) of the self-heating behaviour are indicated [7].

In order to separate the mass loss in each exothermic stage, the DTG curves were curve-fitted using the OriginPro software (OriginLab, Version 8, Northampton, MA) by applying Gaussian functions, as illustrated in Fig. S1. The maximum peaks temperatures for each exothermic stage, for each sample, were carefully selected to give the best fitting results with the lowest possible residue from cumulative peak fitting.

KBr disks for FTIR analysis were prepared using crushed and sieved (< 0.018 mm) samples of the raw coals and densified products that had been vacuum dried (at 30 °C for 24 h). Samples (3.0 mg) were mixed with 300.0 mg of dried KBr. The spectra were recorded by running 64 scans at a resolution of 4 cm^{-1} using a Bruker FTIR instrument (Equinox, IFS-55).

In order to investigate the evolution of chemical structure through the different thermal stages observed in the DTG/DTA curves, TGA experiments were programmed to stop heating after each stage (as determined from the minima of second derivatives of the DTG curves) then cooled down to room temperature. Residual samples were removed from the TGA cup and KBr disks prepared for FTIR analysis.

FTIR peak assignments were based on Painter et al. [20] and the spectral range between 1800 and 1480 cm^{-1} was, for each sample,

Table 1
Characterization of raw and acid washed MW and LY coals.

Properties		MW	LY	Inorganic matter (g/100 g db)	MW		LY	
					Raw	Acid washed	Raw	Acid washed
Moisture (% as received)		60.0	59.0	Al	0.02	0.01	0.67	0.17
				Si	0.10	0.08	1.98	1.55
Proximate Analysis (% dry base)	Ash	1.9	3.5	Ca	0.68	0.03	0.04	0.01
	Volatile	48.4	49.4	Fe	0.28	0.07	0.08	0.04
	Fixed carbon	49.7	47.2	Mg	0.38	0.01	0.08	0.00
Ultimate Analysis (% dry base)	C	67.40	65.70	Na	0.04	0.00	0.14	0.02
	H	4.50	4.70					
	N	0.50	0.6					
	S	0.24	0.66					
	Cl	0.06	0.11					