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In-situ synchrotron IR study on surface functional group evolution of Victorian and Thailand low-rank coals during pyrolysis

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ABSTRACT

In-situ synchrotron FTIR studies were conducted using four Victorian brown coals and one Thailand lignite to examine the evolution of functional groups from the surface of the sample during pyrolysis from room temperature to 550 °C. TGA data showed that the pyrolysis of all coals is comprised of a drying stage (30–200 °C) and devolatilization stage (200–900 °C). FTIR data showed that compared to Victorian brown coals, less surface functional groups were found in Thailand lignite. The loss of functional groups from Thailand lignite was observed during drying, and the devolatilization consisted of two stages. For Victorian brown coals, the concentration of oxygen contained hydroxyl and carboxyl groups decreased during the drying stage, due to the removal of water, and breakdown of weakly bonded alkene and alkyne. When temperature gradually increased during devolatilization stage, more functional groups were released. However, by 550 °C, the groups at the wavenumber of 1700–1340 cm^{-1} (carbonyl, carboxylate, aromatic ring, CH_3 and CH_2 groups) remained in the sample. Based on the spectra taken of two chars from the same brown coals, these groups were not completely removed until 1000 °C.

1. Introduction

Coal currently provides 40% of global electricity needs [1]. Brown coals are of the lowest rank among the coals, but the vast reserves of economically recoverable brown coal make it a large source of fuel for several countries. Victoria has over 430 billion tonnes of brown coal reserves, which account for over 20% the world's low-rank coal reserves. The shallow depth of overburden combined with high coal to overburden ratio (between 0.5:1 and 5:1) make it one of the lowest cost energy sources in the world [2]. The conversion of brown coals into fuel can be carried out through different processes such as pyrolysis, combustion, gasification, and liquefaction. As the initial step in any coal conversion process pyrolysis is important, accounting for up to 70% weight loss of coal [3]. What happens during the pyrolysis process affects the structure of the residual solids (char) and their gasification behaviour, including emission of gaseous pollutants during the subsequent gasification step.

During pyrolysis when the coal particle is heated up, functional groups on the surface of coal decompose and generate gases such as H_2, CO, CO_2, CH_4, and liquid products, leaving the char at the end [4]. The gas yield and char characteristics are largely affected by the change of surface functional groups during pyrolysis of coal. Pyrolysis process is influenced by several factors such as temperature, heating rate, pressure and coal rank. These factors have a significant effect on the char properties and kinetics of the devolatilization process [3,5].

Studies are available on the loss of functional groups on coal coalification process [6,7], oxidation [8], and drying process [9], but on pyrolysis of Victorian brown coal, it is limited. Ibarra et al. investigated the coal structure changes in peat and low-rank coals during the coalification process using Fourier transform infrared (FTIR) spectroscopy [7]. However, this study did not involve the functional group change with temperature. Calemma et al. used FTIR spectroscopy to study the chemical changes during dry oxidation of a sub-bituminous coal at low temperatures from 200 °C to 275 °C [8]. Tahmasebi et al. used FTIR to study the chemical structure changes during drying of Chinese lignite in hot air [9]. Nonetheless, their study did not evaluate the loss of the functional groups during pyrolysis.

In another study, Lin et al. studied the functional group transformation in a Chinese brown coal as a function of temperature up to 700 °C in N_2. The decomposition of aliphatic groups and release of a large amount of oxygen-containing functional groups (heterocyclic, phenolic hydroxyl, and crystalline hydrates) were observed when temperature increased [10]. Zhang et al. investigated the chemical structure change of Victorian Loy Yang coal and Western Australian

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Table 1
Proximate and ultimate analysis of coal samples.

Items	Yallourn	Loy Yang	Morwell	Maddingley	Thailand lignite
Proximate analysis (wt%)					
Moisture (a.d.)	8.92	3.72	11.17	6.63	5.34
Volatile matter (d.b.)	48.18	48.26	49.31	41.33	45.20
Fixed carbon (d.b.)	45.70	45.59	48.65	33.80	3.99
Ash (d.b.)	6.12	6.15	2.04	24.87	50.81
Ultimate analysis (d.b., wt%)					
Carbon	66.35	66.15	60.42	40.08	23.19
Hydrogen	4.92	4.62	4.59	4.53	2.83
Nitrogen	0.39	0.64	1.54	0.32	0.95
Sulfur	0.30	0.31	0.86	1.66	4.00
Ash	6.12	6.15	2.04	24.87	50.81
Oxygen (by difference)	21.92	22.13	30.55	28.54	18.22

a.d. = air dry basis, d.b. = dry basis.

Collie sub-bituminous coal during fast pyrolysis to 600 °C. Aromatic ring system in these coals was not found to significantly change when the temperature increased to 600 °C [11]. However, in their studies, the functional group changes are measured from ex-situ samples. In other word, coal samples firstly pyrolysed in a wire-mesh reactor at a selected temperature, then cooled down to room temperature before taking IR analysis, where the effect of cooling on samples is unknown.

The results in the existing literature are mainly from ex-situ laboratory FTIR spectroscopy, where the sample was subjected to the desired temperature in a gaseous environment and cooled down before taking any measurement. For the laboratory based FTIR, coal samples are required to be crushed to a fine size and dispersed in a Potassium Bromide (KBr) disk and pressed at very high pressure. Hence, a bulk of samples, not any single distinct particle, are measured based on the assumption that particles are uniformly dispersed in the disk [12]. However, because of the high pressure applied during pressing the KBR pellet, the sample can also get destroyed. Another limitation of laboratory-based IR is that samples only can be measured at room temperature, so functional group changes during the pyrolysis process can not be directly observed. In contrast, at synchrotron IR beam line a single particle can be focused, and functional group evolution can be tested as a function of temperature in situ at high resolution. Thereby, the variation and error from heterogeneous differences among particles can be detected, and more precise information on surface functional groups can be obtained. Moreover, the synchrotron IR is capable of observing the particle morphology change during IR measurements [13]. Thus, in-situ synchrotron IR is a useful tool to determine the decomposition steps during the pyrolysis process.

The application of in-situ FTIR on coal is limited to the determination of the strength distribution of hydrogen bond up to 500 °C [14], or the examination of spontaneous combustion at low temperature [15–17]. There is one study to examine the decomposition of the functional groups for Huolinhe brown coal up to 500 °C [18]. They found the groups of methyl and carboxyl decomposed with temperature, whereas the intensity of ester and anhydride initially increased and then decreased. However, the application of in-situ FTIR for the high-temperature pyrolysis of low-rank coals has not been reported so far.

This study for the first-time presents information on the surface functional group evolution during coal pyrolysis by in-situ synchrotron IR. In this study, the effect of temperature on surface functional group evolution of four Victorian brown coals and one Thailand lignite during pyrolysis was investigated at the Infrared Microscopy beamline facility at Australian Synchrotron. To further explore the effect of char preparation temperature, chars pyrolysed at 700–1000 °C in a drop tube reactor were prepared in advance and analysed in the same beamline.

Table 2
Proximate and ultimate analysis of Yallourn and Maddingley char.

Fuel	Pyrolysis Temperature (°C)	Proximate analysis (dry basis)		
		Volatile matter	Fixed carbon	Ash
Yallourn	700	17.79	72.45	9.76
	800	8.29	83.37	8.33
	900	5.18	84.28	10.54
	1000	8.18	81.63	10.19
Maddingley	700	16.24	49.53	34.21
	800	13.08	52.27	34.21
	900	10.91	53.44	34.63
	1000	9.94	54.31	35.73

2. Experimental

2.1. Coal samples

Four Victorian brown coals (Morwell, Loy Yang, Yallourn, and Maddingley), and a Thailand lignite were used in this study. Thailand lignite is from the Mae Moh mine in Thailand. All samples were firstly air-dried and sieved between 20 μm and 38 μm. The proximate and ultimate analysis of the coal samples were given in Table 1.

Coal chars of Yallourn brown coal and Maddingley brown coal were also used to investigate the functional group evolution at different char preparation temperature. These coal chars are derived from coal pyrolysis in a drop tube furnace at four different temperatures – 700 °C, 800 °C, 900 °C and 1000 °C. The proximate analysis of Yallourn and Maddingley char pyrolysed at 700–1000 °C is presented in Table 2.

2.2. Apparatus and procedure

In situ FTIR experiments were conducted using the infrared Micro spectroscopy (IRM) beamline at the Australia Synchrotron. The IRM beamline consists of a Bruker V80 v Fourier transform infrared (FTIR) spectrometer and a Hyperion 2000 IR microscope, which offers high signal-to-noise ratios at between 3 and 8 μm diffraction limited spatial resolutions. Because of this, the beamline is perfect to analyse microscopic samples. In a specially designed Linkam cell with BaF_2 window, the microscope attached to the system allows to pick the particle of interest and focus on it to obtain the information on a single particle during the course of the experiment.

About 0.5 mg sample was used for each run in the experiments and dispersed on BaF_2 disk. The sample chamber was initially purged at 30 °C for 10 min in a flowing nitrogen stream. Then these were heated at the rate of 10 °C/min up to 550 °C, in the presence of ultra-high purity nitrogen to maintain a pyrolysis atmosphere