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Modification of lignites via low temperature ionic liquid treatment

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ABSTRACT

Two lignite samples (150–212 μm) were treated with four ionic liquids (ILs); 1-butylpyridinium chloride ([Bpyd][Cl]), 1-ethyl-3-methylimidazolium dicyanamide ([Emim][DCA]), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and 1-butyl-3-methylimidazolium tricyanomethanide ([Bmim][TCM]) at 100 °C for 3 h to establish the utility of ILs for lignite pre-treatment in conversion processes. ILs are room temperature molten salts that have remarkable physical and chemical properties including high thermal and electrochemical stabilities, low vapour pressures and, critically for this work, the capacity to solubilise a diverse range of materials. Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and optical microscopy were employed in this study to gain insight into the physical and chemical interactions occurring between lignite and ILs at low temperatures. The FTIR results indicate that the majority of the ILs employed were able to break apart the macro-structure of coal resulting in an increase in short chain aliphatic hydrocarbons. Additionally, FTIR analysis revealed a significant decrease in the presence of COOH and CO groups for lignites treated with [Emim][DCM]. The TGA data revealed that the IL treated lignites had significantly lower devolatilisation temperatures than the untreated lignite, indicating an increase in lower molecular weight species after treatment. Microscopy showed a sizeable decrease in particle size after IL treatment due to fragmentation, and these coals appeared to be considerably swollen. Analysis of the recovered ILs showed no denaturing after the treatment process, indicating their recyclability potential in the treatment process.

1. Introduction

Australia has significant reserves of lignite, commonly referred to as brown coal, which is mainly used to generate power. Various models for the average chemical structure of lignite have been proposed; these complex models contain varying amounts of inorganic matter, volatile matter, heteroatomic functional groups, aromatic rings, and aliphatic chains [1–3]. Effective and efficient utilisation of lignite is contingent upon understanding its complex structure, and behaviour under various reaction conditions, hence it is still broadly studied [4–6]. Solvent extraction of lignite has been carried out to gain a greater understanding of its structure, and its ability to be utilised in upgradation and conversion processes [7–10]. Various organic solvents have been shown to be able to solubilise, swell, and depolymerise lignites [11–13]. Typical solvents employed for this include pyridine, *n*-methyl-2-pyrrolidone, tetrahydrofuran and carbon disulfide [14–17].

These solvents are often implemented in coal utilisation and conversion processes; involving the production of liquid fuel substitutes, hypercoal (ash-free coal), chemical feedstocks and distillable chemicals [11,18–20].

Ionic liquids (ILs) are solvents composed entirely of ions that have a melting point below 100 °C [21]. These solvents have attracted significant attention in recent years for a variety of applications, which is attributed to the unique range of properties they possess, including high thermal stability, low vapour pressure and the ability to be customised by altering their cation-anion combination [22].

The use of ILs as solvents in biomass systems has been investigated previously [23–26]. These investigations found that ILs were able to solubilise and depolymerise cellulose and lignin for use as potential feedstocks for liquid fuel and fine chemical production. The mechanism for depolymerisation proposed was based on the disruption of hydrogen bonding that comprises the structure of biomass. It was found that ILs able to strongly hydrogen bond, such as [Bmim][Cl], were the best solvents for this dissolution process.

In comparison, studies on coal and IL interactions are still in preliminary stages [27–30]. Initial investigations into the use of ILs to solubilise coal have been carried out by Painter et al. [27], who observed the ability of [Bmim][Cl] to solubilise and fragment Illinois No. 6 coal. Qi et al. [30] recently showed that there was a trend between the aliphatic content of Victorian brown coals and their ability to be solubilised by low

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molecular weight IL DIMCARB. In an initial investigation, we have previously shown that the ability of [Bmim][Cl] to interact with coal appears to be dependent on the maceral fraction of the coal used, as it was found that coals rich in vitrinite were swollen by IL treatment and coals rich in inertinite were fragmented by IL treatment [28]. It was also found that [Bmim][Cl] was able to extract 30% more of the coal rich in vitrinite when compared to the inertinite rich coal [28].

Additional investigations have shown that specific ILs such as [Bmim][Cl] were able to significantly alter the morphological and thermal properties of sub-bituminous coals [31]. Microscopy revealed that extensive fragmentation was observed after IL treatment, greatly enhancing the porosity of the treated coal particles and thermal decomposition (pyrolysis) studies showed an increase in the presence of lower molecular weight species after IL treatment [31]. Thermal coals that underwent IL treatment were also shown to have been altered, with certain ILs impacting the coals mineral matter content and oxygen functionality [32]. The present investigation examines the effects of IL treatment on two lignites to gain insight into their interactions and assess the viability of IL treatments in coal conversion applications.

2. Experimental

Two lignite samples (coals S and coal K) were employed in this study. The coals were milled and sieved to a particle size range of 150–212 μm. Proximate and ultimate analyses of the coals are shown in Table 1. As can be seen, coal S has a higher carbon and ash yield, whereas coal K has a higher oxygen and moisture content.

Four ILs; 1-butylpyridinium chloride ([Bpyd][Cl]), 1-ethyl-3-methylimidazolium dicyanamide ([Emim][DCA]), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and 1-butyl-3-methylimidazolium tricyanomethanide ([Bmim][TCM]) were purchased from io-li-tec (Heilbronn, Germany) at 99% purity and used in this study.

The coal/IL treatment process was carried out in accordance with the method previously established by our research group [32]. A brief summary of the method is presented here. Samples were prepared in a 1:5 mass ratio of coal to IL, respectively. The IL and coal mixtures were magnetically stirred in sealed jars that were placed in an oil bath at 100 °C for 3 h. Subsequently, the coal-IL mixture was placed in a centrifuge tube and the jar, in which the coal and IL were stirred, was rinsed with distilled water to ensure maximum coal recovery. The resultant coal/IL/water mixture was centrifuged, after which the supernatant was removed from the tube with a pipette. The supernatant water/IL mixture was placed in an oven at 80 °C to evaporate water and recover the IL. The coal samples were dried in an oven at low temperatures (60–80 °C).

The dried coal was then subjected to multiple washes by distilled water to ensure the removal of any IL adsorbed to the coal surface, or within its pores. The distilled water was recovered after each wash and its electrical conductivity (EC) measured. This was carried out by mixing 20 mL of distilled water with the coal sample for 5–10 min, the distilled water was then recovered via filter paper separation. The conductivity of the recovered water was then measured to test for any residual IL. This process was repeated until the conductivity of the recovered water was similar to that of distilled water. The coal sample was recovered from the filter paper separation and dried at low temperatures prior to characterisation.

To confirm IL removal from the treated samples, microanalysis was carried out via an elemental analyser, model PE2400 CHNS/O (PerkinElmer, Shelton, CT) and a PerkinElmer AD-6 ultra microbalance. This method allowed the nitrogen contents of both the raw and treated samples to be compared in order to check for the presence of adsorbed ILs.

Table 1
Proximate and ultimate analyses of the lignites used in this study.

Lignite	Proximate analysis[a]				Ultimate analysis[b]				
	M (%)	A (%)	VM (%)	FC (%)	C (%)	H (%)	N (%)	S (%)	O[c] (%)
S	13.4	20.1	38.7	41.2	65.7	6.2	1.2	0.4	26.5
K	27.2	15.8	46.3	37.9	59.4	5.4	0.7	0.8	33.7

[a] Dry basis, M: moisture content; A: ash content; VM: volatile matter; FC: fixed carbon.
[b] Dry ash free basis.
[c] O calculated by difference.

2.1. Optical microscopy

A Zeiss Optical Microscope Axioskope 40 was utilised to obtain optical micrographs of the samples at room temperature. A small amount of each sample was mounted between a glass slide and cover slip. Images of each sample were then taken at 20× magnification.

2.2. Thermogravimetric analysis (TGA)

Pyrolysis of the treated and untreated (raw) samples was carried out using a TA Instruments Model Q50 V20.10 Build 36 thermogravimetric analyser. 10–15 mg of each sample was placed on a platinum crucible, for analysis. For all experiments, a nitrogen sweep gas flow rate of 100 mL/min was used and a ramp rate of 10 °C/min up to a maximum temperature of 650 °C. Conversion during pyrolysis was calculated via the following:

$$x = \frac{m_i - m_t}{m_i - m_f} \tag{1}$$

where x is the conversion, m_i is the samples initial mass, m_f is its final mass and m_t is the samples mass at time t.

2.3. Fourier transform infrared (FTIR) spectroscopic analysis

A PerkinElmer Spectrum Two spectrometer with a universal ATR sampling accessory was used to carry out FTIR analysis on both the recovered coal and IL samples for a scan range of 400–4000 cm^{-1}.

3. Results and discussion

The average recovery for each of the IL-treated lignites can be seen in Table 2. The highest recovery for both lignites was observed for the [Bmim][TCM]-treated samples. The lowest recovery differed between lignite samples, with the lowest for lignite S being the [Bpyd][Cl]-treated samples and the lowest for lignite K being the [Bmim][Cl]-treated samples. This shows that the interactions between the lignites and ILs are specific to both IL and lignite used for this process.

3.1. Changes in particle size and morphology

After the IL treatment process, optical microscopy revealed changes in particle size and morphology. Micrographs of coal S and coal K treated with water and each of the four ILs are presented in Fig. 1. Fig. 1a–b show coal S and coal K treated with water respectively. It was apparent from the micrograph of raw coal S in water (Fig. 1a) that both fine particles, ~25 μm in size, as well as larger particles, ~150 μm, were present.

Table 2
Average lignite recovery after IL treatment.

Ionic liquid treatment	Recovery (wt.%)	
	Coal S	Coal K
[Bpyd][Cl]	61	64
[Emim][DCM]	73	77
[Bmim][Cl]	69	57
[Bmim][TCM]	83	79

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