



# Physicochemical interactions of ionic liquids with coal; the viability of ionic liquids for pre-treatments in coal liquefaction



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## HIGHLIGHTS

- Interactions between coal and ionic liquids have been examined via SEM and TGA.
- The viability of ionic liquids for pretreatments in liquefaction is investigated.
- Morphological and thermal properties of the coals were altered with pretreatment.

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## ABSTRACT

Three Australian sub-bituminous coals were treated with three different ionic liquids (ILs) at a temperature of 100 °C. The thermal behaviour of these treated coals were compared against raw coals via pyrolysis experiments in a Thermogravimetric Analyser. Morphological comparisons were also made via Scanning Electron Microscopy. Among the studied ILs, 1-butyl-3-methylimidazolium chloride [Bmim][Cl] was found to perform the most consistently in being able to alter the thermal and morphological properties of most of the coals used. It is posited that this may be due to the large difference in charge density between the delocalised charge of the large bmim cation and the chloride anion which allows this IL to disrupt the cross linked network of coal. It was also found that the interactions of the ionic liquids are coal specific, for instance none of the ionic liquids were able to change the thermal properties of coal A. Moreover, the results indicated that among the studied coals, coal R showed the highest mass loss during pyrolysis in TGA and coal C showed the highest amount of swelling and fragmentation in SEM images. The results displayed in this study indicate that the potential for ionic liquids to be used as pre-treatments in coal liquefaction is promising.

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## 1. Introduction

Coal is a heterogeneous material made up of both organic and inorganic components. The differing components of coal influence aspects of its behaviour, such as gasification and combustion reactivity. It is Australia's primary source of energy, making up roughly three quarters of Australia's Electricity generated [1]. Additionally, coal plays a key economic role in Australia's exports; Australia is the 4th largest producer of coal and the largest exporter in the world [1]. Conversely to this, Australia is heavily dependent on imports to satisfy our liquid fuel requirements, especially petroleum. Our dependence on imported liquid fuels has increased from 60% in 2000 to over 90% of our transport fuel demand today [2].

Because of this increasing reliance on imports, our economy is left susceptible to fluctuating market prices. [3].

Coal liquefaction is a process whereby coal is transferred into liquid fuel. There are two types of coal liquefaction; Indirect Coal Liquefaction (ICL), which involves the production of liquid fuels via an intermediate gasification step, where a mixture of Carbon monoxide and Hydrogen (syngas) are produced via the gasification of coal. This gas is then used to construct hydrocarbon chains of a range of lengths via condensation in order to produce liquid fuels [3–5]. Direct Coal liquefaction (DCL) involves the splitting of the convoluted, 3-dimensional cross-linked macrostructure of coal via high temperatures and pressures followed by hydrogenation in order to obtain shorter hydrocarbon chains of desired lengths with the intention of obtaining liquid fuel. This is usually done in the presence of a catalyst [3,6–8].

The mechanisms behind DCL are complex and not fully understood yet, however it is generally agreed upon that the following

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steps take place; the coal macrostructure is broken down into various radicals, hydrogen then caps these radical moieties in order to form shorter hydrocarbon chains with a higher H/C ratio [7,9]. This process is usually done in the presence of a catalyst, which helps to distribute hydrogen into the coal structure using solvents.

A significant issue that is a hindrance to the application of DCL is the large capital and operating costs [10]. The high pressures (15–20 MPa), temperatures (380–450 °C) and amount of hydrogen required for this process means that the initial investment costs associated with commercialising this process are quite high [6,11]. Increasing the efficiency of this process and thus decreasing the operational and capital costs required has been an area of interest for many [12,13]. This can be done by via improved catalysts, optimising process parameters and with various pre-treatments. Pre-treatments are utilised in order to swell and fracture the coal before it undergoes DCL. This is advantageous as it enables the partial breakdown of the coal macro structure, and also allows the porosity of the coal to increase, which facilitates the dispersion of hydrogen donor solvent and catalyst onto the coal structure [9,14].

Numerous studies have focused on the use of organic solvents as pre-treatment of coal, such as toluene, hexane, NMP, pyridine and phenanthridine to fragment, swell or dissolve coal [4]. The organic solvents usually employed however have drawbacks associated with them, these include; cost, losses during their use, degradation, their recovery after use and long term performance. The recent push for industries to employ green processes also means that the toxicity of these organic solvents is another major issue hindering their industrial applicability [15]. A type of solvent that potentially might not have these disadvantages are ionic liquids (ILs). Ionic liquids are salts that have a melting point below 100 °C [16]. The first ionic liquid, ethylammonium nitrate (Fig. 1), was synthesised in 1914 [17]. In the last few decades there has been a surge of interest in these salts, this is largely due to their unique properties. Ionic liquids are green solvents with negligible vapour pressure and they often exhibit exceptional thermal stability. It has been reported that some ILs can be thermally stable up to temperatures of 450 °C [18]. Furthermore, they are not flammable at room temperatures [19]. But the most promising property of ionic liquids is their tunability. ILs are often referred to as designer solvents due to the fact that their properties can be tuned for a specific purpose via changing their ion composition [20]. The amount of ion combinations available are vast; it has been estimated that there are as many as 1018 possible ionic liquids [21].

ILs have been studied as solvents extensively in recent times. Literature suggests their possible use in solvent extraction of biomass and biofuel production [15]. However, the studies on coal and IL interactions are quite limited in the open literature [15,22,23]. Firstly, Painter et al. [22] studied the dispersion and dissolution of Illinois No. 6 coal into different ILs. It was concluded in this study that only certain ILs were able to disperse and fragment some coals. In reply to that, Shah et al. [15] showed that the coal–IL interactions may be coal maceral specific. Shah et al. [15] observed that vitrinite rich coal was found to be swelled during the IL treatment whilst inertinite rich coal was severely fragmented.

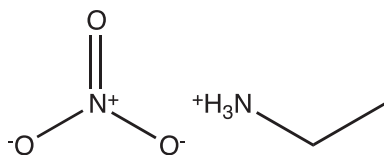


Fig. 1. Molecular structure of the first synthesised ionic liquid (Ethyl Ammonium Nitrate).

Moreover, the dissolution of vitrinite rich coal in IL was found to be >30% compared to inertinite rich coal.

Although few studies are published in this area, the science behind the interactions of different coals and ILs is still not properly understood. The number of coals and ILs studied in the literature are very limited and it is highly recommended that more samples of coals and ILs should be added in the test matrix in order to define/correlate the mechanisms of coal–IL interactions. Therefore, the current study is looking at interactions of three different Australian sub-bituminous coal with three different ILs. More specifically, the study of IL's application in pre-treatment for direct coal liquefaction is quite limited in the existing literature. Therefore, the current paper investigates the viability of ILs for the coal pre-treatment in liquefaction.

## 2. Experimental

Three types of Australian subbituminous coals were used in this investigation, which will be referred to henceforth as C, A and R. These were ground down to a size of roughly 150–212 μm. The proximate and ultimate analysis of these can be seen in Table 1 below.

Three Ionic Liquids were used in this investigation (Table 2):

- 1-Ethyl-3-methylimidazolium dicyanamide [Emim][DCA],
- 1-Butyl-3-methylimidazolium chloride [Bmim][Cl] and
- 1-Butyl-3-methylimidazolium tricyanomethanide [Bmim][TCM]

The above selected ILs were able to dissolve multiple aromatics from several petrochemical streams and hence were chosen based on the COSMO-RS screening carried out by Hansmeier [24].

Samples were made up consisting of coal and ionic liquid at a volume ratio of 20:80 respectively. The IL and coal were placed in a jar with a magnetic stirrer; the jar was then tightly sealed and placed in an oil bath to be heated for 3 h at 100 °C as can be seen in Fig. 2. After 3 h the jar was taken out of the oil bath, this mixture was then washed with 100 ml of distilled water and filtered using filter paper (pore size 11 μm). The water/IL mixture was placed in the oven in order to recover the IL and the coal samples were placed in the oven at low temperatures (80 °C) to dry. However, based on the previous literature on graphite interactions with ionic liquid [19], it was hypothesised that a single water wash may not be sufficient enough to separate IL from coal, as some IL may still remain trapped in pores. Therefore, multiple distilled water washes (5–6 times) were utilised followed by conductivity measurements of the washed sample in order to check for the presence of any IL adsorbed to the coal surface. Two different types of

Table 1  
Proximate and ultimate analysis of the coals used.

	Coals		
	C	A	R
<i>Proximate analysis</i>			
Q (kJ/kg)	18,026	24,956	26,748
Moisture (%)	3.9	1.5	3.7
Ash (%)	32.5	23.0	9.8
Volatile Matter (%)	35.9	50.6	35.9
Fixed Carbon (%)	64.1	49.4	64.1
<i>Ultimate analysis</i>			
Carbon (%)	73.8	78.3	77.2
Hydrogen (%)	4.3	6.7	5.2
Nitrogen (%)	1.1	1.1	2.0
Sulphur (%)	0.3	0.7	0.7
Oxygen (%)	20.5	13.2	15.0

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