Treatment of lignite and thermal coal with low cost amino acid based ionic liquid-water mixtures

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Abstract

Coal is a major resource in Australia, both for power generation and as an export good, however its environmental impact is of significant concern. The structure of coal is inherently complex and contains many heteroatoms, which negatively affect the combustion efficiency and cause pollution. This study reveals that pretreatment of two types of Australian coal, a lignite coal and a thermal bituminous coal, with low cost choline amino acid based ionic liquids, markedly reduces the particle size and heteroatom content. This method is rapid (3h) and proceeds at a low temperature of 70 °C. FTIR, NMR and TGA analysis revealed that pretreated coal has reduced aliphatic carbon, carbonyl groups and sulfur compared to untreated coal. Choline arginate was the best performing pretreatment agent for both types of

coal. This is attributed to multiple hydrogen bond acceptor sites on the arginate anion, which facilitates strong interaction with the coal surface. These results open new pathways towards more energy efficient and cleaner coal, using low cost ionic liquids.

Keywords: Coal; pre-treatment; desulfurization; ionic liquids; choline hydroxide; amino acids.

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1. Introduction

Coal is considered a major resource for the Australian economy, providing both domestic energy (32%, second to oil which was 38%) and revenue from export [1]. The structure of coal is inherently complex and poses significant processing challenges [2]. In general, it is composed of primarily carbon, together with hydrogen, oxygen, nitrogen, sulphur and many other trace elements [3]. It is the presence of these extra elements that reduces the energy efficiency of coal, with oxygen reducing the amount of energy released per kg [4], and sulphur and other elements contributes to the release of toxic gases to the environment [5]. Thus, coal is often pre-treated by some physical or chemical processes prior to combustion to address this concern. Two key objectives of the pre-treatment of coal are softening, swelling and dissolution of coal particles and removal of the extra elements.

Ionic liquids (ILs) are a class of solvents that consist of cations and anions and have melting points under 100 °C [6]. ILs possess some unique characteristics, such as negligible vapour pressure, non-flammability and structural stability. Most importantly, certain ILs can be functionalised for different applications, simply by modifying their cation and anion. Recently, a select class of ILs have received significant attention in the field of lignocellulosic biomass energy conversion [7-9]. It has been shown that certain types of ILs partially dissolve lignocellulosic biomass [7], thereby facilitating their conversion to biofuels. Lignocellulosic biomass is derived from living plant materials, and are primarily comprised of cellulose, hemicellulose and lignin. It was suggested that these ILs work by forming hydrogen bonds with the various components of the lignocellulose, consequently disrupting the cross-linked network present in plant cell walls and thereby facilitating dissolution [9]. Furthermore, the anions of the ionic liquids appeared to play a more important role than the cations in dissolving the biomass, with suitable anions including chloride [10], carboxylates [11], phosphates, phosphonates [12] and amino acid anions [13, 14]. As some types of coal

are fossilized lignin, coal and lignin share many common structures, including the high composition of carbon, the presence of aromatic rings and the types of linkage between their monomeric units. Hence it can be hypothesized that the ILs that solubilize the lignin present in lignocellulosic biomass will have some effect on coal as well.

Study on the use of ILs in coal improvement has been rather limited [15-19]. In our previous investigations [17-19], four types of ionic liquids, namely 1-butylpyridinium chloride ([Bpyd][Cl]), 1-ethyl-3-methylimidazolium dicyanamide ([Emim][DCM]), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]), and 1-butyl-3-methylimidazolium tricyanomethanide ([Bmim][TCM]), were able to alter the thermo-physical state of two types of coals. Treatment with ILs results in a reduction in the size of the coal particles, as well as an alteration in the elemental composition of the coal. TGA analysis showed that the treated coal was composed of a larger portion of lower molecular weight fragments.

So far, one of the major barriers in the utilization of ionic liquids in large-scale operations is their relative high cost, contributed by the cost of the starting materials, their synthesis, purification and relatively low recovery and reuse [20]. Therefore, the objective of this study is to explore the use of cheaper ionic liquids; made from simple acid-base reactions between two naturally occurring chemicals, choline and amino acids; for the pre-treatment of coal. This class of ILs have produced positive results in the field of lignocellulosic biomass processing [13], and have shown success in a single step reaction from biomass to ethanol. In addition, in the present study, instead of using pure ILs, mixture of IL-water has been utilised with the aim to further reduce the overall cost of the process. Comparison of the current work has been established with our previous results with [Bmim][Cl] in order to gauge the efficacy of this relatively simple and inexpensive class of ILs [18].

2. Materials and Methods

2.1. Synthesis of ionic liquids: Choline hydroxide (46 wt% in water), all amino acids, namely L-alanine, L-arginine, L-aspartic acid, glycine, L-leucine, L-lysine, L-phenylalanine, L-valine were purchased from Sigma Aldrich and used in the current work without any further purification. In the synthesis process firstly equal amount choline hydroxide and amino acids (by mole percentage) were mixed together. The resultant mixtures were then heated up to 70 °C and stirred for continuous 3 hours. Specific amount of water was also added to the mixture solution during heating to ensure that amino acids were completely dissolved in the solution. Table 1 shows the structure of the amino acids, along with their added water content.

IL	Cation	Anion	Anion classification	Number of possible H-bonds on anion	Abbrev.	Water (wt%)	pH (100x diluted)
Choline L-alaninate			Non-polar	3	[Ch][ALA]	40.35	11.22
Choline L-argininate			Basic positively charged at pH 7	6	[Ch][ARG]	32.51	12.31
Choline L-aspartate			Acidic negatively charged at pH 7	5	[Ch][ASP]	35.87	6.17
Choline glycinate			Non-polar	3	[Ch][GLY]	42.02	11.07
Choline L-leucinate			Non-polar	3	[Ch][LEU]	59.00	10.71
Choline L-lysinate			Basic positively charged at pH 7	4	[Ch][LYS]	34.73	11.80
Choline L-phenyl-alaninate			Polar	3	[Ch][PHE]	33.19	10.99
Choline L-valaninate			Non-polar	3	[Ch][VAL]	37.38	10.89

91

92 **2.2. Treatment of coal in ionic liquids:** Two types of coal were investigated in this study,

93 a lignite coal with particle size 20 mesh (841 μm), and a thermal bituminous coal with

94 particle size 75-120 μm . Table 2 shows the proximate and ultimate analyses of the coals used.

95 Table 2: Proximate and ultimate analyses of the coals used in this study

Coal	Proximate analysis				Ultimate analysis ^a				
	% M	% A	% VM	% FC	% C	% H	% N	% S	% O ^b
Lignite	10.99	6.61	51.32	31.08	69.89	3.63	1.01	0.34	25.13
Thermal	10.31	16.44	44.19	29.06	71.11	3.80	1.15	0.94	22.99

96 *M: Moisture, A: Ash, VM: Volatile Matter, FC: Fixed carbon. ^aUltimate analyses were carried out on a dry weight and ash*
97 *free basis, ^bcalculated by subtracting C, H, N and S.*

98 Treatment of the two types of coal in the ionic liquids were carried out at a 1:5
99 weight/volume ratio *i.e.* 0.1 g of coal in 0.5 mL of ionic liquids, at 70 °C with stirring for 3
100 hours. At the end of the treatment, a mixture of 50:50 v/v ethanol/water (30 mL) was added
101 and the mixtures were transferred to 50mL Eppendorf tubes. The tubes were then centrifuged
102 at 400 rpm for 30 minutes. The supernatants were collected and dried under vacuum to
103 recover the ionic liquid liquor, while the solids were subjected to further washing with
104 ethanol/water (between 7-15 times) until the electrical conductivity of the discarded washing
105 solution reached that of pure ethanol/water (less than 4 μScm^{-1}). The solids were then dried at
106 110 °C overnight.

107 **2.3. Optical Microscopy:** Optical photographs at 50x, 100x and 200x magnification were
108 obtained on a Zeiss optical microscope Axioskope 40 equipped with a heated stage. Samples
109 were examined at room temperature and at 70 °C.

110 **2.4. Thermogravimetric (TG) Analysis:** A thermogravimetric analyzer (TGA, model
111 Q50 V20.10 Build 36, TA Instruments, U.K.) was used to observe the changes in the thermal
112 behavior of the coals after IL treatment. Each treated coal sample (5-10 mg) was placed in an
113 alumina pan in a nitrogen atmosphere with a flow rate of 100 mL/min. Pyrolysis of the
114 treated coal was then carried out in nitrogen environment from 35 to 1000 °C with a
115 temperature ramp rate of 10 °C/min. Each raw coal sample was also analyzed under the same

conditions for comparison. Multiple runs were performed to ensure the repeatability of results.

2.5. Fourier Transform Infrared (FTIR) Spectroscopic Analysis: FTIR analysis was carried out on a PerkinElmer Spectrum Two spectrometer, with a universal Attenuated Total Reflectance (ATR) sampling accessory and a scan range of 400 – 4000 cm^{-1} . The raw and IL-treated coals were both analyzed. The ILs used in this investigation were also analyzed before and after the treatment process via the same method.

2.6. Nuclear Magnetic Resonance (NMR) Spectroscopic Analysis. ^1H and ^{13}C NMR analysis was carried out on a Bruker AVANCE III 600 MHz on both the pure and recovered IL using D_2O as the solvent. Both standard and water depressed ^1H NMR were performed.

3. Results and discussion

3.1. Dissolution of coal

The eight amino acids chosen cover the three categories of amino acids, namely non-polar side chain (Ala, Gly, Leu, Val), polar side chain (Phe) and electronically charged side chain (acidic: Asp; basic: Arg, Lys). While there have been a few studies on the treatment of coal with ionic liquids [15, 17-19, 21], there has been a very little attempt to illuminate the interaction between the ILs and the coal bulk structure, largely due to the very complex nature of the coal. By examining 8 different amino acids, the objective here is to shed light on these interactions.

Upon treatment with the synthesized ILs, some mass loss was observed for both types of coal. Table 3 lists the recovery of total solids after treatment with ionic liquids. Larger mass loss signifies better dissolution of the coal into the ILs. Lignite dissolves more easily than thermal coal for most cases, despite being larger in size (841 μm and 120 μm , respectively). This is mainly because of the differences in the crosslinking structure and surface area of

both coal types [22]. Lignite being younger coal compared to thermal coal, the structure less cross-linked and less heterogeneous in nature and the surface is porous, has relatively slightly higher surface area, as reported in previous publications [23, 24]. Consequently, lignite dissolved more easily than the thermal coal.

The range of recovery of lignite was large, 31.8 – 91.6 wt%, while that for the thermal bituminous coal was limited to 63.8 – 86.6 wt% (Table 3). This difference further reflects the higher heterogeneity in the structure and lower surface area of the thermal coal. The IL [Ch][Arg] appeared to be the best solution for both types of coal. The elemental analysis of the [Ch][Arg] treated coals showed an elevated amount of nitrogen (4.91 and 4.44 wt% compared to 1.01 and 1.15 wt% in the raw coals, Table 3) which implies that some of this IL adhered so strongly to the coal surface that repeated washing by water/ethanol could not remove them. Strong attachment of ILs to their substrates have been reported for lignocellulosic biomass [25]. While it was not ideal in their case, since the residual IL molecules can inhibit the mixture of cellulase enzymes employed during downstream process, the consequence in the case of coal is certainly not as detrimental. Pre-treatment using the other seven ionic liquids showed no significant increase of nitrogen. However, despite less bonding than [Ch][Arg], reasonable level of interactions must have occurred since the coals still dissolved, albeit to a lesser extent, in these ionic liquids. The specific features of the ILs that interact with the coal will be thoroughly discussed in the last section. Despite the losses of amino acid based ILs in the pre-treatment due to the strong attachment of ILs on coal surface that would increase the operating cost of the overall process, the efficiency of such ILs compared to our previous results[18, 19] and data reported in the open literature is remarkably high [16].

There is a loss of sulphur in all IL pre-treatments, which is a very positive outcome since sulphur contributes to the formation of toxic gas (SO_2) during coal combustion. Currently,

165 sulphur is mostly removed post-combustion by a process called flue-gas desulfurization, most
166 often by absorption to water or alkali [26]. Pre-combustion desulfurization is mostly done by
167 physical separation based on the difference in specific gravity of the organic matter and
168 minerals in coal [27]. In contrast, chemical desulfurization is less common and usually
169 carried out with a strong base (NaOH) [28], by oxidation [29] or reduction [30]. The current
170 study would be most akin to the use of base, since the ILs are quite basic (pH 10.7 – 12.3 for
171 all but [Ch][Asp]). It is likely that the sulphur in the inorganic section of the coal (mostly
172 pyrite FeS) reacts with the base and thus dissolves into the ionic liquids.

173 In order to keep the synthesis as simple as possible and the cost of these ionic liquids low, no
174 attempt was made to remove the water. Furthermore, as the coals contain significant amount
175 of moisture, drying the ionic liquids was deemed uneconomical. Biomass processing with
176 ionic liquid-water mixtures instead of neat ILs is common [7, 13, 31, 32]. Aqueous solution
177 of 65 wt% 1-butyl-3-methylimidazolium methylsulfate was as effective as 90 wt% [7], and
178 concentration as low as 10 wt% ionic liquid was sufficient in the treatment of lignocellulosic
179 biomass [14].

180 Nevertheless, the effect of water on the pre-treatment was investigated. One of the eight ionic
181 liquids, [Ch][Lys], was dried under vacuum to a low water content of 8 wt%. Upon
182 concentration, [Ch][Lys] becomes more viscous and darker in yellow. The result was as
183 expected, with no significant difference between the dilute and the dried ionic liquids (see
184 Table 3).

185 Compared to the neat ionic liquids treatment in our previous work [19], which used neat
186 [Bpyd][Cl], [Emim][DCM], [Bmim][Cl] and [Bmim][TCM] on thermal coal, the recovery
187 was similar (70% – 82%). [Ch][Arg] solution is certainly on par with the best IL in our last
188 study, [Bmim][Cl], in terms of dissolving thermal coal, for their recovery was 63.8% and
189 72% respectively.

Table 3: Recovery of the coal after treatment with ionic liquids and their elemental analysis

*Recovery was calculated as final solid/ starting total solid i.e. moisture was excluded. Ultimate analyses were carried out on a dry weight and ash free basis, ^acalculated by subtracting C, H, N and S. Samples were measured in duplicates.

Coal	Treatment	Recovery (wt%)*	Rank	C	H	N	S	O ^a
Lignite	[Ch][Ala]	76.3	6	69.92 ± 0.15	4.17 ± 0.21	1.76 ± 0.07	0.27 ± 0.01	23.88 ± 0.28
	[Ch][Arg]	31.8	1	65.18 ± 0.15	3.97 ± 0.13	4.91 ± 0.06	0.24 ± 0.15	25.70 ± 0.36
	[Ch][Asp]	91.6	8	66.33 ± 0.02	4.06 ± 0.16	1.64 ± 0.17	0.26 ± 0.01	27.72 ± 0.01
	[Ch][Gly]	35.6	2	68.20 ± 0.14	4.02 ± 0.05	2.00 ± 0.07	0.28 ± 0.17	25.49 ± 0.44
	[Ch][Leu]	59.8	3	68.47 ± 0.06	4.20 ± 0.08	1.64 ± 0.16	0.13 ± 0.06	25.57 ± 0.07
	[Ch][Lys]	78.9	7	69.08 ± 0.01	4.52 ± 0.07	2.23 ± 0.02	0.22 ± 0.03	23.94 ± 0.07
	[Ch][Phe]	73.8	5	66.37 ± 0.02	3.01 ± 0.23	1.67 ± 0.11	0.16 ± 0.05	28.79 ± 0.09
	[Ch][Val]	63.6	4	69.23 ± 0.01	3.94 ± 0.20	1.41 ± 0.06	0.17 ± 0.08	25.25 ± 0.17
	Dry [Ch][Lys]	80.2		67.18 ± 0.08	4.10 ± 0.20	2.4 ± 0.15	0.22 ± 0.04	26.1 ± 0.10
	Raw			69.89 ± 0.50	3.63 ± 0.11	1.01 ± 0.02	0.34 ± 0.06	25.13 ± 0.53
	[Ch][Ala]	86.6	8	70.26 ± 0.26	3.78 ± 0.04	2.55 ± 0.48	0.45 ± 0.11	22.96 ± 0.29
	[Ch][Arg]	63.8	1	68.81 ± 0.07	4.00 ± 0.06	4.44 ± 0.06	0.34 ± 0.05	22.40 ± 0.02
	[Ch][Asp]	79.7	5	71.82 ± 0.57	3.48 ± 0.11	0.70 ± 0.05	0.29 ± 0.12	23.70 ± 0.40
	[Ch][Gly]	85.4	7	68.63 ± 0.27	3.84 ± 0.16	1.07 ± 0.02	0.22 ± 0.08	26.24 ± 0.52
Thermal	[Ch][Leu]	79.8	6	71.71 ± 0.49	3.98 ± 0.19	0.72 ± 0.02	0.28 ± 0.06	23.30 ± 0.23
	[Ch][Lys]	76.3	2	70.26 ± 0.16	3.97 ± 0.05	1.46 ± 0.05	0.28 ± 0.05	24.03 ± 0.02
	[Ch][Phe]	77.4	3	71.79 ± 0.28	4.31 ± 0.15	1.23 ± 0.01	0.15 ± 0.02	22.52 ± 0.40
	[Ch][Val]	78.6	4	70.95 ± 0.14	3.72 ± 0.12	1.26 ± 0.03	0.27 ± 0.15	23.80 ± 0.19
	Dry [Ch][Lys]	78.6		71.89 ± 0.30	3.80 ± 0.05	1.50 ± 0.06	0.25 ± 0.08	22.56 ± 0.45
	Raw			71.11 ± 0.49	3.80 ± 0.15	1.15 ± 0.08	0.94 ± 0.13	22.99 ± 0.84
	[Ch][Ala]							
	[Ch][Arg]							
	[Ch][Asp]							
	[Ch][Gly]							

3.2. Change in particle size of coal

Optical microscopy revealed a reduction in the size of the coal particles in most treatments (Figure 1, blue bar, full histograms of particle size distribution in ESI). Especially effective were the treatment of lignite using [Ch][Arg], [Ch][Gly] and [Ch][Phe], which reduce the size of the lignite particles from 3 – 5 times. The reduction in size correlates quite well with the mass recovered after the treatment, with the treatments that dissolve more of the coal leaving behind smaller fragments. The thermal coal also displayed a reduction in size to about half the raw coal, there is not much difference between the ionic liquids. Similar result was observed for [Bmim][Cl] in our previous study [18], which reduced the size of two types of thermal coal from 100 – 200 μm to around 10 – 50 μm . In a timed experiment, small amount of lignite and thermal coal was mixed with a drop of [Ch][Lys] and monitored over time at 70 °C using the optical microscope (Figure 2). Swelling of the particles appeared as early as 30 minutes and increased with time. The liquor darkened in colour, more significantly so for the lignite than the thermal coal. In contrast, coal treated with water did not change in appearance, there was also no leaking of colours from the coal to the liquid.

Figure 1: Particle size of raw coals and their treated counterparts, and percentage recovery of coal treatment. Blue bar: partical size, red line: recovery %, number on top of blue bar: number of measurements for each sample.

Figure 2: 50x Microscopic profile of lignite and thermal coal soaked in [Ch][Lys] on a heated stage at 70°C. Darkening of the solution and swelling of the particles can be observed.

3.3. Change in thermal properties of coal

The thermal properties of the raw coals and their treated counterparts were studied using TGA (Figure 3). Pyrolysis to 1000 °C caused the lignite and the thermal coal to lose 41.5 wt% and 35.1 wt% of their total solid masses, respectively. Treated lignite showed a slightly higher mass loss (i.e. 42.2 – 47.2 wt%) in comparison to treated thermal coal (35.0 – 40.3 wt%). In TGA, the first derivative of the “weight vs temperature” curve is an important tool, as it provides valuable insights about the materials that might have been overlooked from the original curve. Information such as the onset temperature of a transition, how many transitions/reactions there are, or at what temperature the fastest mass loss occurs, can be found in the first derivative curve. This curve of lignite shows two peaks, the first main peak at 422 °C and a small peak at 650 °C. Treated lignite shows a small additional peak at 252 –

299 °C, together with the same ~420 °C peak and ~650 °C peak. The appearance of the lower temperature peak indicates that a portion of the lignite structure has broken down into lower molecular weight fragments which decompose at a lower temperature. Similar observation was seen for the thermal coal, with one large broad peak at 442 °C and a smaller peak at 642 °C for the raw coal. After treatment with ionic liquids, an additional peak in the range of 271 – 291 °C appeared. These observations were similar to what was observed for the thermal coals that were treated with [Bmim][Cl] which also displayed two peaks at 400 °C and 250 °C [18].

Figure 3: TGA profile of lignite and thermal coal. Left axis: weight percentage. Right axis: first derivative over temperature dw/dt . 100% represents total solid only, water has been excluded.

3.4. Change in chemical composition/functional group on coal

FTIR analysis of the raw lignite (Figure 4) revealed absorption bands of OH ($\sim 3300\text{ cm}^{-1}$, broad, moisture and coal OH groups), aliphatic C-H (2850 cm^{-1}), aromatic C=C (1570 cm^{-1}) and C-O ($1000 - 1300\text{ cm}^{-1}$). Treated lignite showed reduction of the OH, the C-H and C-O bands, meaning some of the aliphatic C-H and alkoxy C-O had been lost to the ionic liquids. The reduction of the OH band is most likely due to the treated coal being dried in the oven after treatment, but can also be due to loss of OH within the coal. [Ch][Arg] and [Ch][Gly] showed the biggest reduction in C-O bands; the ratio of C-O/C=C intensity in the raw lignite was 1.04 while they were 0.64 and 0.67 for [Ch][Arg] and [Ch][Gly].

Raw thermal coal has a weaker OH and CH bands than lignite (Figure 5), reflecting its lower moisture content and its more rigid graphite like structure [33]. There are smaller changes

appeared after treatment with ILs. Only four out of the eight ILs caused a significant reduction in the C-O band, namely [Ch][Ala], [Ch][Arg], [Ch][Gly] and [Ch][Phe]. The ratio of C-O/C=C intensity in the raw thermal coal was 3.47 while they were 1.92, 1.80, 1.57 and 1.99 for [Ch][Ala], [Ch][Arg], [Ch][Gly] and [Ch][Phe], respectively.

The removal of oxygenated functional groups is a desirable outcome, since oxygen reduces the efficiency of converting coal to fuels/chemicals. It is likely that the C-O that was lost belong to hydroxyls (C-O-H) and not ether (C-O-C), since the ILs interact with the coal via hydrogen bonding in which the ILs is the hydrogen bond acceptor i.e. prefer to bond with OH rather than C-O (more discussion to follow in the last section)

Figure 4: FTIR spectra of raw lignite and its treated counterparts

Figure 5: FTIR spectra of raw thermal coal and its treated counterparts

3.5. Effect of the pre-treatment on the ionic liquids

The ionic liquids prior to pre-treatment with the coal have a clear faint yellow colour. ^1H NMR was done to ensure that the molar ratio of choline: amino acid was indeed 1 to 1. No contaminants were seen in the ^1H NMR and ^{13}C NMR. The pH of the ionic liquid solutions (diluted by 100 times, to protect the pH probe) were in the range of 10.7 – 12.3 (Table 1), except for $[\text{Ch}][\text{Asp}]$ which has pH 6.17. This is expected since most amino acids are weak

acids, except for aspartic acid. FTIR of the ionic liquids (see ESI) show absorbance for the amino NH_2 and the carboxylate COO^- groups ($\text{C}=\text{O}$, $1550 - 1610 \text{ cm}^{-1}$), together with other bands signature for each amino acid.

FTIR spectra (see ESI) of the recovered liquors of $[\text{Ch}][\text{Gly}]$, $[\text{Ch}][\text{Lys}]$ and $[\text{Ch}][\text{Leu}]$ show additional appearance of the C-H ($\sim 2850 \text{ cm}^{-1}$) and $\text{C}=\text{O}$ ($\sim 1750 \text{ cm}^{-1}$) bands. The C-H band is in complement to the disappearance of this band from the treated coal (Figure 4). The $\text{C}=\text{O}$ band at 1750 cm^{-1} signifies a $\text{C}=\text{O}$ stretch of a carboxylic group, meaning some of the amino acid carboxylate anion has been protonated and became carboxylic acid. This evidence further supports the hypothesis that the interaction between the ILs and the coal is of H-bonding nature, with the COO^- bonding and eventually deprotonating some hydrogen on the coal. Other ionic liquids show no change in their IR spectra, possibly due to the small concentration of the dissolved coal as compared to the IL concentration.

^1H NMR (Table 4) of the lignite liquors reviewed protonation of the COO^- of the amino acid anion. While the COOH cannot be directly seen on the ^1H NMR (due to the fast exchange with the surrounding H_2O molecules), the change in the electron density of the branching hydrogens can be detected. In some cases, when the COO^- form and the COOH form exchange very fast, an average downfield shift can be observed. In other cases, both forms were observed (ALA and VAL). ^{13}C NMR displayed the protonation of the COO^- as well, with some IL liquors showing both COO^- and COOH (see Table 5). In addition, in some cases, there are extra peaks belonging to the coal observed in the region $150 - 170 \text{ ppm}$ and $57 - 40 \text{ ppm}$, which represent $\text{C}=\text{C}$ and $\text{C}-\text{O}$ respectively. By contrast, the $[\text{Bmim}][\text{Cl}]$ recovered after thermal coal treatment did not show any extra peaks in its ^{13}C NMR spectrum [18], this is likely due to the fact that $[\text{Bmim}][\text{Cl}]$ is a solid at room temperature which makes its recovery slightly different to the choline amino acid ILs.

While there are many changes to the amino acid anion shifts after treatment with coal, the choline cation showed little change in both its ^1H NMR and ^{13}C NMR. This implies that the anion interacts with the coal surface more strongly than the cation, and hence has a more important role in coal pretreatment. This finding is in agreement with the current opinion on lignocellulosic biomass pretreatment [9], in which the anion generally plays a more significant role in determining biomass dissolution than the cation.

Overall, lignite treatment caused more changes to the chemical shifts of the ILs than thermal coal. All but [Ch][Phe] and [Ch][Asp] lignite liquors showed protonation of the COOH, as evident by both the ^1H NMR and ^{13}C NMR. The appearance of C=C and C-O and aliphatic C further confirms the ability of some of these ILs in removing parts of the coal.

Table 4: ^1H NMR assignment of the pure ILs and their recovered liquors from the coal treatment. Choline shifts are not shown in the table, they were fairly constant across all samples and had values of 3.94 (t, CH_2OH), 3.40 (t, NCH_2), 3.09 (s, NCH_3)

A.A	^1H NMR peaks (ppm)		
	Pure IL peak	Lignite	Thermal
Ala	3.25 (q, CH_3)	3.43	3.25
	1.14 (d, CH)	1.19, 1.06	1.14
Arg	3.09 (t, CH_2N)	3.22	3.15
	3.00 (t, CH)	3.00	3.03
	1.39–1.50 (m, $\text{CH}_2\text{CH}_2\text{CH}_2$)	1.43–1.72	1.39–1.63
Asp	3.76 (dd, CH)	3.79	3.78
	2.67 (dd, $\text{CH}_a\text{H}_b\text{COOH}$)	2.71	2.70
	2.56 (dd, $\text{CH}_a\text{H}_b\text{COOH}$)	2.57	2.57
Gly	Gly CH_2 was overlapped by choline CH_3		
Leu	3.23 (dd, CH)	3.29	3.31
	1.56 (m, $\text{CH}(\text{CH}_3)_2$)	1.56	1.57
	1.40 (m, $\text{CH}_a\text{H}_b\text{CH}$)	1.45	1.45
	1.31 (m, $\text{CH}_a\text{H}_b\text{CH}$)	1.38	1.36
	0.81 (dd, CH_3)	0.83	0.83
Lys	3.15 (t, CH)	3.31, 3.24	3.34
	2.61 (t, CH_2NH_2)	2.89, 2.84	2.87
	1.44–1.57 (m, CHCH_2)	1.48–1.67	1.47–1.69
	1.41 (quin, $\text{CH}_2\text{CH}_2\text{NH}_2$)	1.19–1.39	1.20–1.39
	1.25 (quin, CHCH_2CH_2)	1.13	1.14

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Phe	7.26–7.29 (Ph,2H)	7.22–7.28	7.22–7.28
	7.17–7.22 (Ph,3H)	7.14–7.21	7.14–7.21
	3.41(dd,CH)	3.41	3.43
	2.90 (dd,CH _a H _b Ph)	2.91	2.93
	2.75 (dd,CH _a H _b Ph)	2.74	2.75
Val	2.96 (d, CH)	3.33	3.22
	1.83 (m, CH(CH ₃) ₂)	1.83	1.98, 1.85
	0.83 (d,CH ₃)	0.89, 0.81	0.86, 0.78
	0.76 (d, CH ₃)	0.84, 0.75	0.80, 0.72

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310 Table 5: ^{13}C NMR of the amino acid anion of the pure ILs and their recovered liquor after coal treatment.

311 Choline ion shifts are not shown in the table, they were fairly constant across all samples and had values in the range of
 312 67.39 – 67.87 (NCH_2), 55.55 – 55.60 (CH_2OH), 53.74 – 53.86 (CH_3)

A.A.	^{13}C NMR peaks (ppm)		
	Pure IL peak	Lignite	Thermal
Ala	183.54 (COO^-)	182, 178	182.7
	51.38 (CH)	52.39, 50.71	51.27
	20.07 (CH_3)	19.09, 17.54	19.72, 16.91
Arg	182.97 (COO^-)	181.23, 180.82	182.9, 180.85
	157.45 ($\text{C}=\text{NH}$)	156.71	156.87
	55.6 (CH)	55.25	55.47
	41.03 (CH_2NH)	40.82	40.94
	31.77 (CHCH_2)	31.77	31.37
	24.61 ($\text{CHCH}_2\text{CH}_2\text{CH}_2$)	24.42	24.41
		Extra peaks: 164.56, 163.57, 162.56 ($\text{C}=\text{C}$ aromatic); 57.3, 56.26, 30.9, 30.10 ($\text{C}-\text{O}$); 16.9 (aliphatic C)	Extra peaks: 166.03, 163.59, 162.52 ($\text{C}=\text{C}$ aromatic); 57.32, 56.29, 30.9, 30.20 ($\text{C}-\text{O}$); 16.9 (aliphatic C)
Asp	177.37 (branch COOH)	177.40	177.28
	174.11 (COO^-)	174.14	174.09
	52.3 (CH)	52.19	52.14
	36.6 (CH_2COOH)	36.5	36.45
Gly	180.42 (COO^-)	179.94, 178.84	179.71, 178.96
	44.38 (CH_2)	44.3	45.6
		Extra: 175.87, 170.67, 164.04 ($\text{C}=\text{O}$), 57.35, 45.52, 41.94 ($\text{C}-\text{O}$), 16.9 (aliphatic C)	Extra: 164.1 ($\text{C}=\text{O}$), 57.39, 44.14, 41.94 ($\text{C}-\text{O}$), 16.9 (aliphatic C)
Leu	182.96 (COO^-)	181.47	182.71, 178.20
	43.59 (CH)	42.83	42.13, 41.15
	24.35 (CH_2)	24.30	24.56, 24.20
	22.40 (CH_2CH)	22.31	22.56, 22.14
	21.31 (CH_3)	21.21	21.24, 21.03
		Extra: 57.42 ($\text{C}-\text{O}$), 16.8 (aliphatic C)	Extra: 161.43 ($\text{C}=\text{C}$) 57.42 ($\text{C}-\text{O}$), 16.8 (aliphatic C)
Lys	(COO^-) 183.43	182.89, 183.23	184.43
	(CH) 55.59	55.80	55.59
	(CH_2NH_2) 40.14	40.99, 40.55	39.32
	(CHCH_2) 34.28	32.06, 31.70	32.35
	($\text{CH}_2\text{CH}_2\text{NH}_2$) 30.47	27.97	26.94
	(CHCH_2CH_2) 22.24	24.51	21.74
		Extra: 168.06, 156.84 ($\text{C}=\text{C}$)	

Phe	183.43 (COO ⁻)	181.16	180.87
	138.17, 129.45, 128.64, 126.71 (Ph)	138.08, 129.46, 128.67, 126.75	137.96, 129.47, 128.69, 126.79
	57.41 (CH)	57.34	57.27
	40.57 (CH ₂)	40.42	40.26
		Extra peak: 17.00 (aliphatic C)	Extra peak: 16.97 (aliphatic C)
Val	182.03 (COO ⁻)	182.03	181.13, 176.84
	61.74 (CH)	61.74	62.37, 60.82
	31.52 (CH(CH ₃) ₂)	31.21, 30.21	31.19, 29.86
	19.02 (CH ₃)	18.97, 18.43	18.94, 18.25
	16.71 (CH ₃)	17.15, 16.66	17.10, 16.63
		Extra: 163.98, 161.30 (C=C), 11.97 (aliphatic C)	Extra: 163.89, 161.87 (C=C)

3.6. Discussion on features that govern the ability of ionic liquids in dissolving coal

[Ch][Arg] is superior for dissolving both lignite and thermal coal. Previous research concerning lignocellulosic biomass pre-treatment with ILs has shown ions with many H-bond sites are best performing (e.g. [Emim][OAc], [Bmim][HSO₄]) [7, 9, 34]. Both coal and lignocellulosic biomass possess OH groups that extensively H-bond to create a strong cross-linked network. ILs with significant H-bonding capacity intercalate and disrupt this network to effect dissolution. In our previous study, [Bmim][Cl] was the most effective pretreatment agent, and it also has a strong H-bond acceptor Cl⁻ anion [18]. On this basis, the superior effectiveness of choline arginate over other choline amino acids is attributed to the number of hydrogen bond donor/acceptor sites. The R branch of arginate (-CH₂CH₂CH₂NHC(=NH)NH₂) provides 3 extra possible H-bonding sites, in addition to the NH₂ and the COO⁻ groups that are present on all amino acids (Table 1). However, it is not just the number of hydrogen-bonding sites that matter. [Ch][Asp] has 5 H-bond sites, only one less than [Ch][Arg], but is not effective for dissolving coal (rank 8/8 and 5/8 for lignite and thermal coal). However, the aspartate anion is fundamentally different to the arginate ion, in that aspartate is acidic while arginate is basic. In other words, aspartate would be better at hydrogen donating while arginate would be better at hydrogen accepting. This shows that H-

bond accepting ability is crucial in determining the ability of the ionic liquid to dissolve the coal. [Ch][Lys], the other ionic liquid that is similar to [Ch][Arg] in that its has a NH₂ group on the side chain, also worked quite well for thermal coal (ranked 2/8), though not as well with lignite coal (ranked 7/8). The reason for this difference is the topic of continued study. Another factor to take into account when considering the effectiveness of the ILs is their relative molecular sizes. It might be the reason for [Ch][Gly] effectiveness since it has the smallest amino acid, presumably allowing it to insert easily into the porous structure of lignite (ranked 2/8 in lignite pretreatment). Basicity of the ionic liquid/water mixtures also plays an important role, evident by the inertness of [Ch][ASP] (pH 6.17) compared to other amino acid based ILs (pH 10.7 – 12.3). π - π stacking does not appear to be a possible interaction, for [Ch][Phe] coal displays very little difference after treatment. Non-polar amino acids (Ala, Val and Leu) were less effective. Finally, the presence of water does not diminish the effectiveness of the choline amino acid ILs, as evident by the case of dried [Ch][Lys], which behaves similarly to aqueous [Ch][Lys].

4. Conclusion

We have demonstrated the use of relatively low cost ionic liquid-water mixtures in the treatment of coal. Choline arginate and choline glycinate were the two best ionic liquids in this series. Treatment of coal by ionic liquids reduces the decomposition temperature of coals, the size of the coal particles, and removes Sulphur and oxygenated functional groups, all of which are beneficial to downstream combustion of coal. Comparison of results obtained for the different ionic liquids reveals that the ability of the ions to accept hydrogen bonds is critical for coal pre-treatment.

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Table 1

Table 1: List of ionic liquids, their abbreviations, classification and final water content

IL	Cation	Anion	Anion classification	Number of possible H-bonds on anion	Abbrev.	Water (wt%)	pH (100x diluted)
Choline L-alaninate			Non-polar	3	[Ch][ALA]	40.35	11.22
Choline L-argininate			Basic positively charged at pH 7	6	[Ch][ARG]	32.51	12.31
Choline L-aspartate			Acidic negatively charged at pH 7	5	[Ch][ASP]	35.87	6.17
Choline glycinate			Non-polar	3	[Ch][GLY]	42.02	11.07
Choline L-leucinate			Non-polar	3	[Ch][LEU]	59.00	10.71
Choline L-lysinate			Basic positively charged at pH 7	4	[Ch][LYS]	34.73	11.80
Choline L-phenyl-alaninate			Polar	3	[Ch][PHE]	33.19	10.99
Choline L-valaninate			Non-polar	3	[Ch][VAL]	37.38	10.89

Table 2

Table 2: Proximate and ultimate analyses of the coals used in this study

Coal	Proximate analysis				Ultimate analysis ^a				
	% M	% A	% VM	% FC	% C	% H	% N	% S	% O ^b
Lignite	10.99	6.61	51.32	31.08	69.89	3.63	1.01	0.34	25.13
Thermal	10.31	16.44	44.19	29.06	71.11	3.80	1.15	0.94	22.99

M: Moisture, A: Ash, VM: Volatile Matter, FC: Fixed carbon. ^aUltimate analyses were carried out on a dry weight and ash free basis, ^bcalculated by subtracting C, H, N and S.

Table 3

Table 3: Recovery of the coal after treatment with ionic liquids and their elemental analysis

*Recovery was calculated as final solid/ starting total solid i.e. moisture was excluded. Ultimate analyses were carried out on a dry weight and ash free basis, ^acalculated by subtracting C, H, N and S. Samples were measured in duplicates.

Coal	Treatment	Recovery (wt%)*	Rank	C	H	N	S	O ^a
Lignite	[Ch][Ala]	76.3	6	69.92 ± 0.15	4.17 ± 0.21	1.76 ± 0.07	0.27 ± 0.01	23.88 ± 0.28
	[Ch][Arg]	31.8	1	65.18 ± 0.15	3.97 ± 0.13	4.91 ± 0.06	0.24 ± 0.15	25.70 ± 0.36
	[Ch][Asp]	91.6	8	66.33 ± 0.02	4.06 ± 0.16	1.64 ± 0.17	0.26 ± 0.01	27.72 ± 0.01
	[Ch][Gly]	35.6	2	68.20 ± 0.14	4.02 ± 0.05	2.00 ± 0.07	0.28 ± 0.17	25.49 ± 0.44
	[Ch][Leu]	59.8	3	68.47 ± 0.06	4.20 ± 0.08	1.64 ± 0.16	0.13 ± 0.06	25.57 ± 0.07
	[Ch][Lys]	78.9	7	69.08 ± 0.01	4.52 ± 0.07	2.23 ± 0.02	0.22 ± 0.03	23.94 ± 0.07
	[Ch][Phe]	73.8	5	66.37 ± 0.02	3.01 ± 0.23	1.67 ± 0.11	0.16 ± 0.05	28.79 ± 0.09
	[Ch][Val]	63.6	4	69.23 ± 0.01	3.94 ± 0.20	1.41 ± 0.06	0.17 ± 0.08	25.25 ± 0.17
	Dry [Ch][Lys]	80.2		67.18 ± 0.08	4.10 ± 0.20	2.4 ± 0.15	0.22 ± 0.04	26.1 ± 0.10
	Raw			69.89 ± 0.50	3.63 ± 0.11	1.01 ± 0.02	0.34 ± 0.06	25.13 ± 0.53
	[Ch][Ala]	86.6	8	70.26 ± 0.26	3.78 ± 0.04	2.55 ± 0.48	0.45 ± 0.11	22.96 ± 0.29
	[Ch][Arg]	63.8	1	68.81 ± 0.07	4.00 ± 0.06	4.44 ± 0.06	0.34 ± 0.05	22.40 ± 0.02
	[Ch][Asp]	79.7	5	71.82 ± 0.57	3.48 ± 0.11	0.70 ± 0.05	0.29 ± 0.12	23.70 ± 0.40
Thermal	[Ch][Gly]	85.4	7	68.63 ± 0.27	3.84 ± 0.16	1.07 ± 0.02	0.22 ± 0.08	26.24 ± 0.52
	[Ch][Leu]	79.8	6	71.71 ± 0.49	3.98 ± 0.19	0.72 ± 0.02	0.28 ± 0.06	23.30 ± 0.23
	[Ch][Lys]	76.3	2	70.26 ± 0.16	3.97 ± 0.05	1.46 ± 0.05	0.28 ± 0.05	24.03 ± 0.02
	[Ch][Phe]	77.4	3	71.79 ± 0.28	4.31 ± 0.15	1.23 ± 0.01	0.15 ± 0.02	22.52 ± 0.40
	[Ch][Val]	78.6	4	70.95 ± 0.14	3.72 ± 0.12	1.26 ± 0.03	0.27 ± 0.15	23.80 ± 0.19
	Dry [Ch][Lys]	78.6		71.89 ± 0.30	3.80 ± 0.05	1.50 ± 0.06	0.25 ± 0.08	22.56 ± 0.45
	Raw			71.11 ± 0.49	3.80 ± 0.15	1.15 ± 0.08	0.94 ± 0.13	22.99 ± 0.84
	[Ch][Ala]							
	[Ch][Arg]							
	[Ch][Asp]							
	[Ch][Gly]							
	[Ch][Leu]							
	[Ch][Lys]							
	[Ch][Phe]							
	[Ch][Val]							
	Dry [Ch][Lys]							
	Raw							

Table 4

Table 4: ^1H NMR assignment of the pure ILs and their recovered liquors from the coal treatment. Choline shifts are not shown in the table, they were fairly constant across all samples and had values of 3.94 (t, CH_2OH), 3.40 (t, NCH_2), 3.09 (s, NCH_3)

A.A	^1H NMR peaks (ppm)		
	Pure IL peak	Lignite	Thermal
Ala	3.25 (q, CH_3)	3.43	3.25
	1.14 (d, CH)	1.19, 1.06	1.14
Arg	3.09 (t, CH_2N)	3.22	3.15
	3.00 (t, CH)	3.00	3.03
	1.39–1.50 (m, $\text{CH}_2\text{CH}_2\text{CH}_2$)	1.43–1.72	1.39–1.63
Asp	3.76 (dd, CH)	3.79	3.78
	2.67 (dd, $\text{CH}_a\text{H}_b\text{COOH}$)	2.71	2.70
	2.56 (dd, $\text{CH}_a\text{H}_b\text{COOH}$)	2.57	2.57
Gly	Gly CH_2 was overlapped by choline CH_3		
Leu	3.23 (dd, CH)	3.29	3.31
	1.56 (m, $\text{CH}(\text{CH}_3)_2$)	1.56	1.57
	1.40 (m, $\text{CH}_a\text{H}_b\text{CH}$)	1.45	1.45
	1.31 (m, $\text{CH}_a\text{H}_b\text{CH}$)	1.38	1.36
	0.81 (dd, CH_3)	0.83	0.83
Lys	3.15 (t, CH)	3.31, 3.24	3.34
	2.61 (t, CH_2NH_2)	2.89, 2.84	2.87
	1.44–1.57 (m, CHCH_2)	1.48–1.67	1.47–1.69
	1.41 (quin, $\text{CH}_2\text{CH}_2\text{NH}_2$)	1.19–1.39	1.20–1.39
	1.25 (quin, CHCH_2CH_2)	1.13	1.14
Phe	7.26–7.29 (Ph, 2H)	7.22–7.28	7.22–7.28
	7.17–7.22 (Ph, 3H)	7.14–7.21	7.14–7.21
	3.41 (dd, CH)	3.41	3.43
	2.90 (dd, $\text{CH}_a\text{H}_b\text{Ph}$)	2.91	2.93
	2.75 (dd, $\text{CH}_a\text{H}_b\text{Ph}$)	2.74	2.75
Val	2.96 (d, CH)	3.33	3.22
	1.83 (m, $\text{CH}(\text{CH}_3)_2$)	1.83	1.98, 1.85
	0.83 (d, CH_3)	0.89, 0.81	0.86, 0.78
	0.76 (d, CH_3)	0.84, 0.75	0.80, 0.72

Table 5: ^{13}C NMR of the amino acid anion of the pure ILs and their recovered liquor after coal treatment.

Choline ion shifts are not shown in the table, they were fairly constant across all samples and had values in the range of 67.39 – 67.87 (NCH_2), 55.55 – 55.60 (CH_2OH), 53.74 – 53.86 (CH_3)

A.A.	^{13}C NMR peaks (ppm)		
	Pure IL peak	Lignite	Thermal
Ala	183.54 (COO^-)	182, 178	182.7
	51.38 (CH)	52.39, 50.71	51.27
	20.07 (CH_3)	19.09, 17.54	19.72, 16.91
Arg	182.97 (COO^-)	181.23, 180.82	182.9, 180.85
	157.45 ($\text{C}=\text{NH}$)	156.71	156.87
	55.6 (CH)	55.25	55.47
	41.03 (CH_2NH)	40.82	40.94
	31.77 (CHCH_2)	31.77	31.37
	24.61 ($\text{CHCH}_2\text{CH}_2\text{CH}_2$)	24.42	24.41
		Extra peaks: 164.56, 163.57, 162.56 ($\text{C}=\text{C}$ aromatic); 57.3, 56.26, 30.9, 30.10 ($\text{C}-\text{O}$); 16.9 (aliphatic C)	Extra peaks: 166.03, 163.59, 162.52 ($\text{C}=\text{C}$ aromatic); 57.32, 56.29, 30.9, 30.20 ($\text{C}-\text{O}$); 16.9 (aliphatic C)
Asp	177.37 (branch COOH)	177.40	177.28
	174.11 (COO^-)	174.14	174.09
	52.3 (CH)	52.19	52.14
	36.6 (CH_2COOH)	36.5	36.45
Gly	180.42 (COO^-)	179.94, 178.84	179.71, 178.96
	44.38 (CH_2)	44.3	45.6
		Extra: 175.87, 170.67, 164.04 ($\text{C}=\text{O}$), 57.35, 45.52, 41.94 ($\text{C}-\text{O}$), 16.9 (aliphatic C)	Extra: 164.1 ($\text{C}=\text{O}$), 57.39, 44.14, 41.94 ($\text{C}-\text{O}$), 16.9 (aliphatic C)
Leu	182.96 (COO^-)	181.47	182.71, 178.20
	43.59 (CH)	42.83	42.13, 41.15
	24.35 (CH_2)	24.30	24.56, 24.20
	22.40 (CH_2CH)	22.31	22.56, 22.14
	21.31 (CH_3)	21.21	21.24, 21.03
		Extra: 57.42 ($\text{C}-\text{O}$), 16.8 (aliphatic C)	Extra: 161.43 ($\text{C}=\text{C}$) 57.42 ($\text{C}-\text{O}$), 16.8 (aliphatic C)
Lys	(COO^-) 183.43	182.89, 183.23	184.43
	(CH) 55.59	55.80	55.59
	(CH_2NH_2) 40.14	40.99, 40.55	39.32
	(CHCH_2) 34.28	32.06, 31.70	32.35
	($\text{CH}_2\text{CH}_2\text{NH}_2$) 30.47	27.97	26.94
	(CHCH_2CH_2) 22.24	24.51	21.74
		Extra: 168.06, 156.84 ($\text{C}=\text{C}$)	

Phe	183.43 (COO ⁻) 138.17, 129.45, 128.64, 126.71 (Ph) 57.41 (CH) 40.57 (CH ₂)	181.16 138.08, 129.46, 128.67, 126.75 57.34 40.42 Extra peak: 17.00 (aliphatic C)	180.87 137.96, 129.47, 128.69, 126.79 57.27 40.26 Extra peak: 16.97 (aliphatic C)
Val	182.03 (COO ⁻) 61.74 (CH) 31.52 (CH(CH ₃) ₂) 19.02 (CH ₃) 16.71 (CH ₃)	182.03 61.74 31.21, 30.21 18.97, 18.43 17.15, 16.66 Extra: 163.98, 161.30 (C=C), 11.97 (aliphatic C)	181.13, 176.84 62.37, 60.82 31.19, 29.86 18.94, 18.25 17.10, 16.63 Extra: 163.89, 161.87 (C=C)

Ionic Liquids

Hydrogen bonding

Coal

Partially dissolved
Fragmentation
Swelling
Loss of sulphur