



# Pretreatment of coal by ionic liquids towards coal electrolysis liquefaction



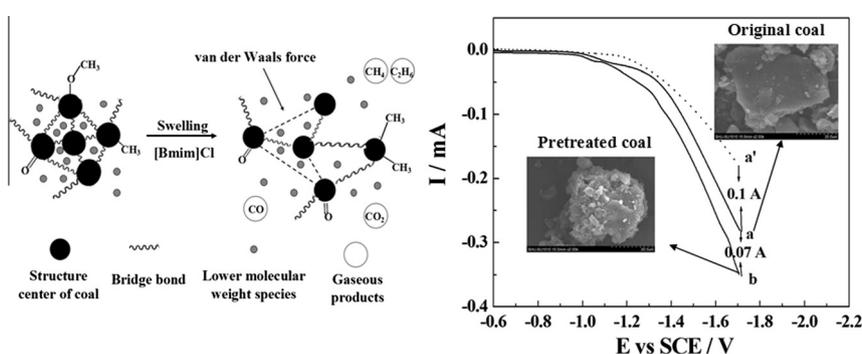
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## HIGHLIGHTS

- Coal is pretreated by ionic liquids (ILs).
- [Bmim]Cl exhibits the best performance of coal extraction and swelling.
- The mechanism for pretreatment of coal in IL is proposed.
- IL-pretreated coal is electrolyzed on a Ni–W–B electrode.
- Pretreatment with IL promotes the coal electrolysis liquefaction (CEL) substantially.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Ionic liquids have been employed to pretreat coal to modify its network structure, and thus to improve the electroreduction activity of coal on a Ni–W–B catalytic electrode. Among the pretreatment solvents, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) exhibits the best performance of coal extraction and swelling. The coal sample is pretreated by [Bmim]Cl at optimized temperature (150 °C), then the pretreated coal is analyzed and characterized by scanning electron microscopy, gas chromatograph, infrared spectroscopy and linear sweep voltammetry. The results show that the coal network is fractured, resulting in a loose and porous structure, which facilitates hydrogenation reactions of coal on the catalytic electrode. A liquefaction yield of 57.6% is realized after electrolysis of coal on the catalytic electrode for 24 h at  $-1.7$  V in a NaOH + H<sub>2</sub>O + tetrabutylammonium bromide mixed electrolyte system, 15% higher compared to the coal without pretreatment (40.3%). The mechanism for the pretreatment of coal in ionic liquids has been proposed.

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## 1. Introduction

Coal is the most abundant fossil fuel in the world, and also a vital global energy source, although consumption of pulverized coal leads to severe environment pollution. Limited growth in petroleum supply and uneven petroleum market results in a significant gap between supply and demand of the liquid fuel [1–3].

Therefore, the development of an economically viable process for direct coal liquefaction (DCL) remains as an important goal for fuel science and technology [4]. Industrial DCL refers to hydrogenation of coal performed usually at 385–425 °C and an elevated H<sub>2</sub> pressure [5], which leads to great waste of energy and high cost of equipment. In recent years, coal electrolysis liquefaction (CEL) under clean and mild reaction conditions has attracted much attentions and has become a promising alternative to DCL [6,7].

Coal is a sedimentary rock with large three-dimensional cross-linked macromolecular network of polynuclear aromatic clusters

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connected by relatively strong bonds, such as ether bridge bonds, etc. [8]. And a small amount of low molecular weight constituents is trapped in the network [9]. Coal is featured with most of its surface covered with micropores less than 1 nm in diameter, which is hard for the access of active  $H^+$  and catalyst to coal reactive sites inside the coal network [10]. Therefore, pretreatment of coal, which can break the coal network, expand the pores and increase the mobility of small molecules trapped in the network of the coal, is essential to CEL. Many studies have reported that in the presence of hydrocarbon solvents, such as tetrahydrofuran (THF), toluene, pyridinium, N-methyl pyrrolidinone (NMP) and other mixed organic solvents, non-covalent interactions within the coal network can be disrupted and relaxed [11–13]. However, these traditional solvents are volatile, toxic, and difficult to be recycled [14]. Hence, highly efficient, green and recyclable solvents are desired.

Ionic liquids (ILs), which are featured with special physico-chemical properties such as low melting point, non-flammability, recyclability and negligible volatility, have been used widely as novel solvents [15,16]. Meanwhile, it has been reported that ionic liquids can be used to fragment, disperse, and partially dissolve coal. For example, Cummings et al. have reported that ionic liquid can swell and disrupt the network of coal, and is a potential solvent to be used to pretreat coal for DCL [17]. Lei et al. have reported that with the increase of the oxygen content and the decrease of carbon content, the extract yield of coal with 1-butyl-3-methylimidazolium chloride significantly increases [18].

In this paper, ILs are employed to pretreat coal at optimized temperature. The pretreated coal is characterized by scanning electron microscopy (SEM), gas chromatograph, and infrared (IR) spectroscopy. The pretreated coal sample is electrolyzed on a catalytic electrode (Cu/Ni–W–B) in  $NaOH + H_2O +$  tetrabutylammonium bromide (TBAB) mixed electrolyte system. Electrochemical hydrogenation of the pretreated coal has been studied by linear sweep voltammetry (LSV), and the liquefaction products are analyzed.

## 2. Experimental

### 2.1. Regents and apparatus

Coal sample is from Shenhua Group of China, and it is a typical lignite used for DCL. Lignite is the coal of the lowest rank, and it is an important energy resource due to the enormous reserve. In addition, lignite has the advantages of high reactivity, low mining cost and low content of heteroatoms such as sulfur, nitrogen [19,20]. Therefore, Shenhua coal is chosen as a coal liquefaction model in this work. The coal was crushed, ball milled and sieved to <200 mesh. The obtained coal particles were washed with 1 mol/L  $H_2SO_4$  for 5 h, and then filtered and dried in vacuum for 24 h at 110 °C [21,22]. Ionic liquids including 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-butyl-3-methylimidazolium bromine ([Bmim]Br), 1-hexyl-3-methylimidazolium chloride ([HMim]Cl), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim]OTf), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF<sub>4</sub>) and 1-butylpyrrolidinium tetrafluoroborate ([BPy]BF<sub>4</sub>) with purity 99% were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Science. N-methyl-2-pyrrolidone (NMP), TBAB and NaOH were obtained from Sinopharm Chemical Reagent Co., Ltd. (China).

The electrochemical measurements were carried out using a CHI660D electrochemical workstation (CHI, China). IR spectra were recorded within 400–4000  $cm^{-1}$  region on an AVATAR 370 Fourier transform infrared spectrometer (Nicolet, America). SEM images were taken on a scanning electron microscope (JEOL JSM-6700F, Japan) at 15 kV. The species in the gas sample were analyzed by a gas chromatograph (KC Chromatograph, GC-900A) equipped with

hydrogen flame ionization (FID) and thermal conductivity (TCD) detectors. 1 g coal and 10 g IL were sealed in a glass tube to perform the pretreatment experiment. After the pretreatment, 1 mL of gas was taken from the sealed sample tubes by using an injector, and then injected into the GC immediately. Alkanes were analyzed using FID detector, aluminum oxide as the chromatographic column and nitrogen (99.99%) as the carrier gas with a flow rate of 11 mL/min. The temperature of oven, gasification chamber and detector is 40 °C, 110 °C and 110 °C, respectively. Carbon monoxide and carbon dioxide was analyzed using the TCD detector, the chromatographic column is 5 Å molecular sieve column and the carrier gas is helium (99.99%) with a flow rate of 5 mL/min. The temperature of oven, gasification chamber and detector is 50 °C, 110 °C and 110 °C, respectively.

### 2.2. Extract yield and swelling measurements

Extraction experiments of coal with ILs were carried out according to the following procedure: First, ionic liquid (10.0 g) was put in a dry flask and mixed with coal (1.0 g) at a specific temperature for 2 h under magnetic stirring. Second, the insoluble components were separated by a vacuum filter with a polytetrafluoroethylene membrane (particle retention size is 1.2  $\mu m$ ). Third, soluble components were precipitated from the IL solution using deionized water as a back-extractant, and then the precipitates were separated from the aqueous solution by an air filtration pump. The extracts were dried overnight at 70 °C. The extract yield (EY) is calculated according to the following equation:

$$EY = M_1/M_0 \times 100\% \quad (1)$$

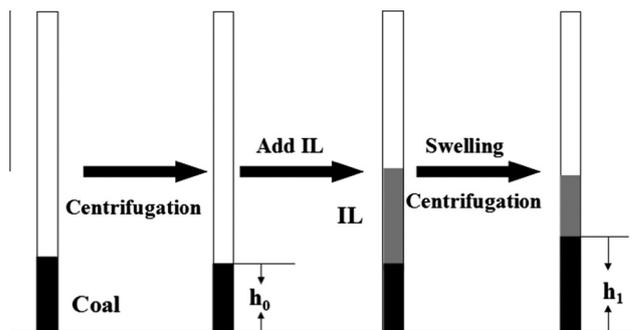
where  $M_1$  is the mass of extracts, and  $M_0$  is the mass of coal sample (1.0 g).

Volumetric method was used to measure the swelling ratio ( $Q$ ) of the sample [23]. As shown in Scheme 1, coal sample (0.1 g) was placed in a 4 mm inner diameter glass tube and centrifuged for 30 min at 1500 rpm. The height of the coal layer was measured as  $h_0$ . Then 0.6 mL of solvent was added and mixed with the sample. The sample was again centrifuged, and the height of the coal layer  $h_1$  was measured. The swelling ratio was calculated according to the following equation:

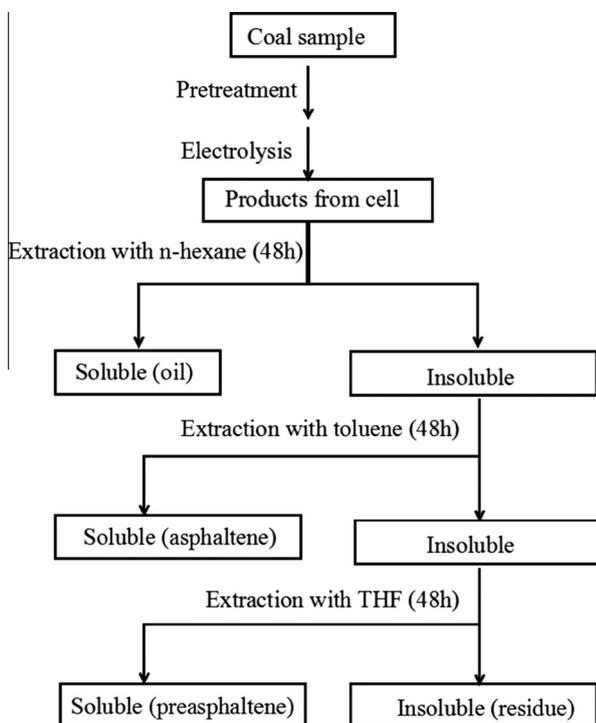
$$Q = h_1/h_0 \quad (2)$$

### 2.3. Pretreatment of coal samples

Coal (1.0 g) and IL (10.0 g) were mixed in glass tubes for the pretreatment, which was carried out under controlled temperature, time and stirring. Then the sample was cooled down to room temperature and the mixture was washed by water thoroughly to remove the IL, and then dried in vacuum at 70 °C overnight. The IL can be reused after removal of water under vacuum [24].



Scheme 1. Procedure of volumetric method for measuring the swelling ratio of coal.



Scheme 2. Separation procedure of coal liquefaction products.

#### 2.4. Electrolysis procedure

Electrochemical experiments were carried out using an H-type electrolytic cell, whose compartments were separated by a microporous membrane. A saturated calomel electrode (SCE), a platinum sheet (3 cm × 3 cm) and an electrocatalytic Cu/Ni-W-B (2 × 2 cm) electrode are employed as reference electrode, counter electrode and working electrode, respectively [21]. The electrolyte in the cathode part is 50 mL, consisting of 1 mol/L NaOH, 0.5 mol/L TBAB, and 20 g/L coal. TBAB as a phase transfer catalyst can improve the dispersion of coal in electrolyte, which promotes the reaction of insoluble fractions with active H<sup>+</sup> on the catalytic electrode [25,26]. The composition and volume of electrolyte in the anode part is the same as the cathode solution except coal. A magnetic stirrer was placed in the cathode compartment. The electrolysis experiment was performed in an oil bath (70 °C) at −1.7 V for 24 h using a potentiostat–galvanostat device (ZF-9, Shanghai).

The final liquefaction mixture was separated by Soxlet solvent extraction with n-hexane, toluene and tetrahydrofuran (THF) in turn [27]. As shown in Scheme 2, the liquid and solid products from the cell were separated into oil (n-hexane soluble), asphaltene (toluene soluble but n-hexane insoluble) and preasphaltene (THF soluble but toluene insoluble). And the liquefaction ratio was defined as the percentage of the coal that was converted into asphaltene, preasphaltene and oil during the liquefaction [28].

### 3. Results and discussion

#### 3.1. Coal pretreatment by ionic liquids

##### 3.1.1. Ionic liquid selection

Ionic liquid is selected based on the extraction and swelling performance of coal. As shown in Table 1, it is clear that the ILs based on [Bmim]<sup>+</sup> cation exhibit better extraction performance than that of [Hmim]<sup>+</sup> and [Bpy]<sup>+</sup> based ionic liquids. Moreover, among the [Bmim]<sup>+</sup> based ILs, the Cl<sup>−</sup> anion shows better result compared with Br<sup>−</sup>, OTF<sup>−</sup> and BF<sub>4</sub><sup>−</sup>. It is possibly due to the interactions

Table 1

Extract yield and swelling ratio of coal at 90 °C for 2 h in the presence of ILs and NMP.

Solvent	Extract yield (EY, daf) (%)	Swelling ratio (Q)
[Bmim]Cl	18.51	1.73
[Bmim]Br	16.87	1.70
[Bmim]OTF	6.81	1.37
[Bpy]BF <sub>4</sub>	5.27	1.29
[Bmim]BF <sub>4</sub>	11.56	1.63
[Hmim]Cl	14.91	1.68
NMP	9.85	1.41

between imidazolium-based ILs with coal particles, such as the  $\pi$ – $\pi$  conjugation between the imidazolium cation and aromatic rings [29], and larger charge density and electronegativity of Cl<sup>−</sup> ions compared with other anions [30]. Extract yield of the coal sample in [Bmim]Cl reaches to 18.51% at 90 °C. In contrast, the extract yield under the same condition in NMP, which is a strong polar solvent, is only 9.85%.

Table 1 also shows the swelling ratios of coal in different solvents. The swelling ratio in [Bmim]Cl is 1.73, which is the highest among the solvents including other ILs and NMP at the same temperature. After swelling, approximately 30% (V:V) of [Bmim]Cl is soaked in coal by calculating the height change of [Bmim]Cl. It should be noted that the swelling ratio increases with increasing extract yield, suggesting that the interactions between coal macromolecules such as hydrogen bonds could be broken because of the coal swelling behavior, leading to the improvement of solubility in the solvent [30]. These results indicate that [Bmim]Cl exhibits the best performance to extract and swell coal. Therefore, [Bmim]Cl is adopted as the pretreatment solvent in our following experiments.

As [Bmim]Cl is a hydrophilic IL, the recycling of [Bmim]Cl can be performed by evaporating water from the final filtrate. The recovery of [Bmim]Cl is approximately 97% and the extract yield and swelling ratio of recycled [Bmim]Cl remain at the same level as those of the fresh [Bmim]Cl. Therefore, pretreatment of coal with [Bmim]Cl is feasible and cost-effective.

##### 3.1.2. Optimization of pretreatment temperature

Temperature is a key factor during the pretreatment of coal [31]. Optimization of pretreatment temperature is performed from 90 to 200 °C, concerning the decomposition temperature of [Bmim]Cl at 210 °C. Fig. 1 shows appearances of Shenhua coal mixed with [Bmim]Cl at different temperatures. For comparison, [Bmim]BF<sub>4</sub> and [Bmim]OTF are also studied. [Bmim]Cl melts at about 65 °C

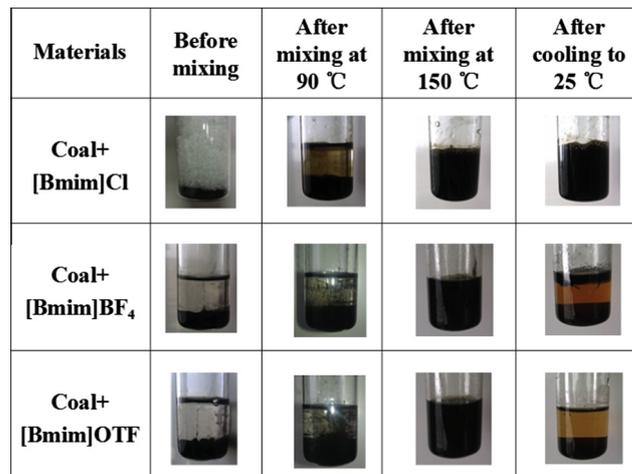


Fig. 1. Appearance of coal mixed with specific ILs (10% coal by weight) (from left to right): initial mixing at 25 °C, after heating to 90 °C and 150 °C for 2 h respectively, and after cooling to 25 °C from 150 °C (without stirring).

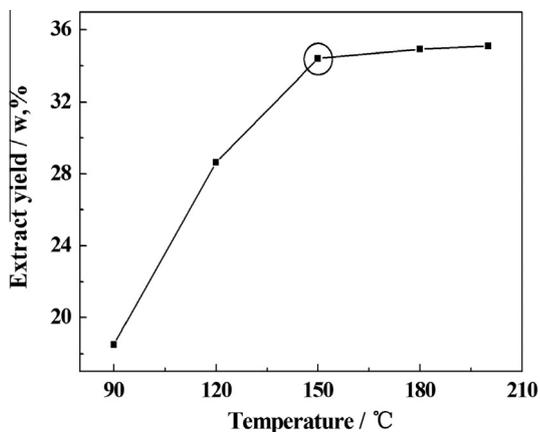


Fig. 2. Extract yield of coal with [Bmim]Cl at different temperature. Coal:[Bmim]Cl (w/w) = 1:10, time = 2 h.

[32], and after mixing with coal sample at 90 °C for 2 h, the color of [Bmim]Cl turns into brown, while the other two ILs are still transparent. Upon heating to 150 °C, a black dispersion is formed, and appears unaltered upon cooling down to room temperature. However, [Bmim]BF<sub>4</sub> and [Bmim]OTF do not result in appreciable dispersion of the coal samples after cooling down to room temperature, due to aggregation of coal particles. The results indicate that temperature plays an important role in pretreating coal and [Bmim]Cl has better ability to disperse and dissolve coal than other ILs at the same temperature.

Fig. 2 shows extract yields of coal samples with [Bmim]Cl at different temperatures. With increasing temperature, extract yield sharply increases before 150 °C, after which, the extract yield nearly reaches constant of 35% from 150 °C to 200 °C. The yield at 150 °C (34.4%) is almost 2 times of that at 90 °C. This could be due to the fact that the aggregated structure of coal can be

fragmented at 150 °C in ionic liquids (as discussed below), resulting in higher extract yield of coal in [Bmim]Cl [31]. Therefore, 150 °C is adopted as the pretreatment temperature.

### 3.2. Effect of pretreatment on coal structure

#### 3.2.1. Characterization of IL-pretreated coal

Fig. 3 shows SEM images of the original coal (sample A) and the [Bmim]Cl-pretreated coal (sample B). In comparison with the original coal, the [Bmim]Cl-pretreated coal exhibits more loose stacking structures. It is probably due to the fact that interactions between coal particles are broken during the pretreatment, and the coal particles are dissociated and rearranged in the presence of [Bmim]Cl [33]. In addition, more small particles are distributed over the surface of the pretreated coal. It is supposed that the small particles in the coal network could be released from the macromolecule network and dissolve into [Bmim]Cl, and then are precipitated on the surface of coal particles by using water as a back-extractant.

In order to further determine the effect of IL pretreatment on the cross-link structure of coal, gaseous products produced during the process have been analyzed. Fig. 4 shows the gas chromatograms of gaseous products obtained from the treatment without (b) and with [Bmim]Cl (a) detected with TCD detector (A) and FID detector (B), respectively. The major peaks of CO, CO<sub>2</sub> and C<sub>1</sub>–C<sub>7</sub> hydrocarbons are identified by retention times. From Fig. 4A, it is obvious that the yields of CO and CO<sub>2</sub> increase during the [Bmim]Cl pretreatment. From Fig. 4B, pretreatment with [Bmim]Cl results in new hydrocarbons products of C<sub>2</sub>H<sub>4</sub> and n-C<sub>4</sub>H<sub>10</sub>, and obvious increase of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and i-C<sub>5</sub>H<sub>12</sub>. The results strongly suggest that chemical bonds in coal particles could be broken during the pretreatment by using [Bmim]Cl.

IR spectra are recorded to further investigate the effect of IL pretreatment on the chemical bonds of coal. Fig. 5 shows IR spectra of the original coal (a), the [Bmim]Cl-pretreated coal (b) and [Bmim]

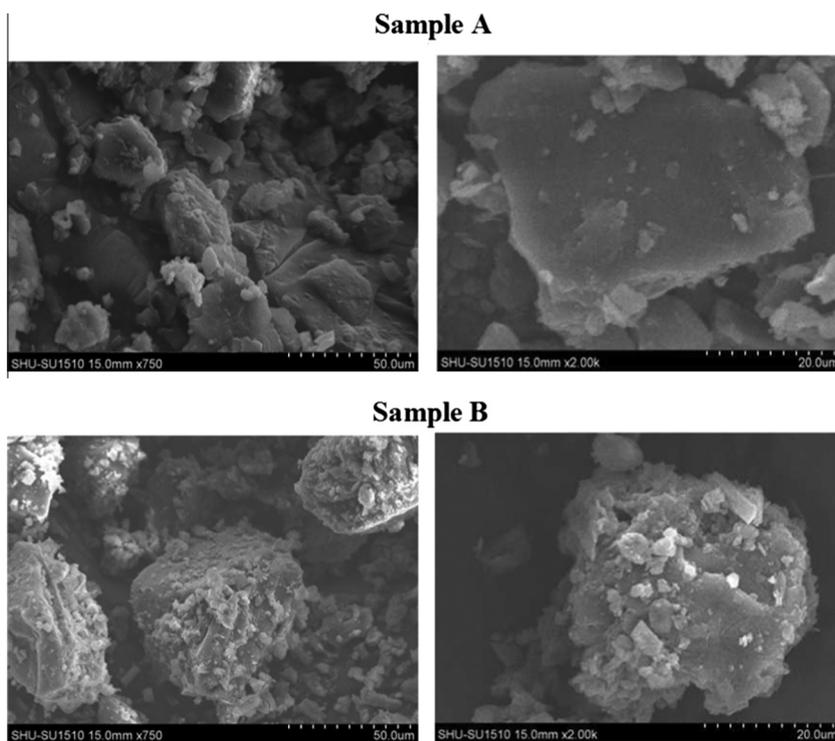


Fig. 3. SEM images of the coal particles surface: SEM micrograph of the original coal (Sample A); SEM micrograph of the [Bmim]Cl-pretreated coal (Sample B).

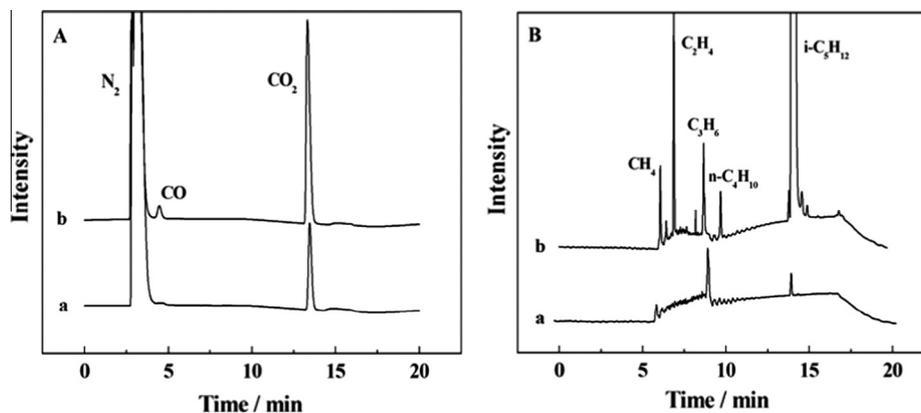


Fig. 4. Gaseous products generated from coal pretreatment under different conditions with a TCD detector for CO and CO<sub>2</sub> and a FID detector for alkanes: pretreatment at 150 °C for 10 h (a); pretreatment at 150 °C for 10 h with [Bmim]Cl (b).

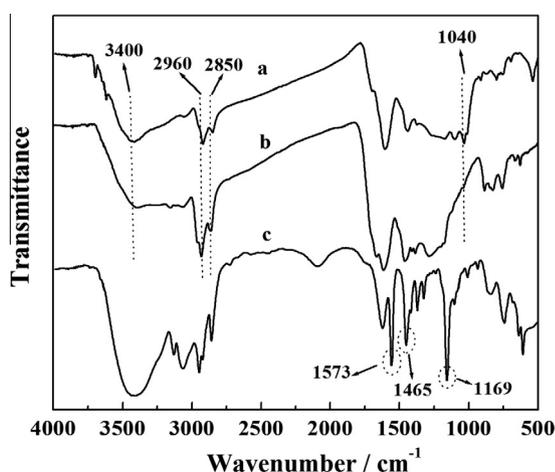


Fig. 5. IR spectra of the original coal (a), the [Bmim]Cl-pretreated coal (b) and [Bmim]Cl (c).

Cl (c). The coal pretreated by [Bmim]Cl shows decrease in the intensity of the broad peak near 3400 cm<sup>-1</sup>, which is assigned to the self-associated OH– hydrogen bond in coal [34,35]. The absorption peaks at 2960 and 2850 cm<sup>-1</sup> are attributed to the stretching vibration absorption of –CH<sub>3</sub> and –CH<sub>2</sub>– bonds respectively. The

ratio of peak height at 2960 to the one at 2850 cm<sup>-1</sup> increases after the pretreatment with [Bmim]Cl, indicating that the terminal group –CH<sub>3</sub> increases during the pretreatment [36]. The peak at 1040 cm<sup>-1</sup>, corresponding to the –C–O– stretching vibration, decreases significantly after the pretreatment [37,38]. In addition, the characteristic absorption peaks of [Bmim]Cl at 1573, 1465 and 1169 cm<sup>-1</sup> (curve c) are not observed in curve b, which proves the removal of [Bmim]Cl after washing with deionized water [39].

### 3.2.2. Mechanism of IL pretreatment of coal

It is known that coal particles are associated through bridge bonds such as covalent bonds, ionic linkages, hydrogen bonds, van der Waals forces and so on [40]. Of these associative interactions, hydrogen bonds and ether linkages play key roles to keep the macromolecular structure of low rank coals [41]. According to the above results, the possible mechanism of the pretreatment on the coal structure is proposed in Fig. 6. It is reasonable to assume that the pretreatment of coal with [Bmim]Cl can break bridge bonds, such as OH– self-associated hydrogen bonds, aliphatic bridges and –C–O–, consequently, resulting in structural relaxation of the pretreated coal and escape of lower molecular weight species such as aliphatic, and oxygen-bound carbons from the network [42]. To verify the proposed mechanism, further experiments are necessary and still in progress.

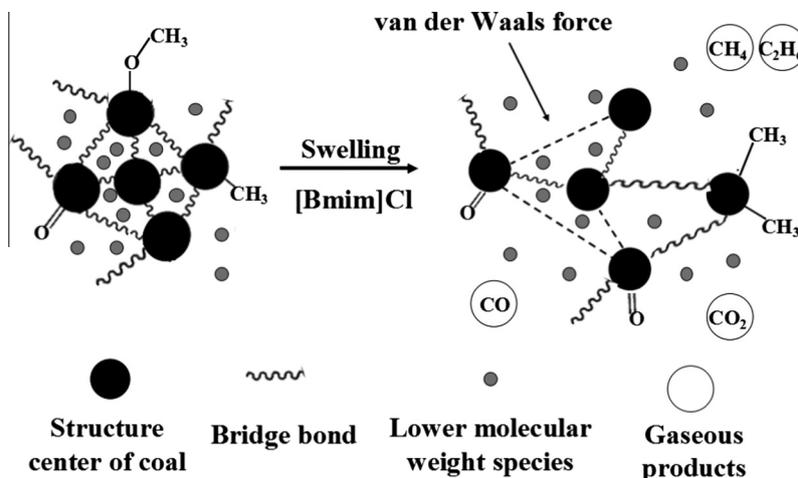


Fig. 6. Schematic mechanism of IL-pretreatment of coal.

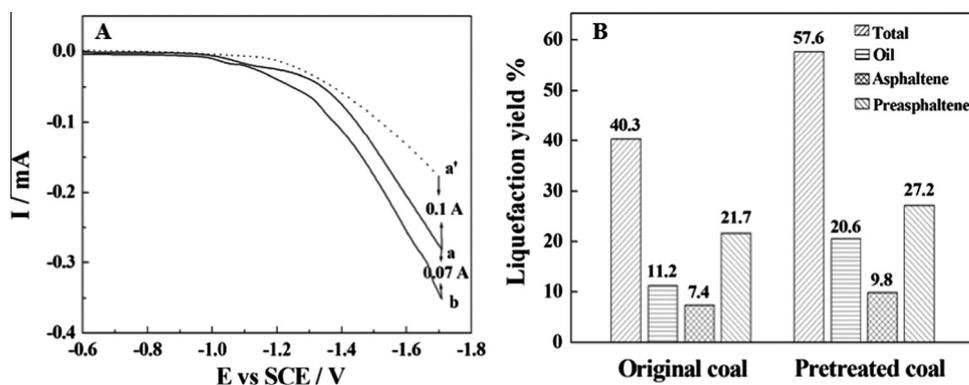


Fig. 7. LSV curves of the blank electrolyte without coal (a'), the original coal (a) and the [Bmim]Cl-pretreated coal (b) at 70 °C with a scan rate of 50 mV/s (A). Effect of pretreatment on the liquefaction yield of coal (B).

### 3.3. Electrolysis of IL-pretreated coal

Fig. 7A shows the electroreduction results of coal. LSV curve a', a and b are obtained for blank electrolyte, original coal and [Bmim]Cl-pretreated coal, respectively, at 70 °C with a scan rate of 50 mV/s. As shown in Fig. 7A, it can be observed the reduction currents (curve a and b) are enhanced when coal is introduced into the system after  $-1.0$  V, indicating that the reaction of coal electroreduction occurs. The difference between the current with coal (a) and without coal (a') is the net current of coal electroreduction on the electrode [22]. And at  $-1.7$  V, the net current is the largest, therefore  $-1.7$  V is chosen for the optimum electrolytic potential. The net current of pretreated coal electroreduction is 0.17 A at  $-1.7$  V, 0.07 A higher than that of the original coal. The enhanced current should be due to the loose structures of coal and release of low molecular weight species that are easily reduced on the catalytic electrode. These results indicate that pretreatment of coal with [Bmim]Cl can promote the coal electroreduction substantially.

To evaluate the effect of pretreatment on CEL, liquefaction yields of the original coal and the [Bmim]Cl-pretreated coal are determined, and the results are shown in Fig. 7B. After electrolysis at  $-1.7$  V for 24 h, the liquefaction yield of [Bmim]Cl-pretreated coal reaches to 57.6%. The yield of solid product is 38.2% and the rest (approximately 4%), such as minerals and acidic functional groups, are dissolved in the alkaline electrolyte [43]. It can be seen that the total liquefaction yield of [Bmim]Cl-pretreated coal is much higher than that of original coal (40.3%). All the components of oil, asphaltene, preasphaltene increase by different degrees, and especially oil increases from 11.2% to 21.6%. In our previous work [44], the coal sample pretreated by  $\gamma$ -ray irradiation gives a liquefaction yield of 58.5%, which is quite close to the present result of [Bmim]Cl-pretreated coal. Considering the complexity of irradiation equipment, pretreatment by ionic liquids is a more economical and practical method for CEL. Moreover, the present liquefaction yield is close to that of industrial DCL (65–73%) and the operation condition (70 °C, 1 atm) is much milder than that of DCL method and the cost of pretreatment is relatively low as well because of the recycling of [Bmim]Cl [40]. However, CEL is still at laboratory level, more work should be done before it can be applied to commercial scale of coal liquefaction. But as an easily-operated and environmental-benign process with low cost, the present CEL method is promising in coal liquefaction research.

## 4. Conclusion

The effect of pretreatment with ionic liquids on the coal structure and coal electrolysis liquefaction activity has been

investigated. The extract yield and swelling measurements results show that [Bmim]Cl is particularly effective in dissolving and swelling the lignite coal. After pretreatment of coal at 150 °C for 10 h, loose stacking structure is formed on the coal particle surface, and bridge bonds in coal particles are broken. The pretreated coal gives a liquefaction yield of 57%, which is 13% higher than that of original coal.

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