



# Pretreatment of coal by ionic liquids towards coal electrolysis liquefaction



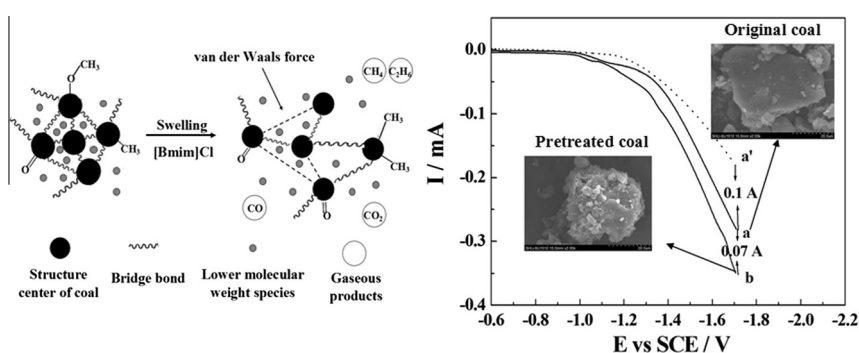
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## HIGHLIGHTS

- 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:

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

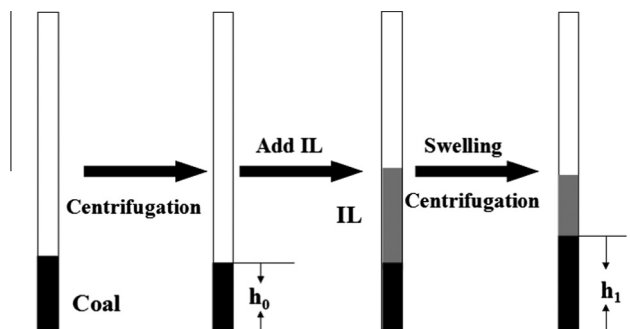
where  $M_1$  is the mass of extracts, and  $M_0$  is the mass of coal sample (1.0 g).

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.

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