



Extractive de-sulfurization and de-ashing of high sulfur coals by oxidation with ionic liquids



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ABSTRACT

The environmental consequences of energy production from coals are well known, and are driving the development of desulfurization technologies. In this investigation, ionic liquids were examined for extractive desulfurization and de-ashing in industrially important high sulfur sub-bituminous Indian coals. The ionic liquids, namely, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (IL1) and 1-*n*-butyl-3-methylimidazolium chloride (IL2) were employed for desulfurization of a few Indian coal samples in presence of HCOOH/H₂O₂ and V₂O₅. Results show the maximum removal of 50.20% of the total sulfur, 48.00% of the organic sulfur, and 70.37 wt% of the ash in this process. The ionic liquids were recovered and subsequently used for further desulfurization. FT-IR spectra reveal the transformation of organic sulfur functionalities into the sulfoxides (S=O) and sulfones (–SO₂) due to the oxidative reactions. The sulfate, pyrite and sulfides (aryls) signals in the near edge X-ray absorption fine structure (NEXAFS) of the oxidized coal samples showed sulfur transformation during the desulfurization process. The study demonstrates the removal of significant amount of inorganic as well as organic sulfur (aryls) components from the original high sulfur coal samples to make them cleaner.

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1. Introduction

Fuel is viewed as the food of an industry, and is therefore critical for the development level of any national economy. Clean energy production is therefore a pressing issue for development of a modern and sustainable economy. Coal has been an important source of energy to industry despite of its hazards to the communities. In India, over 70% of the electricity is produced from burning coal; in China, the number is over 80%. The serious negative effects of sulfur on the environment from coal use are well known. Sulfur compounds are converted to sulfur oxides during combustion, and these ultimately lead to acid rain. Sulfur dioxide and other combustion related pollutants from sulfur-containing fuels also lead to environmental concerns such as smog, global warming and water pollution [1,2]. Environmental regulations impose stringent limits for sulfur levels, providing an additional motivation to develop methods to remove sulfur from various fossil fuels. Therefore, the removal of sulfur and mineral matters to produce clean coal is very important [3–5]. Hence, process development is required to make this fossil fuel energy consumption both efficient and environmentally friendly. The current industrial method for removal of sulfur from liquid fuels is hydrosulfurization (HDS),

which may not be effective at removing heterocyclic sulfur compounds such as dibenzothiophene (DBT) and its derivatives, especially 4,6-dimethyldibenzothiophene (4,6-DMDBT) from coals [6]. On the other hand, oxidative desulfurization (ODS) is a promising technology for the reduction of sulfur at low temperature and at atmospheric pressure. ODS is a two stage process of oxidation followed by liquid extraction [7]. Sulfoxides and sulfones produced after ODS have an increased polarity and are preferentially extracted by highly polar solvents. However, other properties such as the boiling and freezing points, and the surface tension need to be carefully considered to evaluate the potential for separation and recovery of the solvent for recycling and reuse [8,9]. ODS technology of coal is still at laboratory research stage. Reaction selectivity, safety and cost are important concerns for the selection of the oxidant, catalyst and operating conditions for ODS in coal utilization. Because of limited reserves of high rank coals and environmental concerns, an advanced and non-toxic process for the conversion and cleaning of low-rank, high sulfur coal needs to be developed urgently. Thus, the objective of this study is to initiate the development of an advanced, non-hazardous coal desulfurization process that can be carried out under mild conditions, such as atmospheric pressure and room temperature. Such a method is expected to enhance the efficient and environmentally friendly utilization of coal by industry.

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1.1. Ionic liquids in coal

The recent interest in the use of ionic liquids (IL) for green chemistry processes and the development of alternative energy technologies has largely been gaining attention for the cleaner use of fuels [10–15]. Attractive properties of ILs include non-volatility, solubility for organic/inorganic compounds, good thermal and chemical stability, non-flammability, recyclability, and their environmental friendliness. These properties make ILs suitable extractants for sulfur compounds [16–19]. Since the earliest application for desulfurization by ILs was reported in 2001 [20], several studies have examined this application [21–23]. These results show the potential of ionic liquids that contain fluoride and chloride ions in the sulfur removal from liquid fuels. However, coal desulfurization using ILs is still a challenging task as several outstanding issues remain to be resolved in industry, including the recovery of useful hydrocarbon fuels from refractory sources as well as the solvent and catalyst recycling and minimization of waste. Ionic liquids have received great attention as a new kind of “green solvent” for desulfurization [24].

1.2. High sulfur Indian coals

The sub-bituminous types of coals from North-Eastern region (NER), India contain high sulfur (~2–8%) with the majority of sulfur being organically bound and low ash content. The physico-chemical properties of these coals are abnormal in comparison to the other similar types of coals in the world. The majority of sulfur in these coals was found to be of organic forms (75–90%), which are difficult to remove chemically [25]. There are five types of organic sulfur functionalities found in NER coals: aliphatic or aromatic thiols; aliphatic or mixed sulfides; aliphatic or aromatic disulfides; heterocyclic thiophenic and thioketonic compounds. Different chemicals have been used for the desulfurization of coals including metal salts, different oxidizing agents, inorganic acids, and alkali hydroxide bases [26–30]. These chemicals usually impart hazards to the environment and to chemists working with processes to remove sulfur from coal. Thus, for extractive desulfurization of high sulfur Indian coals, ionic liquids (ILs) have been included in the current study as green solvents. FT-IR and NEXAFS spectroscopy were used to study the molecular nature of the sulfur transformation during the process.

2. Materials and methods

2.1. Coal samples and chemicals

Chemicals used in the laboratory component of this study, including the ionic liquids (ILs), are: H₂O₂ (30%), HCOOH (85%), *N,N*-Dimethyl formamide (DMF), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (IL1), *n*-hexane, V₂O₅, 1-*n*-butyl-3-methylimidazolium chloride (IL2) (Sigma Aldrich and Merck). The representative high organic sulfur coal sample namely MK was collected from Nagaland Coalfield (N26°19'7"; E94°30'44") and the other two (T1 and T2) were collected from the coalfields of Assam (N27°13'–27°23'; E95°35'–96°00') of North-East India. The samples were ground to ~0.211 mm fractions for further analyses.

2.2. Physico-chemical characterization

The proximate analysis and sulfur analysis were carried out in Proximate Analyser (Model: TGA701, Leco, USA) and Sulfur Analyser (Model: Leco, 144DR) respectively. The forms of sulfur are determined by the ASTM method [31]. The percent of organic sulfur was calculated by difference. The C, H and N were determined

in CHN analyzer (Leco). The calorific value (GCV) were determined by following the methods described in Indian Standard Methods (IS:1350 (Part-II)-1969). Fourier Transform Infrared (FTIR) spectra of the coals and treated samples were recorded in a Perkin–Elmer system 2000, model 640B at wavelength range of 4000–400 cm⁻¹ using a KBr pellet with the same weight of the dried coal samples and KBr. The peak areas were calculated from the software associated with the system.

2.3. NEXAFS analysis of coals

The Sulfur 1s NEXAFS spectra of coal samples before and after the treatment were performed at the Canadian Light Source, using the Soft X-ray micro-characterization Beamline (SXRMB). The InSb(111) double crystal mono-chromator was used for the NEXAFS measurements. The powder sample was mounted using double-sided, conducting carbon tape, and loaded into a vacuum chamber (base pressure of 1 × 10⁻⁸ torr). A 4-element Si(Li) drift detector was used to record the Sulfur 1s NEXAFS spectra in fluorescence mode. Representative sulfur model compounds include Benzo thiophene, di-benzo sulfide, phenyl sulfoxide, dibenzo thiophene sulfone, FeSO₄·7H₂O and Pyrite. All reference compounds were obtained from Aldrich (>97%) and used without further treatment.

2.4. Extractive desulfurization of coal with ILs and their alkali extraction

30 g of coal sample (~0.211 mm size) were oxidized with a mixture of 13.2 ml of 20% HCOOH and 75 ml of 20% H₂O₂ in the reflux conditions for 1 h. The temperature was recorded as 70–80 °C during the course of reaction. The oxidized coal samples were then filtered and washed with water until the pH of the filtrate became neutral. To test the roles of ionic liquids, another two experiments were performed. In these experiments, 30 g coal samples (~0.211 mm size) were oxidized with the mixtures of 13.2 ml of 20% HCOOH and 75 ml of 20% H₂O₂ in the same reflux conditions for 1 h in presence of the IL1 and IL2 (0.5 g each) respectively. V₂O₅ (~0.5 g) was also added to both of these sets of experiments. The hydrofluoric acid and hydrochloric acid generated during extraction were neutralized with dilute alkali (NaOH) and sufficient distilled water. The filtrate containing sulfur-loaded ILs was kept for recovery and recycling purposes [32]. Each of the ionic liquid mediated oxidized coal samples are again mixed with 1 N NaOH (100 ml) and refluxed for 1 h. The filtered clean coal samples are then washed with 1 N HCl solution and hot distilled water till neutralization and oven dried for 1 h. The oven dried coal samples were used for further analysis. The liquid waste including NaOH, HCl and other acid solutions were neutralized (pH = 7.0) by using limestone and the resulting salt solutions were flushed down the drains after mixed with excess of waters in order to ensure complete neutralization. Researchers had attempted to use different types of ILs for desulfurization to extract dibenzothiophene (DBT) from model diesel fuel [32,33]. The Bronsted acidic ionic liquid promotes the catalytic reactions and the thiophenic sulfur compounds can be removed from coal in a suitable solvent system. The major organic sulfur compounds present in Indian coals include methyl phenyl sulfide, thiophenol, diphenyl sulfide, thiophene, benzothiophene, dibenzothiophene, etc. [34].

2.5. Recovery of ionic liquids (ILs)

As shown in Fig. 1A, the color of the filtrate solution containing IL1 is dark green and that from IL2 is yellow. Upon centrifuging these filtrates with absolute alcohol, the insoluble V₂O₅ and other impurities are separated out from the mixture. Absolute alcohol

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