

Desulphurization of Coal Soluble Using Ionic Liquids

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1 Introduction

Because of limited reserves and environmental concerns, an advance process for the conversion and cleaning of low-rank coal needs to be developed. Numerous studies on solvent extraction as one method of converting coal to liquids have been reported. For example, the hyper coal process can be used to obtain clean coal with less than 200 ppm of ash content.[1-3] This process is effective for sub-bituminous and bituminous coals but not for brown coals. Miura et al. have carried out solvent extraction with different types of coal, including brown coal, using organic solvents and reaction conditions of 350°C and 10MPa. [4-6] The solute obtained in this process showed low ash content. However, the distribution of sulphur forms in the products of these extraction processes has not been clarified.

Hydrodesulphurization is widely used in oil refining. It is carried out at high temperature with high-pressurized hydrogen along with catalysis. The objective of this study is to develop an advanced desulfurization process that can be carried out under mild conditions, such as atmospheric pressure and room temperature. The process is expected to be used for clean fuel production. The authors have been investigating the selective removal of organic sulphur, taking into consideration the different forms of sulphur present in model fuels. [7-9] Several studies have been carried out on the application of ionic liquids, and some studies have indicated the potential of ionic liquids containing fluoride and chloride ions for sulphur removal. [10-12] However, hydrogen fluoride and hydrochloric acid are generated from these ionic liquids during hydrolysis.[13,14] Mochizuki et al. demonstrated that the ionic liquids could remove dibenzothiophene as one of model organic sulphurs using halogen-free ionic liquids.[9] Dibenzothiophene is known to be thermally stable and difficult to remove by conventional desulfurization processes.

In a series of studies on the development of advance desulfurization process, coal soluble was prepared by heating low-grade coals at a temperature of 350°C for 1 h in 1-methylnaphtalein as a solvent according to the Miura's process. [15] The sulphur distribution from the raw coals to products (soluble, residue and deposit) was investigated and the chemical forms of sulphur in the raw coals and coal soluble were identified by XANES analysis. The extraction behaviour of organic sulphur from the coal soluble using the ionic liquids is investigated.

2 Experimental

2.1 Preparation of coal soluble

Table 1 shows ultimate analysis of the sample coal, Thailand lignite, Mae Tan coal. Average particle size of the sample was 0.35 mm. The dried Mae Tan coal was mixed with 1-methylnaphtalein (1-MN) and heated at 350°C for 1 h in an autoclave. The coal was separated into extract, Residue and gaseous product. The extract was further separated into solvent-soluble fraction, Soluble, and solvent-insoluble fraction, Deposit. [15] Here, Soluble is used in this study.

2.2 Preparation of ionic liquids

Five types of ionic liquids shown in Table 2 were prepared by adding dialkyl sulphates to alkyl imidazoles according to the method devised by Holbrey et al. [9] Dialkyl sulphates (Nacalai tesque, EP) were added to alkyl imidazoles (Tokyo Kasei, GR) in toluene and placed

Table 1 : Ultimate analysis of Mae Tan coal and its soluble [%, dry basis]

Sample	C	H	N	S
Raw coal	50.0	3.4	0.7	1.1
Soluble	81.0	6.8	0.9	1.3

Table 2 : Ionic liquids (1-alkyl (R₁)-3-alkyl (R₂) imidazolium alkyl (R₃) sulfate) prepared

Ionic liquid	Abbre.	R ₁	R ₂	R ₃
1,3-Dimethylimidazolium methyl sulfate	MMIMMeSO ₄	Methyl	Methyl	Methyl
1-Ethyl-3-methylimidazolium methyl sulfate	EMIMMeSO ₄	Ethyl	Methyl	Methyl
1-Ethyl-3-methylimidazolium ethyl sulfate	EMIMeEtSO ₄	Ethyl	Methyl	Ethyl
1-Ethyl-3-ethylimidazolium ethyl sulfate	EEIMEtSO ₄	Ethyl	Ethyl	Ethyl
1-Butyl-3-ethylimidazolium ethyl sulfate	BEIMEtSO ₄	Butyl	Ethyl	Ethyl

in an ice bath under a nitrogen atmosphere. The mixture was then stirred at room temperature for 1 h. After the reaction, the solution was found to have separated into two phases. The upper phase, consisting of organic solvents, was recovered by decantation, and the lower phase, consisting of the ionic liquids, was washed several times with toluene. The ionic liquid phase was heated at 75°C, and aspiration was carried out to remove unreacted organic solvents.

2.3 Extractive desulfurization

The coal soluble dissolved in 1-MN was mixed with the ionic liquid. This mixed solution was heated at 200°C for a certain time interval with agitation. After the extraction, the mixed solution was cooled to separate the ionic liquid and the soluble. Multi-step extraction was carried out by changing the ionic liquid.

2.4 Analyses

Some improvements to the ASTM (D2492) method applied were applied to analysing sulphur forms (pyritic, ferrous sulphide, sulphate, and organic sulphur) in raw coal. Sulphur K-edge X-ray absorption near edge structure spectroscopy was applied to specifying the forms of organic sulphur in raw coal and soluble. XANES measurements were carried out at beam line 11B of Photon Factory in the National Laboratory for High Energy Physics. Si (111) monochromators were used to vary the incident X-ray energy. The beam irradiated the samples fixed on a nickel plate under 10^{-8} atm in a vacuum chamber. Data were recorded in the fluorescence mode in the region of the S K-edge at room temperature. Sulphur forms in the samples were specified by comparing the XANES spectra obtained to the ones for model compounds.

Elemental analysis was conducted by using HCN coder (Yanaco, MT-700) and Carbon and Sulphur analyser (HORIBA, EMIA-220V). Sulphur content of soluble was determined by an ion chromatograph analyser (DIONEX, DX120) installed with an auto combustion instrument (Mitsubishi Kagaku, AQF-100). The phase change of ionic liquid with temperature was observed by a differential scanning calorimeter (Shimadzu, DSC-60 Plus).

3 Results and Discussion

3.1 Sulphur-form analysis

Chemical analysis of soluble is shown in Table 1. While carbon and hydrogen contents of soluble are higher than those of raw coal, sulphur content also increases to 1.3 wt%. This indicates that the solvent extraction does not remove organic sulphur efficiently, Figure 1 shows the results of XANES analysis of Mae Tan raw coal and soluble. Raw coal contains various kinds of sulphur species. A strong peak is observed around 2472.6 eV which is attributable to thiophene. Small peak of pyritic sulphur is also observed at 2480.5 eV. On the contrast, XANES analysis of the soluble shows two distinct peaks

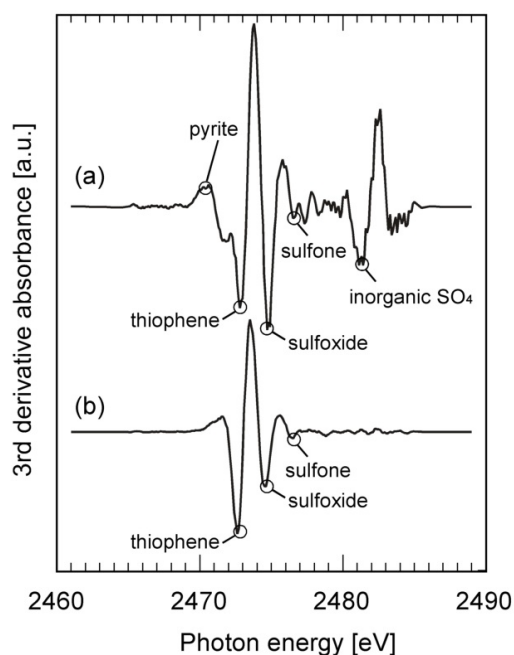


Figure 1 : Sulphur XANES spectra of (a) raw coal and (b) soluble for Mae Tan coal

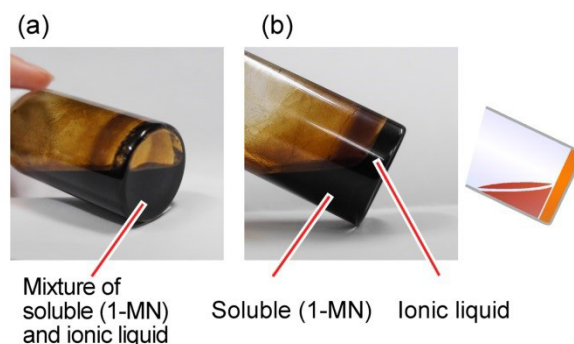


Figure 2 : Photos of mixture of soluble and ionic liquid at (a) above 120°C and (b) room temp.

of thiophene and sulfoxide. The ionic liquid is expected to remove thiophene as the major species of organic sulphur in the soluble.

3.2 Selection of ionic liquid

When the ionic liquids and soluble were mixed and heated for the extraction of sulphur, it became a homogeneous solution which was difficult to separate both liquids after the experiment. While EMIMMeSO₄, EMIMEtSO₄, EEIMEtSO₄ and BEIMEtSO₄ are liquid at room temperature, MMIMMeSO₄ shows the phase change depending on the temperature. According to the differential scanning calorimetry of MMIMMeSO₄, MMIMMeSO₄ is solid at room temperature and becomes melt above 70°C. It indicates that the mixed solution of soluble and MMIMMeSO₄ can be separated when the solution is cooled to the room temperature after the extraction experiment above 70°C. Figure 2 represents the picture of the mixture of soluble and MMIMMeSO₄ at 120°C and room temperature. Two phases of soluble and

ionic liquid can be seen due to the phase change of the ionic liquid.

3.3 Effect of extraction temperature

Table 3 shows change in removal extent of model organic sulphur with extraction temperature. The model fuel was prepared from organic compounds, benzothiophene, 1, 2 ethanedithiol, benzenethiol and diethyldisulfide with 1-MN as a solvent. The model fuel was mixed with MMIMMeSO₄ at a weight ratio of 1:1 and the mixture was heated at the temperatures from 100 to 200°C. Sulphur content of the model fuel was 200 ppm. Thiophene was extracted preferentially and the removal extent of sulphur increased with the increase of temperature.

3.4 Extraction of sulphur from the soluble

The coal soluble dissolved in 1-MN was mixed with MMIMMeSO₄ and heated at 200°C for the treatment time from 1 to 6 h. The sulphur content decreased with the treatment time and attained to the equilibrium value at 3 h. Figure 3 shows the result of multistep extraction. With the repeated extraction, the sulphur content in the soluble decreased linearly with the number of extraction.

Table 3 : Change in the removal extent of sulphur in the model fuel with extraction temperature

S compound	Removal extent [%]		
	100°C	150°C	200°C
Benzothiophene	25.4	18.6	44.1
1,2-Ethanedithiol	12.1	15.0	26.2
Benzenethiol	0.0	0.0	13.0
Diethyldisulfide	0.0	0.0	4.4

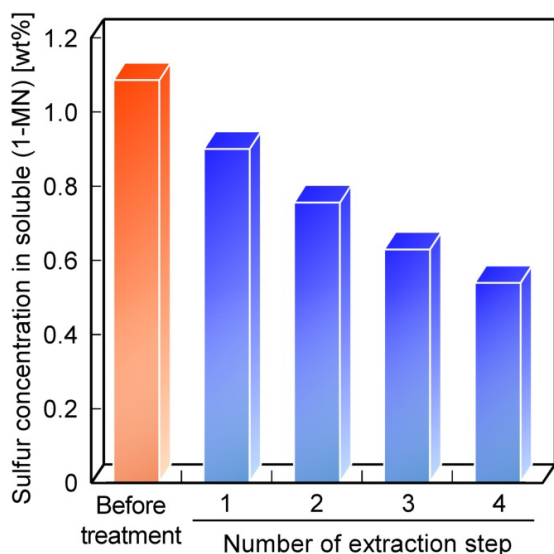


Figure 3 : Change in sulphur concentration in soluble with number of extraction step

4 Conclusion

We found an appropriate ionic liquid for the extraction of organic sulphur and for the separation from the coal soluble after the extraction. MMIMMeSO₄ shows the phase change from solid to liquid around 70°C. MMIMMeSO₄ and the coal soluble could be separated easily by cooling from the extraction temperature to a room temperature. According to the extraction experiment using model compounds of organic sulphur and 1-MN as a solvent, MMIMMeSO₄ extracted thiophenic sulphur preferentially. The removal extent of sulphur increased with the increase of temperature from 100 to 200°C. For the coal soluble, the multi-step extraction with the use of MMIMMeSO₄ is effective to lower the sulphur content.

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