



Sulfur Removal From Indian Coals By Using Green Solvents

Kakoli Khound

Coal Chemistry Division

CSIR-North East Institute of Science & Technology, Jorhat, India

Binoy K Saikia

Coal Chemistry Division

CSIR-North East Institute of Science & Technology, Jorhat, India

Bimala P Baruah

Coal Chemistry Division

CSIR-North East Institute of Science & Technology, Jorhat, India

Abstract:

Ionic liquids (IL), now a days have been used in different chemical reactions as green solvents. Here in this investigation, attempts have been made to obtain cleaner fuels from ligno-bituminous Indian coals. A high sulphur coal sample from North-Eastern region (NER), India with high sulphur (2-8%) and low ash contents have been tried for desulfurization with per acids and Ionic Liquids (IL). It has been observed that the percentage of oxidative desulfurization with IL increases about by 10% in comparison to the single oxidative process with per acids alone. The reaction mechanism involved during this process studied has also been discussed. The physico-chemical properties and FTIR spectral analysis of the coal sample before and after treatment have also been reported. FTIR bands for S=O in the range of 1050-1020 cm^{-1} confirms that the coal sample have been oxidized in ILs. The oxidized sulfur functionalities can easily be removed by extraction.

Keywords: Oxidation of coals; Ionic liquids; green solvents; Indian coals

Introduction

Coal is a heterogeneous mixture of organic and inorganic matter. The North-Eastern region (NER) of India contains the sub-bituminous type coals with high sulfur & low ash contents. The Sub-Bituminous coals of North-Eastern region (NER) of India with high sulfur and low ash content were taken for desulfurization. Chemicals employed for desulfurization are either oxidizing agents such as $\text{Fe}_2(\text{SO}_4)_3$, FeCl_3 , H_2O_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , NaClO_4 , Peroxoacetic acid, perchloric acid, performic acid, HNO_3 , Chlorinolysis, aqueous NaOH followed by HCl treatment, $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ etc.¹. The sulfur in the coals of North-East India is in the range of 2-8% with about 75-90% of them being in the organic form. As five types of organic Sulfur functionalities are present in Assam coals, that is, aliphatic or aromatic thiols, aliphatic or mixed sulfides, aliphatic or aromatic disulfides, heterocyclic compounds of thiophenic types etc.² Oxidative desulfurization (ODS) has received attention as a method for achieving lower Sulfur content in fuels and it has been applied both in coal and oils. Green solvent (IL) have also been used in ODS involving various oxidizers like H_2O_2 , ozone⁴

In the last few decades, there emerged a new class of green solvents, that is, room temperature ILs, which has some novel and desirable properties like non-volatility, excellent solubility for organic/inorganic compounds, good thermal/chemical stability and nonflammability. They have been used in some domains such as extraction, absorption, catalysis and in electrochemistry⁷. In this work, the oxidative desulfurization by 1- n-butyl,3-methyl imidazolium tetrafluoro borate (IL) and 30% V/V H_2O_2 as oxidant is used. The structures of the ILs are shown in Figure 1.

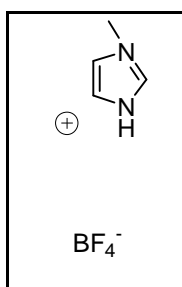


Figure 1: Structures of the IL 1- n-butyl,3-methyl imidazolium tetrafluoro borate

Experimental

The coal sample under study is taken from NE Coalfields. The coal sample was ground to -0.211 mm (72 BS) fractions and used for different experiments. The proximate analysis was carried out by Proximate Analyzer (TGA701, Leco, USA). The total sulphur determination and forms of sulphur analysis were performed by using Sulphur analyzer (Model: 144DR, Leco) following the standard methods (IS: 1351) respectively. The percent of organic sulphur was calculated by difference. The Fourier Transform infrared (FTIR) spectra of the sample was recorded in Perkin-Elmer system 2000 (model 640B) in the wavelength range of $4000\text{-}400\text{ cm}^{-1}$, using a KBr pellet. Equal amount of coal sample and KBr were used during recording of each FTIR spectra. Hydrogen peroxide (30%), formic acid (85%), N,N-Dimethyl formamide (DMF), 1- n-butyl,3-methyl imidazolium tetrafluoro borate (IL), n-hexane, V_2O_5 were the chemicals (Merck/Aldrich) used in the experiments.

Oxidation (Ods) Of Coals In Il In Presence Of V_2O_5

The ionic liquid (IL), 1- n-butyl,3-methyl imidazolium tetrafluoro borate $[\text{Bmim}]\text{BF}_4$ are mixed with n- hexane in (1:10) proportions and is added to the -0.211 mm sized 30 gm coal sample followed by the addition of 0.5 gm of V_2O_5 catalyst and stirred vigorously. Then 13.2 ml of 20% formic acid was added followed by the addition of 75 ml of 20% H_2O_2 was added to the mixture for 1 hour at atmospheric pressure. The oxidized coal sample were filtered and washed with DMF. The oven dried coal sample were kept for further analysis. The simple scheme of the ODS as follows:

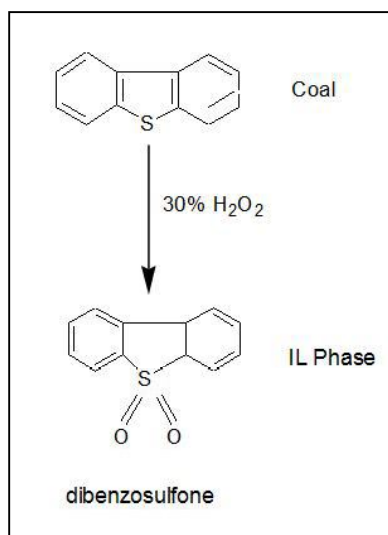
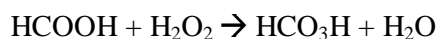


Figure 2: Simple scheme of the ODS

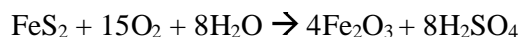
Results And Discussion

The Table 1 shows the physico-chemical properties of the raw and treated coals along with the extent of desulphurization in presence of ionic liquid. The extent of desulphurization and deashing of the coal sample were found to be 32.67 and 28.28% respectively in presence of the ionic liquid. Oxidation of organic sulfur compounds to sulfoxides, sulfonic acids and sulfones through an electrophilic addition mechanism. The probable reactions taking place during this oxidation of coal are as following:

1. Formation of performic acid



2. Oxidation of pyrites by performic acid to hematite iron and sulfuric acid.



3. Oxidation of organic sulfur compounds to sulfoxides, sulfonic acid and sulfones by an electrophilic addition mechanism.

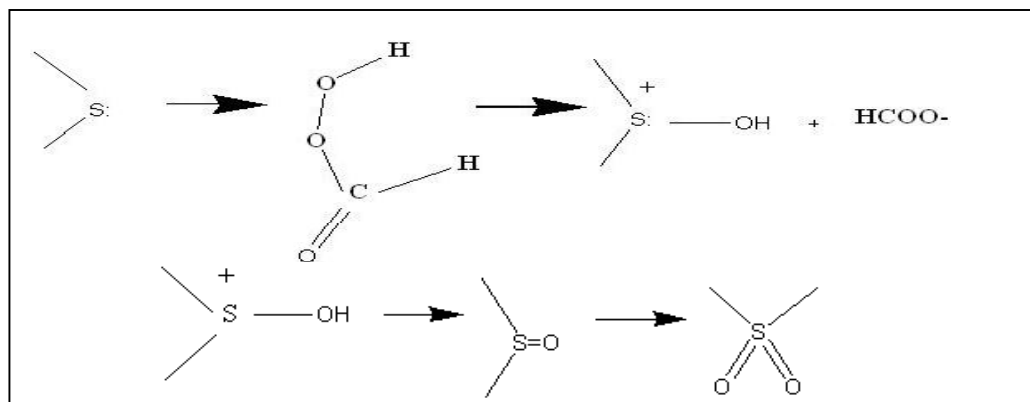


Figure 3

Coal	M	Ash	VM	FC	TS	Py-S	Sulphate-S	Organic-S	Desulphurization (%)*	Deashing (%)*
Raw Coal	3.01	1.91	41.4	53.7	2.48	0.47	0.45	1.55	-	-
Oxidized coal	1.98	1.83	41.9	54.3	1.92	0.17	0.11	1.64	22.58	4.18
Coal+H CO ₃ H+ V ₂ O ₅ +I L	4.61	1.37	40.7	53.3	1.67	0.18	Nil	1.13	32.67	28.28
Coal+H CO ₃ H+V ₂ O ₅ +IL+ NaOH	3.34	1.38	40.8	54.5	1.68	0.11	Nil	1.12	32.26	27.75

Table 1: Chemical analysis of the raw, oxidized, IL extracted and (IL + alkali) extracted coal sample (%wt dry basis)

FTIR study of the raw and the oxidized coal sample

Absorption bands in the region below 550 cm^{-1} are due to the stretching vibration of S-S bonds of sulfides and C-S bonds in primary and secondary thiols. FTIR spectra have shown that organically bound sulfur has been converted to sulfoxides (S=O) and sulfones ($-\text{SO}_2$). On oxidation, the vibration bands in the region of $1415\text{-}1380\text{ cm}^{-1}$ and $1200\text{-}1185\text{ cm}^{-1}$ are due to the presence of organic sulfates. The stretching frequencies in the range $1070\text{-}1030\text{ cm}^{-1}$ are due to the presence of sulfoxides in the coal sample. The bands in the range of $1050\text{-}1020\text{ cm}^{-1}$ are due to the formation of S=O. These regions are also seen in the raw coal sample due to the presence of sulfate ($-\text{SO}_4$). The bands below 800 cm^{-1} are due to the presence of mineral matter present in coal.

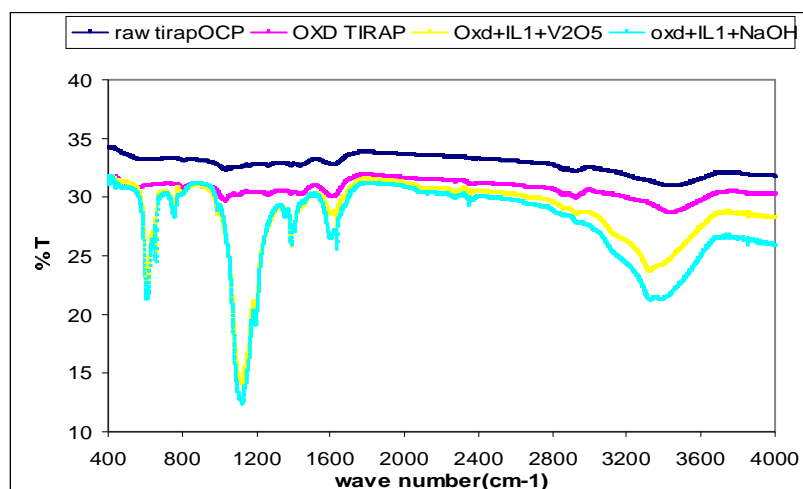


Figure 4: FTIR spectra of the raw, oxidized and IL treated coal sample

Conclusion

Ionic liquid was found to be suitable with the NER coals of India. The percentage of oxidative desulfurization with IL increases about by 10% in comparison to the single oxidative process with per acids alone and is the eco-friendly for using industrially.

Acknowledgements

Authors are thankful to the Director, CSIR-NEIST, Jorhat for his interest to this works.

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