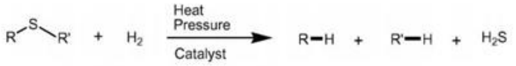
Deep Sulfur Removal from Model Fuels by Extracting Desulfurization with Ionic Liquids

NAYAN P. TALAVIYA[1], HARDIK MIROLIYA[2], BHAGYESH CHOTHANI[3], TEJAS DESAI[4]
[1,2,3,4] *Department of Chemical Engineering, Chhotubhai Gopalbhai Patel Institute of Technology (CGPIT), Bardoli, Gujarat, India*

Abstract -- ILs have drawn more and more attention to the environment friendly solvents and extractive desulfurizations with ILs were studied. 1-butyl 3-methylimidazoli -um bromide, 1-butyl 3-methylimidazolim chloride, 1-butyl 3-methylimidazolium tetraflouroborate, and 1-butyl 3-methylimidazolium hexaflourophosphate were synthe - sized. Model fuels were prepared by adding sulfur compounds in the real fuels. The effect of S-compound removal on extraction with ILs were investigated. The highest extraction with 77.4% S-compound were removed by [BMIM]Cl.

I. INTRODUCTION

Sulfur compound in fossil fuels such as gasoline, diesel and kerosene is the biggest challenge for oil refiners today. Sulfur is found in fuels in organic Sulphur compounds (e.g. Sulfides, thiophene). [1, 2] Which is a major source of acid rain and air pollution. To protect the environment against SOx pollution, the European union currently limits the Sulphur level in light oil to 350ppm and soon it will be decreased to 50ppm. [3] Major portion of the crude oil are used as fossil fuel. It occurs naturally in the ground and takes millions of years to form again. The Sulfur content is expressed as a percentage of Sulphur by weight and varies from less than 0.1% to more than 5% depending on the type and source of crude oils. [4] The Sulphur content present in fuels produces SOx, and NOx, which is very harmful for environment. So that, much attention has been paid to production and use of more environment friendly transportation fuels with minimum concentration of Sulphur and nitrogen compounds. Hydro-denitrification (HDN) and hydro desulphurization (HDS) are conventional methods to remove these compounds in industrial process. [5] the reactivity of sulfur compounds with catalysts of HDS depends on the molecular structure of Sulphur containing compounds. The main disadvantage of HDS are high operating temperatures (>3000C), high pressures (4 MPa), high energy costs, and large reactor size. [6]



Scheme 1 Hydrodesulfurization (HDS) process used for removal of sulfur compounds.

To this end, alternative methods, such as hydro desulfurization were studied, among which extractive desulfurization (EDS) is a most preferable method. Because of its simplicity in operating condition. [7] In past decades, vast researches are going on EDS using ILs. The result gives good future for ILs-EDS as a potential alternative method. In 2001, A. Bosman et al. applied the ILs-EDS technique to remove S compounds in fuel oils for the first time. These ILs were acidic in nature. Since then, many researchers have made use of ILs as solvents for the removal of S-compounds. ILs are organic Salts with Organic anions having melting points less than 1000C. There is no emission of volatile organic or inorganic compound in the environment, So that ILs are environment friendly solvents and known as "Solvent of the future".

In the present work, Imidazolium based ionic liquids like 1-butyl 3-methylimidazolium bromide [BMIM]Br, 1-butyl 3- methylimidazolium chloride [BMIM]Cl, 1-butyl 3- methylimidazolium tetrafluoroborate [BMIM]BF_4 , 1- butyl 3-methylimidazolium hexafluorophosphate [BMI - M]PF_6 were synthesized. FTIR, 1H-NMR, UV spectra analysis were carried out for the characterization of ILs. [8]

II. EXPERIMENTAL PROCEDURE

2.1. Chemical and materials

IL used in the experiment was synthesized using analytical grade chemicals. The details of the chemicals used are as follows: 1-methylimidazole

(CAS 616-47-7, Acros, 99%),1-bromobutatne (CAS 109-69-3, Acros, min 99%),NaBF4(CAS-237-340-6,98%),1-chlorobutane(CAS 109-69-3), KPF6(CAS 17084-13-8) Acetone (CAS 20003-L25, 99.5%), Ethyl Acetate (CAS 20108-L25, 99.5%), Dibenzothiophene (DBT) (CAS 132-65-0,Acros, 98%), n-dodecane (CAS 94094-93-6, Acros, 99%), Benzothiophene (BT) (CAS 95-15-8, 99%), Thiophene (T) (CAS 110-02-1, 99%), 3-methylthiophene (3-MT) (CAS 616-44-4, 98%). All chemicals were purchased from SRL chem. All chemicals were used without any further purification. Real fuels were purchased from Local Petroleum Pump, Surat, Gujarat (India).

2.2. Synthesis of IL

2.2.1. Synthesis of [BMIM]Br

10.8 g (0.08 mol) of bromobutane, 8.2 g (0.1 mol) of 1-methyimidizole, and 30ml of acetone were mixed in three round neck bottomed flasks fitted with a reflux condenser for 48 h at 70 0C with stirring until formation of two phases. The top layer contains unreacted material which was decanted, and 30 ml ethyl acetate was added with comprehensive mixing. Decanted ethyl acetate was followed by adding fresh ethyl acetate twice. Then, the reaction mixture was washed with ethyl acetate to eliminate unreacted material. After the third decanting of ethyl acetate, remaining solvent was removed by heating at 70 0C. The obtained pale-yellow liquid was vacuum distilled for 2hr and the intermediate product was placed for vacuum drying at 80 0C in a vacuum drying oven.

2.2.2. Synthesis of [BMIM]BF4

6.57 g (0.03 mol) [BMIM]Br, 3.29 g (0.03 mol) NaBF4 and 30ml acetone were added to the single mouth flask with a definite amount of acetone as solvent, for 10 h at 40 0C under vigorous stirring. The reaction mixture was filtered, and vacuum distilled for 2hr. Dichloromethane was added to the residue of [BMIM]Br and NaBF4, and white solids precipitated were obtained. Then, the solid precipitate was separated by filtration. Finally, the product was vacuum dried in an oven at 80 0C for 2 h to remove the traces of dichloromethane.

2.2.3. Synthesis of [BMIM]Cl

17.408g (0.1 mol) of chlorobutane, 10.497 g (0.1 mol) of 1-methyimidizole, and 30ml of acetone were mixed in three round neck bottomed flasks fitted with a reflux condenser for 48 h at 65 0C with stirring until formation of two phases. The top layer contains unreacted material which was decanted, and 30 ml ethyl acetate was added with comprehensive mixing. Decanted ethyl acetate was followed by adding fresh ethyl acetate thrice. After the third decanting of ethyl acetate, remaining solvent was removed by heating at 70 0C. The obtained pale-yellow liquid was vacuum distilled and the intermediate product was placed for vacuum drying at 80 0C in a vacuum drying oven.

2.2.4. Synthesis of [BMIM]PF6

6.57 g (0.03 mol) [BMIM]Br, 5.521 g (0.03 mol) KPF6 and 30ml acetone were added to the single mouth flask for 10 h at 600C under vigorous stirring. The reaction mixture was filtered, and vacuum distilled for 2hr. Dichloromethane was added to the residue of [BMIM]Br and KPF6, and white solids precipitated were obtained. Then, the solid precipitate was separated by filtration. Finally, the product was vacuum dried in an oven at 80 0C for 2 h to remove the traces of dichloromethane.

2.3 Preparation of Model Liquid Fuel

A model liquid fuel with 500 ppmw aeromatic compound of sulfur (DBT) was prepared in n-dodecane. Similarly, the model liquid fuels were prepared by dissolving Benzothiophene, Thiophene, and 3-Methylthiophene individually in n-dodecane respectively. Actual diesel and gasoline with total sulfur content of 570 and 85 ppmw respectively were used.

Composition of model fuels (MFs)			
System	Sulfur Compound	Sulfur Content [ppmw]	Hydrocarbon Solvent
MF-1	Dibenzothiophene	50 - 1000	n - Dodecane
MF-2	Dibenzothiophene	50 - 1000	n - Hexane
MF-3	Dibenzothiophene	50 - 1000	n - Heptane
MF-4	Dibenzothiophene	50 - 1000	n - octane

Table 1: Composition of model fuel

2.4 Extractive Desulfurization of the Model Liquid Fuel

The desulfurization experiments were carried out in a 100ml two-necked flask by mixing of model liquid fuel (10 ml) and specific amount of IL with the mass ratio between model liquid fuel to IL as 5:1 at 30℃ in a water bath for 30 min with vigorous stirring. On completion of the reaction, after separation the upper phase (model fuel) was withdrawn and analyzed to determine the concentration of S in model liquid fuels. (%) removal of S can be calculated by the following equation as:

(%) S-removal= [DBT]Initial – [DBT]Final / [DBT]initial x 100

2.4.1. Sulphur content analysis:

The model liquid fuel was analyzed by X-Ray fluorescence spectrometer to determine the concentration of DBT in the model fuels before and after desulfurization.

III. RESULTS AND DISCUSSION

The experiment conducted for desulfurization of various model fuels using different ionic liquid like [BMIM]Cl, [BMIM]Br, [BMIM]BF4, [BMIM]PF6. The progress of desulfurization was studied at 30 0C with mass ratio of model fuel and ILs is respectively 5 and 1. The time for extraction is 30 min and initial sulphur concentration is 500 ppmw.

3.1 Effect of S-compound on extraction with [BMIM]Cl

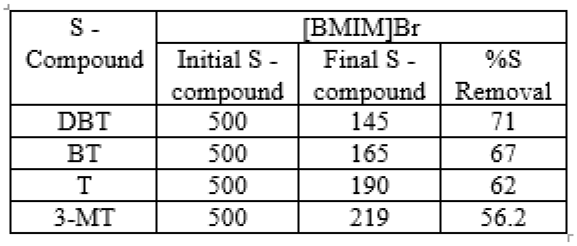
The Sulfur compound decreased from DBT, BT, T and 3-MT is 500 to 113 ppmw (S-removal 77.4%), 145 ppmw (S-removal 71%), 207 ppmw (S-removal 58.6%) and 232 ppmw (S-removal 53.6%) respectively. The mass ratio of model fuel/ILs is 5:1 and the extraction time is 30 min. (Table 2, Fig 2 & 3)

S - Compound	[BMIM]Cl		
	Initial S - compound	Final S - compound	%S Removal
DBT	500	113	77.4
BT	500	145	71
T	500	207	58.6
3-MT	500	232	53.6

Table 2: Effect of S-compound on extraction with [BMIM]Cl

3.2 Effect of S-compound on extraction with [BMIM]Br

The Sulfur compound decreased from DBT, BT, T and 3-MT is 500 to 145 ppmw (S-removal 71%), 165 ppmw (S-removal 67%), 190 ppmw (S-removal 62%) and 219 ppmw (S-removal 56.2%) respectively. The mass ratio of model fuel/ILs is 5:1 and the extraction time is 30 min. (Table 3, Fig 3 & 4)



S - Compound	[BMIM]Br		
	Initial S - compound	Final S - compound	%S Removal
DBT	500	145	71
BT	500	165	67
T	500	190	62
3-MT	500	219	56.2

Table 3: Effect of S-compound on extraction with [BMIM]Br

3.3 Effect of S-compound on extraction with [BMIM]BF$_4$

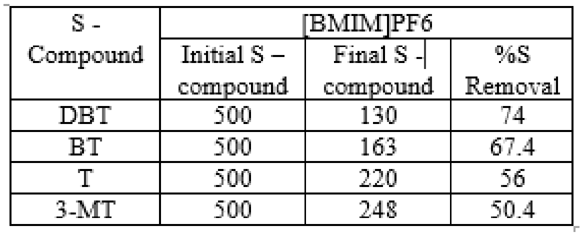
Similarly, The Sulfur compound reduced from DBT, BT, T and 3-MT is 500 to 125 ppmw (S-removal 75%), 170 ppmw (S-removal 66%), 227 ppmw (S-removal 54.6%) and 262 ppmw (S-removal 47.6%) respectively. The mass ratio of model fuel/ILs is 5:1 and the extraction time is 30 min. (Table 4, Fig 5 & 6)

S - Compound	[BMIM]Bf4		
	Initial S - compound	Final S - compound	%S Removal
DBT	500	125	75
BT	500	170	66
T	500	227	54.6
3-MT	500	262	47.6

Table 4: Effect of S-compound on extraction with [BMIM]BF$_4$

3.4 Effect of S-compound on extraction with [BMIM]PF$_6$

Similarly, The Sulfur compound reduced from DBT, BT, T and 3-MT is 500 to 130 ppmw (S-removal 74%), 163 ppmw (S-removal 67.4%), 220 ppmw (S-removal 56%) and 248 ppmw (S-removal 50.4%) respectively. The mass ratio of model fuel/ILs is 5:1 and the extraction time is 30 min.(Table 5, Fig 7 & 8)



S - Compound	[BMIM]PF6		
	Initial S – compound	Final S - compound	%S Removal
DBT	500	130	74
BT	500	163	67.4
T	500	220	56
3-MT	500	248	50.4

Table 5: Effect of S-compound on extraction with $[BMIM]PF_6$

The Sulfur compound decreased from DBT, BT, T and 3-MT is 500 to 145 ppmw (S-removal 71%), 165 ppmw (S-removal 67%), 190 ppmw (S-removal 62%) and 219 Ppmw (S-removal 56.2%) respectively. The mass ratio of model fuel/ILs is 5:1 and the extraction time is 30 min. (Table 3, Fig 3 & 4)

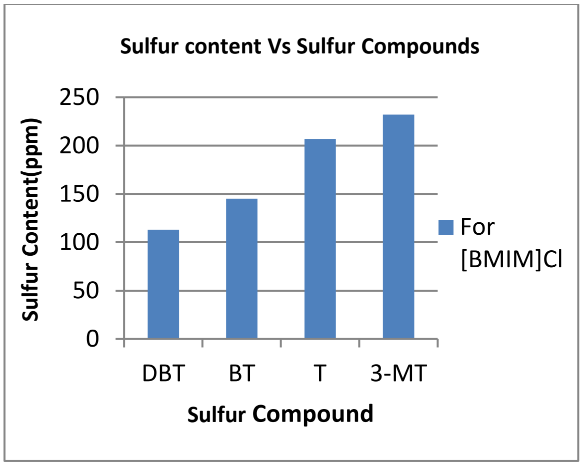


Fig 1: S-compound removal by [BMIM]Cl

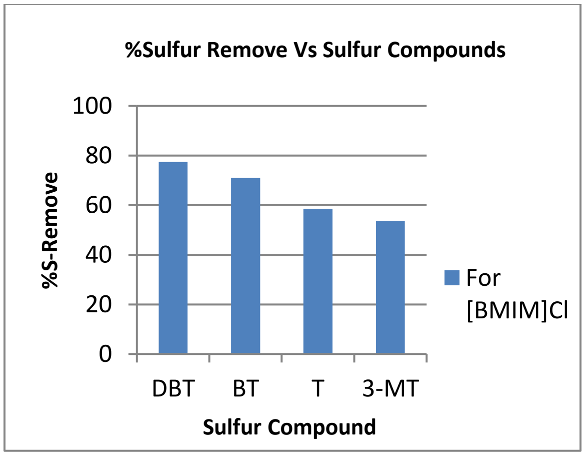


Fig 2 : %S-compound removal by [BMIM]Cl

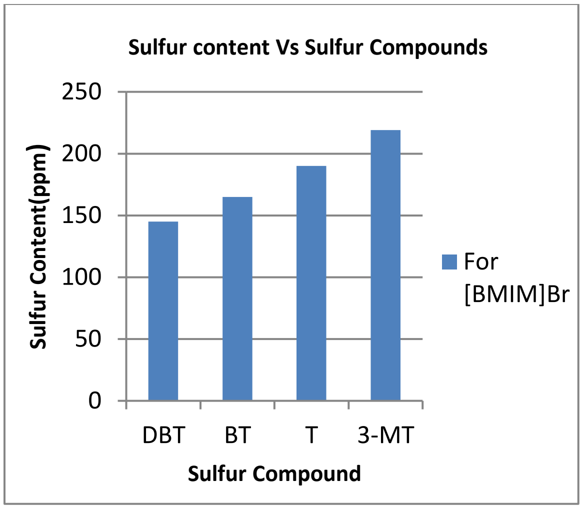


Fig 3: S-compound removal by [BMIM]Br

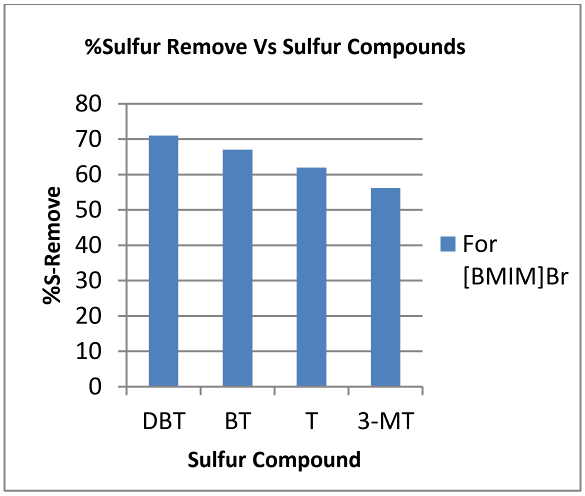


Fig 4 : %S-compound removal by [BMIM]Br

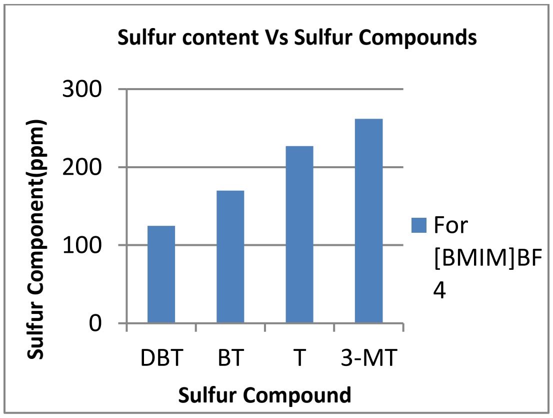


Fig 5: S-compound removal by $[BMIM]BF_4$

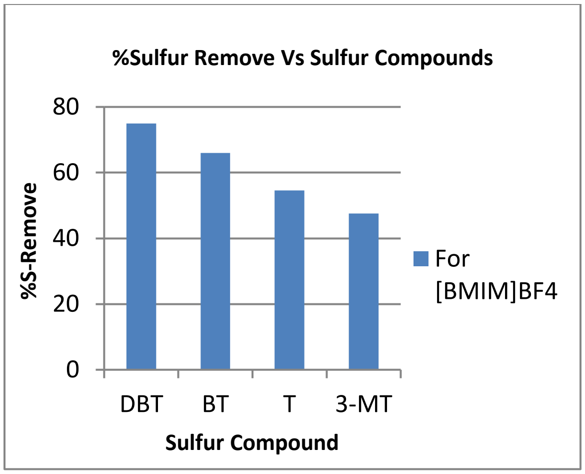


Fig 6 : %S-compound removal by [BMIM]BF$_4$

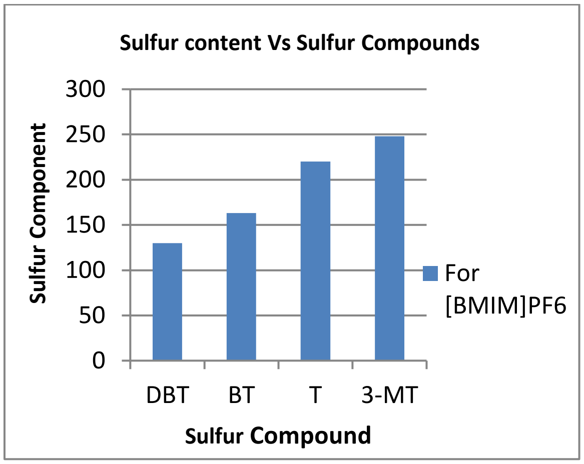


Fig 7: S-compound removal by [BMIM]PF$_6$

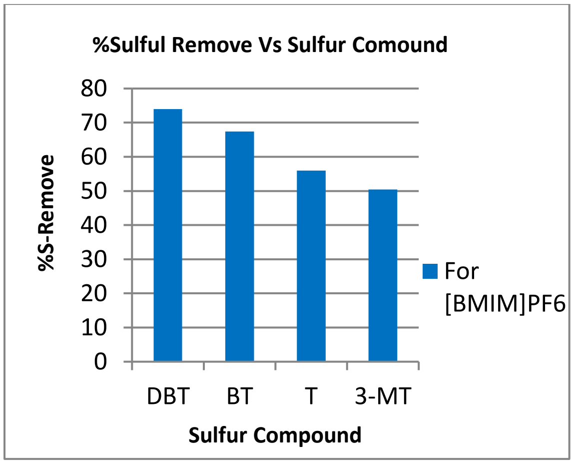


Fig 8 : %S-compound removal by [BMIM]PF$_6$

IV. CONCLUSION

Imidazolium based ILs are most effective extractive solvents for EDS process. ILs-EDS process removes especially S-compound that are not possible in common HDS process. [BMIM]Cl is most efficient solvent for the removal of DBT containing liquid fuels and it can remove 77% of S-compound for single stage extraction at 300C in 30 min with mass ratio of 5:1. The S-compound removal efficiency chain of imidazolium based ILs is [BMIM]Cl> [BMIM]Br> [BMIM]PF^6>[BMIM]BF$_4$.

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