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Polymeric-based deep eutectic solvents for effective extractive desulfurization of liquid fuel at ambient conditions

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ABSTRACT

In this work, the extractive desulfurization of liquid fuel was investigated using a new polymeric DES based on the salt tetrabutyl ammonium bromide (TBAB). Two different light grades of Polyethylene glycol (PEG) were used as hydrogen bond donors. Central Composite Design (CCD) was employed to optimize the operating conditions. The solvents showed high sulfur removal efficiency of DBT and thiophene in simulated fuel. Using a solvent to fuel volume ratio of 1:1 ($V_{DES}/V_{Fuel} = 1:1$), the extraction efficiency reached 82.40% and 62.16% in the first extraction stage at room temperature. Effect of solvent to volume ratio, time, temperature, initial concentration and speed of mixing on extraction efficiency were investigated. The results showed that increasing the speed of mixing has a great influence on the extraction efficiency. The deep desulfurization of the simulated fuel was also carried out in multiple extraction stages. Using a volumetric ratio of $V_{DES}/V_{Fuel} = 1:1$, the DBT and thiophene extraction efficiencies were 100% and 95.15% respectively after three extraction stages. On the other hand, the volumetric ratio of $V_{DES}/V_{Fuel} = 3:1$, achieved efficiencies of 100% and 97.79% after two extraction stages only. This is the minimum number of extraction cycles so far reported using quaternary ammonium based eutectic solvents. Moreover, the deep desulfurization of real diesel was achieved using six extraction stages. Finally, the used DES was successfully regenerated and reused five times without significant loss of solvent activity, which is of utmost necessity from an economical and practical point of view.

1. Introduction

One of the long-standing problems facing petroleum refining industries is the presence of sulfur compounds in fuel oils. Sulfur causes many technical problems in pipelines, pumping, and refining equipment. Moreover, sulfur compounds present in fuels lead to the emission of sulfur oxide gases, thereby indirectly causing serious harm to the public health and environment. In the last few decades, environmental concern has increased. Therefore, governments all over the world are implementing strict standards and regulations to protect the environment from industrial activities impact. The maximum sulfur compounds content in the gasoline and diesel fuels has been limited to less than 15 ppm in many countries (Srivastava, 2012).

In the petroleum refining industry, the conventional and well-known used technique to remove the sulfur in fuel is the hydrodesulphurization method (HDS) (Zhang et al., 2012a; Sepulveda et al., 2011). Despite its wide spread, this technology has many disadvantages such as the high demand of hydrogen consumption, severe operating conditions and high cost due to the use of expensive catalysts. Adding to these difficulties, the HDS technology has a low removal efficiency to some sulfur compounds such as benzothiophenes (Srivastava, 2012; Campos-Martin et al., 2010). These obstacles encour-

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Table 1 – List of chemicals used in this work and their specifications.

S/N	Name	Chemical formula	Purity (%)	Supplier
1	Tetra-butylammonium bromide (TBAB)	$C_{16}H_{36}BrN$	>99.0	Sigma–Aldrich, USA
2	Dibenzothiophene	$C_{12}H_8S$	>98.0	Sigma–Aldrich, USA
3	Thiophene	C_2H_4S	>99.0	Merck Chemicals, Germany
4	Cyclohexane	C_6H_{12}	99.98	Fisher Scientific, UK
5	*Iso*-octane	C_8H_{18}	>99.0	Merck Chemicals, Germany
6	*n*-Decane	$C_{10}H_{22}$	>99.0	Merck Chemicals, Germany
7	Toluene	$C_6H_5CH_3$	>99.7	Honeywell Chemicals, Germany
8	Acetone	C_3H_6O	>99.5	Sigma–Aldrich, USA
9	Acetonitrile	C_2H_3N	>99.0	VWR International, USA
10	Methanol	CH_4O	>99.0	VWR International, USA
11	Polyethylene glycol 200	$C_{2n}H_{4n+2}O_{n+1}$	>99.5	Merck Chemicals, Germany
12	Polyethylene glycol 600	$C_{2n}H_{4n+2}O_{n+1}$	>99.5	Merck Chemicals, Germany

aged researches to explore different alternatives processes such as oxidation, adsorption, bio-desulfrization, and other techniques (Zhang and Zhang, 2002). Much attention has recently been devoted to Extractive Desulfurization (EDS) where a solvent is used to extract the sulfur compounds from the fuel via liquid–liquid extraction. The EDS is a desirable alternative because of the lower energy consumption. It can be performed at mild operating conditions without the use of hydrogen. In addition, it does not affect the chemical structure of the compounds in the fuel oils (Zhang et al., 2004; Asumana et al., 2010).

Different organic solvents, such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and other volatile organic compounds (VOC) have been used as extraction solvents in EDS (Ban et al., 2013). The use of organic solvent was associated with challenges due to their volatilely, flammability, toxicity and the sulfur removal efficiency is not significant (Kulkarni and Afonso, 2010). To overcome these challenges, researchers have used variety of structures of available ILs to remove sulfur compounds since they are favorable due to their slight volatility, good solubility for many organic and inorganic compounds and thermal stability (Wilkes, 2004). However, the use of ILs has some limitations such as the poor efficiencies in the extractive desulfurization and some of the ILs are hazardous and toxic. Thereby, their applications in the industry will present great challenges as they may cause environmental pollution (Zhang and Zhang, 2002; Su et al., 2004; Qi et al., 2015).

To avoid many drawbacks of using ILs, recent studies have targeted developing more environmental friendly solvents. Deep eutectic solvents (DESs) are classified as new family of ionic liquids (Zhang et al., 2012b). They gained intensive interest in the research community as a green alternative for ILs because of the number of benign characteristics, their excellent physical and chemical properties, being much cheaper, nontoxic, inexpensive, generally biodegradable and their synthesis procedure can be done at conditions close to room conditions (Mjalli et al., 2014a,b; Hayyan et al., 2013; Gano et al., 2014). The use of DESs in the extraction desulfurization process has shown extraordinary performance as compared with most of ionic liquids (Campos-Martin et al., 2010).

Most reported types of deep eutectic solvents are based on mixtures of quaternary ammonium or phosphonium-based salts with a variety of other chemical species that can serve as hydrogen bond donors. Recently, the extractive desulfurization of liquid fuels was adopted using a group of ammonium-based deep eutectic solvents (Li et al., 2013). Salts were chosen from Choline chloride (ChCl), tetramethyl ammonium chloride (TMAC), and tetrabutyl ammonium chloride (TBAC), while HBDs were chosen from malonic acid (MA), glycerol (Gl), tetraethylene glycerol (TEG), ethylene glycol (EG), polyethylene glycol (PEG), and propionate (Pr). The study disclosed that the type of the hydrogen donor associated with the salt in the DES structure has a great impact on the performance of the desulfurization process. A high desulfurization efficiency was obtained using the DES made of TBAC salt and PEG. This was mainly due to the hydrogen bond formed between PEG and benzothiophene (BT) as a representative sulfur compound in the fuel (Li et al., 2013, 2012a). PEG has many favorable properties such as its low viscosity, high boiling point, low vapor pressure, low toxicity as well as low cost, which makes it a good choice for the synthesis of DESs. In addition, it has been approved by the Food and Drug Administration (FDA) for internal consumption and has been studied as a green solvent for effective extractive desulfurization of liquid fuel (Jaiswal et al., 2012; Kianpour and Azizian, 2014).

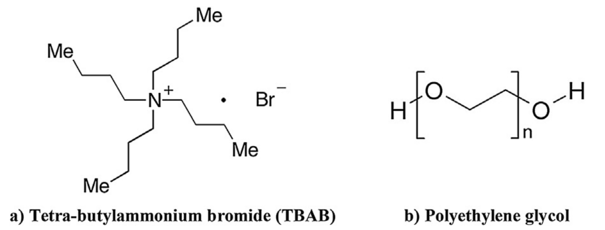

Fig. 1 – Chemical structure of the DES constituents used in this work.

In this work, the extraction efficiency of new deep eutectic solvents based on tetra-butyl ammonium bromide (TBAB) and Polyethylene glycol is investigated. The quaternary ammonium salt TBAB was mixed with one of two low molecular weight grades PEG namely PEG-200 and PEG-600 for DES synthesis. These systems showed excellent sulfur extraction ability. Additionally, the effect of some important process parameters such as mixing time, solvent volume fraction and speed of mixing on the extraction efficiency were investigated. In order to determine the effect of these multiple parameters and their interactions, a systematic approach was adopted. Design of experiments (DOE) was used to model the results and provide us with a full insight of the interactions among the studied process parameters. Among the different design of experiments techniques, the Response Surface Methodology (RSM) was adopted for this task (Meng et al., 2015). The purpose of this analysis was to estimate the effect of key factors on the response of extraction efficiency and determine the optimal operating conditions for simulated fuel desulfurization.

2. Experimental methodology

2.1. Chemicals used

The details of the chemicals used and specifications are shown in Table 1. Fig. 1 shows the chemical structure of the chemical ingredients for the DESs.

2.2. Preparation of the deep eutectic solvent and the fuel

The DESs used in this study were prepared with TBAB as the organic salt and either PEG200 or PEG 600 as HBDs. Initially, the screening process started using different molar ratios of TBAB and PEG from 3:1 to 1:3. The ratio chosen for this work is 1:2 (TBAB:PEG).