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Towards a sulfur clean fuel: Deep extraction of thiophene and dibenzothiophene using polyethylene glycol-based deep eutectic solvents



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ABSTRACT

In this work, extractive desulfurization of model fuel containing dibenzothiophene (DBT) and thiophene (Th) as sulfur compounds was carried out using 16 different Deep Eutectic Solvents (DES) based on polyethylene glycol (PEG) and its precursors. The aim of this study is the reduction of the sulfur content of fuels below the environmental regulation (10 ppm), using PEG-based DES as low-cost extraction media under mild conditions and to compare their extractive performance with that of PEG alone, which by itself is a green solvent. For that purpose, 7 different quaternary ammonium and phosphonium salts were combined with four different molecular weight grades of PEG and PEG precursors such as ethylene glycol and triethylene glycol. The best results were obtained for the DES composed of tetrabutylammonium chloride (TBAC) and PEG400, which showed that it is possible to achieve, in single extraction step, 85% and 68% of extraction efficiency, and deep desulfurization in 2 and 3 cycles, for DBT and Th, respectively. In addition, this DES is not soluble in the model fuel and its extraction capacity is independent on the starting sulfur concentration. Finally, after being reused six times, TBAC:PEG400 DES still maintained 53% and 17% of its capacity, for DBT and Th removal, respectively, and after a regeneration step the performance of the DES was fully recovered.

1. Introduction

Energy, as an essential factor for growth and development, has become the driving force of modern economy. Currently, fossil fuels account for 81% of the global energy mix. Although changes to include a greater contribution from renewable energies are predictable, fossil fuels will remain dominant during the coming decade. By 2040, it is foreseen that fossil fuels will still satisfy 77% of total energy demand. The road transportation sector is a main responsible for the fossil fuels demand and concomitantly, for the increasing air pollution, which has become an important issue around the world [1,2]. In particular, the effect of fuels impurities in air quality has been an important subject [3]. Sulfur, as a natural constituent of crude oil, is the impurity with the highest environmental impact. Its presence in fossil fuels gives rise to several problems not only in petroleum processing and fuel combustion but also in exhaust gases emissions, with a major influence in public health and environment. Sulfur oxides, mainly, sulfur dioxide, is the

main combustion product of sulfur and it has been recognized as a precursor of acid rain and air pollution [4]. Consequently, tighter regulations, particularly in fuels for the transport sector, have been legislated worldwide. At this moment, according to the European Union Directive, gasoline and diesel fuels in Europe should not exceed 10 ppm of total sulfur content [5]. The same limit exists in USA [6], and we are moving towards near zero-sulfur liquid fuels.

The current industrial technology for the removal of organic sulfur compounds from fuels is hydrodesulfurization (HDS), requiring a high temperature and pressure catalytic process. Typically, HDS involves catalytic treatment with hydrogen, converting the existing sulfur compounds to sulfur dioxide which is then removed from the flue gas by amine scrubbing [7,8]. However, HDS technology possess two major drawbacks: the high cost of operation and the low effectiveness in removing refractory heterocyclic sulfur compounds (e.g. dibenzothiophene (DBT)) [9]. Therefore, many research groups and industries have been engaged in the development of innovative complementary

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Table 1
List of chemicals used in this work and respective abbreviations.

	Name	Abbreviation	Chemical formula	Purity (%)	Supplier
Salt (HBA)	Choline chloride	ChCl	$N(CH_3)_3(C_2H_5OH)Cl$	≥ 98	Sigma-Aldrich
	Tetrabutylammonium chloride	TBAC	$N(C_4H_9)_4Cl$	≥ 97	Sigma-Aldrich
	Tetrabutylammonium bromide	TBAB	$N(C_4H_9)_4Br$	≥ 97	Sigma-Aldrich
	Tetrabutylphosphonium bromide	TBPB	$P(C_4H_9)_4Br$	98	Sigma-Aldrich
	Tetraethylammonium bromide	TEAB	$N(C_2H_5)_4Br$	98	Sigma-Aldrich
	Tetrapropylammonium bromide	TPAB	$N(C_3H_7)_4Br$	98	Sigma-Aldrich
	Tetrahexylammonium bromide	THAB	$N(C_6H_{13})_4Br$	99	ACROS organics
HBD	Glycerol	Gly	$C_3H_8O_3$	≥ 99	Sigma-Aldrich
	Ethylene glycol	EG	$C_2H_6O_2$	≥ 99.5	Carlo Erba
	Triethylene glycol	TEG	$C_6H_{14}O_4$	99	Sigma-Aldrich
	Polyethylene glycol 200	PEG200	$C_{2n}H_{4n+2}O_{n+1}$	–	Sigma-Aldrich
	Polyethylene glycol 300	PEG300		–	Fluka
	Polyethylene glycol 400	PEG400		–	Sigma-Aldrich
	Polyethylene glycol 600	PEG600		–	Sigma-Aldrich
Model fuel	n-heptane	n-heptane	C_7H_{16}	> 99	Fisher Chemical
	Thiophene	Th	C_4H_4S	> 99	Sigma-Aldrich
	Dibenzothiophene	DBT	$C_{12}H_8S$	98	Sigma-Aldrich

technologies for fuels desulfurization. Extractive desulfurization (EDS) is one of the most promising desulfurization processes due to its simple operation, low cost and benign effects on the final fuel quality [9,10]. However, the commonly used extractants are organic solvents, which brings again environmental and health concerns due to their volatility and flammability.

Since 2001 [11], ionic liquids (ILs) have been widely explored as alternative solvents for sulfur removal, and although these compounds have many desirable properties, such as non-flammability, non-volatility and high tunability, on top of high extraction efficiencies, they also present major disadvantages like, the high cost and, in some cases, toxicity problems [12,13].

To overcome those limitations, Deep Eutectic Solvents (DES) have been recently proposed as alternative to ILs, since DES can be seen as a low cost and more environmentally friendly ionic solvent [14–16]. The first DES was reported by Abbot [16], who pointed out that eutectic mixtures of urea and a variety of quaternary ammonium salts are liquid at room temperature and also highlighted their interesting solvent properties. In general, these systems are obtained by mixing two or more compounds, namely, an hydrogen bond donor (HBD) and an hydrogen bond acceptor (HBA) in a certain molar ratio, in order to obtain a eutectic mixture [14,17]. In 2013, Li et al. [18] introduced for the first time DES in the desulfurization field. Since then, around twenty studies have been published addressing the use of different DES for sulfur removal, including in extractive desulfurization [18–28] and oxidative desulfurization [29–33]. Among the proposed DES, quaternary ammonium salts are very often used to prepare DES, but some phosphonium salts have also been recently tested [20,34]. Regarding hydrogen bond donors or complexing agents, the most used compounds in desulfurization comprise acids, glycols and metal ions.

In the first reported study [18], the authors evaluated a variety of DES based on several ammonium salts combined with a wide range of HBD, and concluded that the DES formed by tetrabutylammonium chloride (TBAC) and polyethylene glycol (PEG) was able to extract 82.83% of the initial concentration of benzothiophene (BT), in optimal conditions. These authors and others [18,35] also address the extraction mechanism, which is proposed to take place through the establishment of an hydrogen bond between the active hydrogen of the extractant and the sulfur atom of S-containing molecules. Taking these results into account, in 2014, Kianpour et al. introduced the use of pure PEG for extractive desulfurization of fuel, as a cheap, green, effective and non-toxic solvent, in order to replace the toxic organic solvents and the expensive ILs, reaching higher extraction efficiencies (69% and 76% for BT and DBT, respectively) than those reported with ILs [36]. After that, also Wang et al. [37] used pure PEG200 as extractant this time

coupled with a catalytic oxidative system. More recently, PEG was also used as part of a ternary DES, combined again with a quaternary ammonium salt and metal ions [24].

Inspired by these previous studies, a systematic study on the use of salt:PEG DES as extraction media for the removal of Th and DBT, as model sulfur compounds present in fuels, was performed, aiming at developing a methodology that comply with the current legislation, which imposes that total sulfur content in fuel must be less than 10 ppm. For that purpose, a systematic study on the PEG-based DES was carried out, through the use of a wide range of quaternary ammonium salts and one phosphonium salt, which were combined with four different molecular weight grades of polyethylene glycol and with PEG precursors such as ethylene glycol and triethylene glycol. To give a step forward towards the applicability and sustainability of these processes the mutual solubility of both liquid phases (DES and fuel) and the reusability and recyclability of the selected DES was also demonstrated.

2. Experimental

2.1. Materials

The chemicals used in this work are listed in Table 1, as well as their purities and suppliers. All compounds were of high purity and used without any further purification.

2.2. DES and model fuel preparation

The DES used in this study were prepared combining ammonium or phosphonium-based salts (ChCl, TBAC, TBAB, TBPB, TEAB, TPAB and THAB), as HBAs, with one HBD (Gly, EG, TEG, PEG200, PEG300, PEG400 and PEG 600). Although Gly is not a PEG precursor, it was also considered in this study as HBD due not only to its chemical similarity to PEG precursors, but also to its wide availability and low cost. Each combination of organic salts and HBDs was selected by screening different molar ratios from 1:1 to 1:5. The general organic salt:HBD ratio chosen for this work was 1:2, except in those cases where that molar proportion did not yield a homogeneous liquid DES at room temperature.

The preparation procedure followed in this work was simply based on mixing and heating the organic salt/HBA and the HBD. The specific process is as follows: the appropriate amount of each raw compound, according the chosen molar ration as shown in Table 2, was placed in a sealed flask and heated to 323.15 K, with continuous and vigorous stirring (≈ 800 rpm), for one hour or until a clear and homogenous liquid was obtained. After that, the liquid was slowly cooled to room

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