



Oxidative desulfurization of fuels promoted by choline chloride-based deep eutectic solvents



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ABSTRACT

In this study, a new type of “green solvents” named deep eutectic solvents (DESs) has been synthesized by combining hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs). Choline chloride (ChCl) was chosen as typical HBA, and polyethylene glycol (PEG), 1,3-butylene glycol (BG), ethylene glycol (EG), glycerol (G), propionate (Pr), malonic acid (MA) and urea (U) were chosen as HBDs. The extraction and catalytic oxidative desulfurization (ECODS) system was evaluated with phosphotungstic acid (HPW) as catalyst and 30 wt% H₂O₂ as oxidant. Among all the neutral, acid and basic DESs, choline chloride/2polyethylene glycol (ChCl/2PEG) showed the best performance and 99.1% of dibenzothiophene (DBT) could be eliminated from model oil at 50 °C within 3 h. Interestingly, the volume ratio of DES to model oil was just 1:10, which was much less than the amount of extractant in the literature. The gas chromatography–mass spectrometer (GC–MS) analysis demonstrated that DBT sulfoxide (DBTO) and sulfone (DBTO₂) were the products of oxidation of DBT. The desulfurization efficiency of the five sulfides in ECODS system occurred in the following order: DBT > 4-MDBT > 4,6-DMDBT > 3-MBT > BT.

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1. Introduction

Over the past few decades, air contamination has become an increasingly serious global issue from the standpoint of environmental protection. One of the primary sources is the large emissions of sulfur oxides (SO_x) generated throughout the fuel combustion process. Sulfur oxides have brought great harm, which not only undermine catalytic converters leading to increased discharge of CO and NO_x but also form acid rain [1–4]. Therefore, reducing the sulfur content in the fuel with sulfur levels below 10 ppm has attracted worldwide attention.

At present, the traditional industrial desulfurization technology is hydrodesulfurization (HDS) [5]. HDS has been proved to be efficient in eliminating mercaptans, sulfides, disulfides, thiophene, BT and its derivatives [6]. However, it is difficult to approach ultra-low sulfur (<10 ppm S) because of poor effect on refractory sulfides such as DBT and its derivatives [7]. Moreover, high temperatures and high pressures with large quantities of hydrogen are required during the HDS process which result in high cost and energy con-

sumption [8]. Thus, there is an urgent need of inexpensive and energy-saving alternative methods for ultra-deep desulfurization. So far, plenty of alternative desulfurization methods with mild conditions have been extensively investigated. Several desulfurization techniques such as oxidation [9–12], extraction [13,14] and adsorption [15] have been used to eliminate sulfur species from fuel oil in the laboratories. Among these, oxidative desulfurization (ODS) is suggested as one of the most effective technologies for its easy removal of refractory sulfur compounds in mild conditions. These refractory sulfur compounds can be converted into corresponding sulfoxides and sulfones effectually, and then be removed from fuel via simple extraction, adsorption, distillation or biodegradation [16–18].

Ionic liquids (ILs) are considered to be “green solvents” for their characteristic physical and chemical properties including non-volatility, non-emission, recyclable, non-explosive, chemical stability and easy-handling [8,13,19–22]. During the past few years, the application of ILs in ECODS system for ultra-deep desulfurization has become a research hotspot [13,23–25]. Nevertheless, most of ILs also own many shortcomings including exorbitant price, possible toxicity, difficulty to synthesis, poor biodegradability, biocompatibility and sustainability [26–28]. In addition, high purity of the reaction was needed since impurity can seriously affect their

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physicochemical properties and experimental results [29]. For the reasons above, the industrial application of ILs is hindered.

In recent years, a new kind of intermediary deep eutectic solvents (DESs) has been exploited. It was reported by Abbott [30] firstly which can be formed by naturally mixing two or more compounds named hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) in a certain molar ratio. These compounds can be associated with each other depending on hydrogen bond interactions [31]. DESs have the physicochemical characteristics similar to ILs, such as a melting point close to room temperature, similar starting materials, undetectable vapor pressure, non-volatility, non-flammability, wide liquid temperature range and special solubility for many compounds [32,33]. However, unlike most of ILs, DESs are cheaper to be produced, easier to be synthesized and biodegradable [26,34,35]. Up to present, DESs have been synthesized in bulk quantities and widely applied to various fields including metal deposition, oxide dissolution [36], catalysis [37], organic synthesis [29], material preparation [38], electrochemistry [39], substance dissolution, separation process [40] and other processes [41–43]. Recently, more and more researchers have scored remarkable achievements in the application of DESs for the desulfurization of fuel [44–50]. For example, Gano using FeCl₃-based DES for desulfurization and extraction efficiencies as high as 64% and 44% for DBT and thiophene could be achieved with the solvent in a single stage extraction [44]. Li utilized the DES TBAB/HCOOH on removal of BT, DBT, and TS. The results showed that the sulfur removals with BT, DBT, and TS were 81.75, 80.47, and 72% in a single stage, respectively [45]. Though the extractive desulfurization with DESs is a promising method, the desulfurization efficiency is still low after one-step extraction. Then Lü synthesized different DESs and it is worthwhile to note that the removal of DBT can reach 91% upon the addition of H₂O₂ [46]. Yin also have successfully taken advantage of DESs ChCl/p-TsOH and TBAC/p-TsOH to achieve deep desulfurization through oxidation [47].

In this paper, different DESs were synthesized and served as extractants to apply in the ECODS system consisted of HPW as catalyst and 30 wt% H₂O₂ as oxidant. It was found that the DESs prepared with ChCl and PEG could showed wonderful activity in removing BT, DBT, 3-methylbenzothiophene (3-MBT), 4-methylbenzothiophene (4-MDBT) and 4,6-

dimethylbenzothiophene (4,6-DMDBT) from model oil at 50 °C within 3 h. Furthermore, desulfurization efficiency can be greatly promoted using only a few amount of DES. The reaction mechanism was proposed as well according to the gas chromatography–mass spectrometer (GC–MS).

2. Experimental

2.1. Preparation of model oil and DESs

BT, DBT, 3-MBT, 4-MDBT and 4,6-DMDBT were dissolved in *n*-octane to prepare model oils with tetradecane as an internal standard. The sulfur content of these model oils is 500, 500, 500, 500 and 500 ppm, respectively.

The DES ChCl/2PEG was simply synthesized by combining choline chloride (ChCl) with polyethylene glycol (PEG-200) at molar ratio of 1:2 in a flask. Then the mixture was heated up to 80 °C by a thermostatic oil bath in rotational speed of 800 rpm. The reaction process was maintained for 3 h. The method was also applied to synthesize ChCl/[1,3-Butyleneglycol] (ChCl/2BG), ChCl/2Ethylene glycol (ChCl/2EG), ChCl/2Glycerol (ChCl/2GI), ChCl/2Propanoic acid (ChCl/2Pr), ChCl/Malonic acid (ChCl/MA, molar ratio is 1:1) and ChCl/2Urea (ChCl/2U).

2.2. Desulfurization procedure

A certain amount of phosphotungstic acid (HPW), H₂O₂, ChCl/2PEG and model oil were added into a self-made two-necked flask in this order. The mixture was stirred vigorously at the set temperature with water bath for 3 h under atmospheric pressure. From the reaction phenomenon, it can be seen that the catalyst could be dissolved in DES phase but hardly in oil phase. Other DESs and catalysts such as tungsten acid (H₂WO₄), sodium tungstate dehydrate (Na₂WO₄·2H₂O), tungsten trioxide (WO₃), ammonium tungstate [(NH₄)₁₀W₁₂O₄₁·xH₂O] were also experimentally evaluated.

When the reaction finished, the supernatant model oil was separated from the DES phase by a simple decantation and analyzed through gas chromatography–flame ionization detection (GC–FID) as reported in the past [51–53]. The concrete method is listed in Supplementary material.

3. Results and discussion

3.1. Effect of different desulfurization systems on DBT removal

The solubility of the extractant in model oil is one of the most important factors that will lead to cross-contamination. The solubility of synthetic DESs was analyzed by ¹HNMR and the results are shown in Fig. 1. The solvent used for ¹HNMR was chloroform-*d* (CDCl₃). According to the analysis of ¹HNMR, it can be seen that the DESs are insoluble in *n*-octane except ChCl/2GI, ChCl/2Pr and ChCl/MA. The peak at 10.34 ppm belongs to the active hydrogen on the carboxyl of propionic acid while the peak at 11.97 ppm belongs to active hydrogen on the carboxyl of malonic acid. The chemical shift peaks at 2.54 ppm and 2.77 ppm are peaks of hydroxyl in glycerol. Therefore, the three DESs could not be used as ideal extractants in the ECODS system.

To explore the capacity of DESs on desulfurization, DBT was selected as a typical sulfide. Three desulfurization systems including extractive desulfurization (EDS), extractive and oxidative desulfurization (ECODS) and extractive and catalytic oxidative desulfurization (ECODS) were carried out to select the best system under atmospheric pressure at 50 °C. As shown in Table 1, the mere extraction efficiency of the three DESs was not ideal and even decreased when H₂O₂ was added. The phenomena might be attributed to

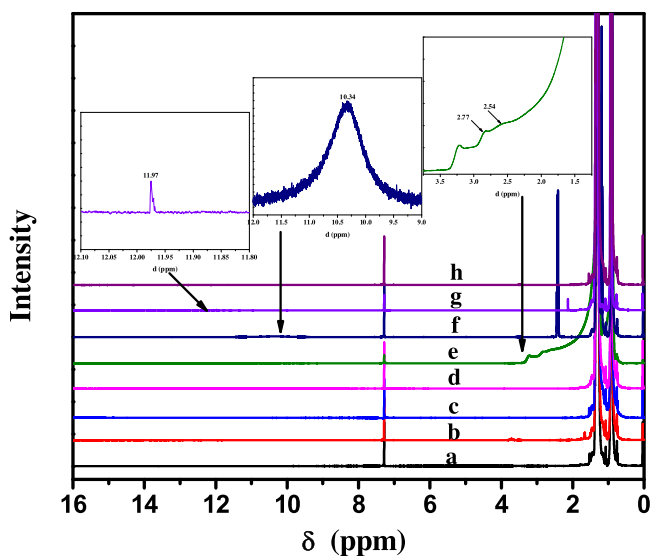


Fig. 1. ¹HNMR analysis of the solubility of different DESs. a. *n*-octane; b. ChCl/2PEG + *n*-octane; c. ChCl/2EG + *n*-octane; d. ChCl/2BG + *n*-octane; e. ChCl/2GI + *n*-octane; f. ChCl/2Pr + *n*-octane; g. ChCl/MA + *n*-octane; h. ChCl/2U + *n*-octane.

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