



Full Length Article

Extractive deep desulfurization of diesel using choline chloride-glycerol eutectic-based ionic liquid as a green solvent



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HIGHLIGHTS

- NMR of ChCl-G eutectic-based ionic liquids.
- Effect of stirring speed and extraction time.
- Effect of ChCl-G:oxidized model oil filtrate volume ratio and multistage extraction.
- Effect of sulfur species was investigated.
- ChCl-G showed 100% sulfur removal with two time extraction.

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ABSTRACT

Today there are serious regulations to reduce the sulfur content of fuel because the SO_x produced during the combustion of fuel containing sulfur species make the air polluted and have dangerous environmental impacts. With the aim to replace the present volatile, flammable and toxic organic solvents or inefficient, corrosive and expensive ionic liquids (ILs), the choline chloride-glycerol (ChCl-G) eutectic-based ionic liquid (EIL) was introduced as a green, effective, non-toxic, non-corrosive and also recyclable for extractive desulfurization (EDS) of oxidized dibenzothiophene (DBTO₂) from model oil in this work for the first time. ChCl-G showed excellent sulfur removal and it showed a high extraction efficiency of 97.06% within 20 min. Using ChCl-G, the DBTO₂ concentration was reduced from 100 ppmw to 0 ppmw within two extraction cycles achieving deep desulfurization. Effect of some important parameters including stirring speed, extraction time, ChCl-G:oxidized model oil filtrate volume ratio, multistage extraction and sulfur species (DBTO₂ and oxidized 4,6-dimethyldibenzothiophene (4,6-DMDBTO₂)) were investigated. It was found that the optimum condition for EDS were stirring speed of 300 rpm, 20 min of extraction time, 1:5 ChCl-G:oxidized model oil filtrate volume ratio and two cycles of extraction. The feasibility of ChCl-G for extraction of different sulfur species was observed in the order of DBTO₂ > 4,6-DMDBTO₂. The spent ChCl-G was regenerated and showed an extraction efficiency of 88.34% within 3 cycles. The results of the present work hopefully provide useful information for further industrial application of ChCl-G as an efficient green solvent for EDS of diesel fuel.

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1. Introduction

Sulfur species has been known for many centuries. It occur uncombined in nature, and when it is oxidized to sulfur oxide (SO_x) it becomes a major pollutant [1]. Sulfur content is usually expressed as the weight percentage of sulfur species in the fuel, because there are many different sulfur species in petroleum derived fuels. Diesel fuel contains high quantities of sulfur species. European emission standards and preferential taxation have forced

oil refineries to dramatically reduce the level of sulfur species in diesel fuel. Therefore, the removal of these sulfur species from diesel fuel is one of the prime important processes in refining industry [2].

High levels of sulfur species in diesel fuel are harmful to the environment because, upon combustion, they prevent the use of catalytic diesel particulate filter to control diesel particulate emissions, as well as more advanced technologies, such as nitrogen oxides (NO_x) adsorbents to reduce emissions. The current fuel combustion engines and exhaust-cleaning catalyst are quite sensitive to sulfur species in which high sulfur level can cause faster deterioration of the engine and catalyst [3]. Sulfur species can cause detri-

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mental effects by saturating the reduction sites on the catalyst, causing the space availability for the reduction of NO_x to decrease [4]. This leads to poisoning of the metal catalyst lowering the efficiency of catalytic converters in automobiles [5].

Moreover, sulfur in diesel fuel is oxidized during combustion, producing sulfur dioxide (SO₂) and sulfur trioxide (SO₃) that have been identified as among the compounds that contribute to acid rain, ozone depletion and air contamination which causes serious diseases in the human respiratory system. The acid formed in this way can accelerate the erosion of historical buildings. It can be transferred to soil, damage the foliage, depress the pH of the lakes with low buffer capacity and endanger the marine life [6]. Furthermore, SO₂ can be the cause of sulfate aerosol formation. The aerosol particles have an average diameter of 2.5 μm that can be transported into the lungs and cause irritation to the lungs and respiratory problem such as lung cancer. In order to reduce the negative effects on human health and the environment, reduction of sulfur content in fuel oils is desirable [7]. Therefore, the production of ultra-low sulfur diesel (ULSD) has become a major task of refineries all over the world. This is due to the stringent environmental regulations which are placing considerable pressure on refinery operators to reduce sulfur content in fuels to 10 ppmw [8].

Generally, removal of organic sulfur from fuel is difficult, because sulfur can only be detached from the organic molecule when certain chemical bonds are cleaved. Breakage of such bonds requires high temperature and pressure. Hydrodesulfurization (HDS) is the conventional sulfur species removal method. This method requires high temperature (300–400 °C), more active catalysts (CoMo and NiMo), longer residence time and high hydrogen gas pressure ranging from 20 to 100 atm (needed for kinetic and catalyst stability purposes) in order to produce fuels that have a lower level of sulfur species [9]. It uses hydrogen supply to break the sulfur species into hydrogen sulfides (H₂S) which is then converted into elemental sulfur and used to produce sulfuric acid (H₂SO₄). Meanwhile, the excess hydrogen is recycled back to the HDS process. The number of hydrogen cycles required may be high depending on the targeted sulfur content level [10].

HDS eliminates the aliphatic and alicyclic sulfur species [11], but more active catalysts are needed in order to achieve the very low sulfur content because the available catalyst is less effective for the hydrogenation of benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivatives [12]. As a result, these sulfur species still remain in the diesel fuel [13]. There is also the problem of undesirable side reactions such as increased coke formation and the saturation of olefins which can result in decrease in octane/cetane number due to hydrogenation side reactions [11]. Therefore, employing HDS for removal of these sulfur species is extremely costly as it occurs under more extreme operating conditions such as elevated temperature and elevated pressure. In order to overcome such a formidable challenge, the renovation of the current sulfur removal plants and the installation of new desulfurization facilities are inevitable. The prohibitive desulfurization cost for refractory sulfur species has obliged researchers to find more efficient and economic alternatives [6].

Extractive desulfurization (EDS) is a well-established process that can be carried out at/or around ambient temperature and pressure. The key to an EDS process is to find a good extractant featuring the following attributes, for example, good extractive ability for the sulfur species, ease of regeneration of the used extractant, contamination-free to the fuels, non-toxicity, environmentally benign, and high stability for repetitive uses [14]. EDS is based on the fact that sulfur species are more soluble compared to hydrocarbons in an appropriate solvent. To make the process efficient, the solvent must be carefully selected to satisfy a number of requirements. The sulfur species must be highly soluble in the solvent. The solvent must have a boiling temperature different than

that of the sulfur species, and it must be inexpensive to ensure economic feasibility of the process [15].

Chemical industry has reduced the use of solvents while focusing more on the development of sustainable green chemistry [16]. In petroleum refining industry, sulfolane and furfural are commercial extraction solvents that are mostly used for aromatics extraction from different petroleum fraction. Since part of the sulfur species in petroleum are in the form of aromatic species, these two solvents are suitable for EDS [17]. However, the regeneration of used solvents is much harder and not economically feasible due to volatility limitations. Other molecular solvents like polyalkylene glycol, imidazolidinone, pyrimidinone, and dimethyl sulfoxide, have also been patented. However, their abilities for EDS are not sufficient and solubility in the fuel is noticeable, which may cause cross contamination. Compared to molecular solvents, some ILs showed high extractability for sulfur species, which indicates that ILs might be a novel and competitive extractive solvent [18].

ILs has been applied in the petrochemical industry especially in catalytic processes, extractive distillation and liquid-liquid extraction process for desulfurization. Their negligible vapour pressure allows the extracted product to be separated from the ILs through low pressure distillation with potential energy savings. In addition, as a result of their negligible vapour pressure, they are able to be regenerated. The use of ILs for extraction of sulfur species from diesel fuel was first described by Bosmann et al. in 2001 [19]. Based on the initial idea to extract the sulfur species by chemical interaction, the extraction of DBT with Lewis and Brønsted acidic ILs was majorly investigated. They indicated that such Lewis-acid based interactions enhance the extraction power of ILs that permit complex formation of sulfur species and ILs. They also identified that extraction of diesel fuel is much more complicated due to the complex chemical composition of diesel fuel which includes many different sulfur species and other impurities like organic nitrogen and oxygen compounds [20]. EDS process using ILs can be a complementary technology for the HDS process, with some studies reported. These studies indicate that the ILs have high extraction ratios and greater selectivity compared to molecular solvents because of the unique solvent characteristics of ILs [10].

However, most ILs work at the disadvantage of high cost for bulk applications, they are relatively expensive (due to expensive raw materials, long preparation and purification procedures) and some of them even have very low tolerance to moisture [21], limited solute solubility, and high viscosity [22]. Furthermore, their toxicology has yet to be examined and some studies suggest for further assessment of their applicability as green media [23]. Because of these reasons it does not make ILs technology competitive with conventional solvents [24].

Recently emerging alternatives to the conventional ILs are deep eutectic solvents (DESs) or also known as eutectic-based ionic liquids (EILs) or analogs ILs [25]. This third generation of ILs is emerging with structure comprising of biodegradable and readily available ions, such as natural bases (choline), amino acids, and naturally occurring carboxylic acids [26]. Together with this third generation of ILs, EILs represent promising alternatives by virtue of their simplicity in preparation and biodegradability, as well as because of their lower associated cost and can be custom built to suit certain and targeted application by the proper selection of their startup ingredients [27].

This paper focused on the development of choline chloride-glycerol (ChCl-G) eutectic-based ionic liquid (EIL) for the extraction of sulfur species in model oil and diesel fuel. Reaction parameters include stirring speed, extraction time, ChCl-G:oxidized model oil filtrate volume ratio, multistage extraction and sulfur species. Regeneration of ChCl-G was also investigated. The optimized extraction conditions were further employed for extractive deep desulfurization of diesel fuel.

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