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# Polyethylene glycol as a green solvent for effective extractive desulfurization of liquid fuel at ambient conditions

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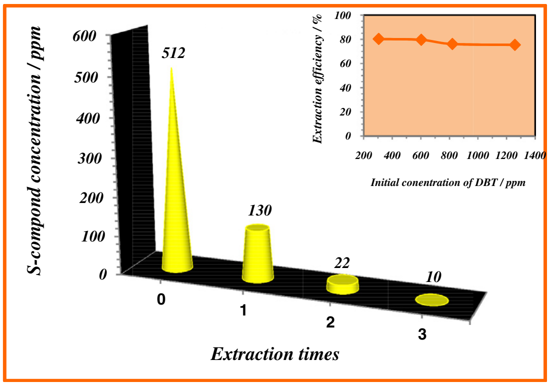
## HIGHLIGHTS

- PEG was introduced as a green and effective solvent for EDS for the first time.
- Extraction performance of PEG is temperature and initial sulfur content independent.
- The BDT content was reduced from 512 to 10 ppmw only within three extraction cycles.
- Regenerated PEG could effectively extract DBT from fresh model fuel.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Today there are serious regulations to reduce sulfur content of fuels because the $SO_x$ produced during the combustion of fuels containing sulfur compounds make the air polluted and have dangerous environmental impacts. With the aim of replacement of the present volatile, flammable and toxic organic solvents or inefficient, corrosive and expensive ionic liquids (ILs), the polyethylene glycol (PEG) was introduced as a green, effective, non-toxic, non-corrosive and also recyclable molecular solvent for extractive desulfurization (EDS) of benzothiophenic compounds from liquid fuel in this work for the first time. PEG shows excellent EDS and it has the higher extraction efficiency for dibenzothiophene (DBT) (76% within 90 s) than those of ILs. Using this extractant, the BDT content was reduced from 512 to 10 ppmw (98%) only within three extraction stages, the minimum number of cycles within shortest time reported up to now, and the deep desulfurization was achieved. Effect of some important parameters including initial concentration of sulfur compound, PEG dosage, time and temperature of extraction on the EDS process was investigated. It was fond that extraction performance of PEG is independent to temperature and initial sulfur content, which is an excellent finding for industrialization. The feasibility of PEG for extraction of different thiophenic compounds was observed in the order of dibenzothiophene > benzothiophene > 4,6-dimethyldibenzothiopene. Finally, the PEG was reused in several cycles and then it was regenerated by adsorption method. The results of the present work hopefully provide useful information for future industrial application of PEG as an efficient green solvent for the EDS of liquid fuels.

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## 1. Introduction

In the recent years, air pollution has become an increasingly important subject worldwide from the environmental point of view. One of the major sources of air pollution is $SO_x$ compounds produced during the combustion of fuels containing sulfur compounds [1–4]. Sulfur oxides can destroy catalytic converters used to reduce CO and $NO_x$ emissions from an internal combustion engines and also have side effects such as acid rain and ozone depletion [5–8]. Therefore, many governments in the world have forced their petroleum refinery industries to reduce sulfur content in the fuels to near zero-levels (<10 ppm S) by 2012 [1,7].

Hydrodesulfurization (HDS) process, converting sulfur compounds to $H_2S$ and corresponding hydrocarbons at very high temperatures (300–400 °C) and pressures (20–100 atm of $H_2$) [8], is the major industrial technique for the removal of sulfur compounds from the fuels. This classical process not only reduces the octane/cetane number of fuel due to saturation of olefins, but also has a limited capacity to efficiently eliminate the refractory benzothiophenic compounds, e.g. dibenzothiophene (DBT), while these compounds take a major part of the sulfides [6] in fuels [7–9]. Therefore, to meet low sulfur-level by the HDS process, severe operation conditions and high economic investments are necessary. For this reason, exploration of convenient and energy-saving processes to reduce the sulfur content of hydrocarbon fuels and therefore reduce the production of $SO_x$ has become a hot research area. At the present, there are various non-hydrodesulfurization approaches including extraction, adsorption, biodesulfurization, oxidation and membrane separation [8]. But replacement of the HDS technique with the existing technologies needs to improve them.

Extractive desulfurization (EDS) process can be carried out at mild and simple conditions and it does not change the chemical structure of the compounds and consequently has no effect on the quality of liquid fuels [5,10]. So, this technique seems to be more appropriate process and it has become the object of active research in recent years. Different organic solvents, such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile and 1-methyl-2-pyrrolidinone (NMP) have been used as extractive solvents in desulfurization [11]. Nevertheless, the commonly used solvents are volatile, flammable, toxic and they have serious consequences for the environment [4]. Therefore, it can be of great significance to explore new environmentally friendly and also cheap, effective and recyclable solvents to improve the extractive desulfurization process. Because of low vapor pressure and thermal stability, ionic liquids (ILs) are considered to be “green solvents” to replace the volatile organic solvents [12]. During the past few years, many studies have been done on desulfurization by ILs [1,3,7,12]. But extractive desulfurization by ILs has many problems including: unexplored ecosystem impacts, costly expensive [1,12], high viscosity of ILs (which decreases diffusion coefficient and interphase area and therefore diffusion rate during the extraction process) [4,13] and corrosion damages caused by halogen-containing ILs [3]. Moreover, because of rather low desulfurization efficiency by extraction with IL, either large volumes of ionic liquid for an efficient liquid–liquid extraction process must be used [7] or extraction should be integrates with oxidative desulfurization process [5]. Whereas oxidative desulfurization has several major problems, which hindered the industrial application of extractive oxidative desulfurization, such as decreasing the quality of fuel because of non-excellent selectivity to the organosulfur compound (hydrocarbons can also be oxidized), difficult post-treatment of sulfoxides and sulfones produced during the oxidation process, the reaction’s safety and the high cost of the oxidant [5,14].

Recently, it has been reported that hydrogen bond formed between the active hydrogen of amine-based protic ILs or ammonium-based deep eutectic solvents as extractant and the sulfur atom of S-containing molecules in fuels accounts for the higher extraction efficiency [4,12]. On the other PEG, as a proton donor solvent [15], not only has a very low vapor pressure (<0.01 hPa at 20 °C for PEG-200) and applicability over a wide temperature range because of high boiling point (b.p. >150 °C) [16] but also, in comparison with the synthesized ILs, it has several advantages such as low viscosity (dynamic viscosity 58–85 mPa s at 20 °C) [16], non-toxicity (which approved by the Food and Drug Administration (FDA), USA) [17–19], corrosion inhibition [20,21], cheap and easily obtained molecular solvent [4]. Based on recently reported works [4,12] and the mentioned characters of PEG, it seems that PEG is a good (green, cheap and effective) option for extractive desulfurization. So these points inspire us to investigate the efficiency of pure PEG, as an immiscible liquid with organic phase, for extractive desulfurization of liquid fuel in the present work.

## 2. Experimental section

### 2.1. Materials

The details of the analytical grade chemicals used are as follows: PEG-200 (Merck), heptane (Merck, purity >99%), activated granular carbon (Merck, size 850–1000 μm), BT, DBT and DMDBT (Sigma–Aldrich, mass fraction purity of >98%).

### 2.2. Extractive desulfurization process

The initial concentration of model fuels was 500 ppmw except for defined tests and they were prepared by dissolving BT, DBT and DMDBT in to *n*-heptane, separately. In the all experiments, defined amount of model liquid fuel containing DBT (as a typical sulfur compound) and PEG with volume ratios PEG/fuel 1:1 (excluding for certain experiments) transferred into a 50 ml glass bottle and the system was placed in a stirred thermostatted batch system at desired temperature (±0.1 °C). In a typical kinetic run, the binary mixture was stirred, stopped at desired time intervals and sampling was conducted for further quantification. In the other experiments, the mixture was stirred vigorously for 5 min and then the sulfur content of the model fuel was determined. The quantification of initial and final sulfur content in the fuel phase, using UV/Visible spectrophotometer (PG Instrument Ltd., T-80) at the related $\lambda_{max}$ [22], allowed the determination of the extraction efficiency (*E.E*%) based on: $E.E(\%) = (1 - C_t/C_0) \times 100$; where $C_0$ and $C_t$ are initial and at any time concentration of sulfur compound (ppmw). To use the spent PEG in the next cycle, the upper organic phase was removed and the used PEG was exposed to the fresh model fuel with fixed volume ratio of PEG/model fuel as 1:1 for the next extraction stage. Regeneration of spent PEG was achieved by adsorption. For this purpose, a bottle containing spent PEG and activated granular carbon as a common adsorbent with the mass ratio PEG/adsorbent 50:1 was placed in a constant temperature shaker (n-BioTEK, NB-304) and shaked at 150 rpm for 24 h and then regenerated PEG was used again in a new EDS experiments.

## 3. Results and discussion

### 3.1. Effect of extraction conditions on sulfur removal

Extraction process may be affected by some factors including phase ratio of extractant to model fuel, initial sulfur content of

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