



# Desulfurization of fuels with sodium borohydride under the catalysis of nickel salt in polyethylene glycol

Xianglong Meng, Lu Li, Kan Li, Pin Zhou, Hongbo Zhang, Jinping Jia, Tonghua Sun\*

School of Environmental Science and Engineering, Shanghai Jiaotong University, Dongchuan Road 800, Shanghai 200240, China

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## ABSTRACT

A facile transportation fuel reductive and extractive desulfurization process is studied using polyethylene glycol as extraction solvent, which is economical and environmental friendly, and sodium borohydride as reductant in this work. Several important parameters including sodium borohydride and nickel chloride dosage, stirring rate, temperature and polyethylene glycol/oil volume ratio are investigated. The total sulfur desulfurization efficiency for the simulated fuel reaches nearly 97% in this process after 1 h reaction at the temperature of 10 °C with sodium borohydride/sulfur molar ratio = 15, nickel chloride/sulfur molar ratio = 3, polyethylene glycol/oil volume ratio = 1. Furthermore, the desulfurization efficiency can be enhanced to 99% in a two-step desulfurization process. All components were detected by GC or GC-MS, and the possible desulfurization mechanism is deduced. The results show that sulfur compounds can be removed by direct desulfurization. The desulfurization performance of recycled polyethylene glycol and regenerated polyethylene glycol was also investigated and the desulfurization efficiency was 92% and 90% respectively, indicating polyethylene glycol can be regenerated in this process. Finally, actual transportation fuels (e.g. gasoline, diesel) were investigated and it revealed that polyethylene glycol and sodium borohydride can be applied in actual fuel extractive and reductive desulfurization.

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## 1. Introduction

Sulfur compounds, which are initially existing in fuels, can be released to the environment as sulfur oxides (SO<sub>x</sub>) (Mortaheb et al., 2012) during combustion. Due to the cause of environmental pollution and toxic effect to the three-way catalysts in vehicles, stringent regulations of ultralow-sulfur fuels have been implemented (Song, 2003). In order to meet the demand for automobile fuels, lots of desulfurization processes have been developed in recent years (Srivastava, 2012). Hydrodesulfurization (HDS), as the most widely applied industrial desulfurization method, is effective for aliphatic and acyclic sulfur compounds, but is less effective for benzothiophene (BT), dibenzothiophene (DBT) and their derivatives (Shafia and Hutchingsb, 2000). Furthermore, it may reduce the octane/cetane number of fuel due to saturation of olefins. Besides these, high investment and operating costs are needed for operation (Guo et al., 2012). Therefore, many researchers put their efforts into the improvement of the conventional HDS and the

development of other alternative technologies with non-hydrodesulfurization, such as oxide desulfurization (ODS) (Zhao et al., 2007; Nie et al., 2013), extractive desulfurization (EDS) (Rashid et al., 2014; Yu et al., 2016), absorptive desulfurization (Xu et al., 2013; Yang et al., 2017), bio-desulfurization (Bhatia and Sharma, 2006; Gonsalvesh et al., 2013), electrochemical desulfurization (Tang et al., 2015), and pervaporative desulfurization (Mitra, 2012).

Among the methods illustrating above, EDS can be carried out at ambient conditions without using costly hydrogen. More importantly, the process does not alter the chemical structure of compounds in fuels, and thus little effect on fuel qualities. Yu et al. developed an extractive desulfurization (EDS) system with polyether-based ionic liquids (ILs) as extractants and the desulfurization rates of BT, DBT and 4, 6-dimethyldibenzothiophene (4, 6-DMDBT) in simulated gasoline can reach 84.7%, 91.4%, and 81.0% respectively (Yu et al., 2016). Kianpour et al. used PEG as solvent for EDS and the extraction efficiency for DBT was 76% within 90 s (98% with three extraction stages) (Kianpour and Azizian, 2014). To enhance the desulfurization efficiency, EDS is always combined with other desulfurization processes (e.g. ODS, reductive desulfurization). Zhang et al. used acidic ionic liquid *N*-

\* Corresponding author.

E-mail address: [sunth@sjtu.edu.cn](mailto:sunth@sjtu.edu.cn) (T. Sun).

carboxymethylpyridine hydrosulphate ( $[\text{CH}_2\text{COOHPy}]\text{HSO}_4$ ) as the extractant and catalyst and hydrogen peroxide as the oxidant for EODS, sulfur removal of simulated oil could reach 99.7% (Zhang et al., 2011). Jiang et al. also used ionic liquid and  $\text{H}_2\text{O}_2$  for EODS, the S-content of actual hydrogenated diesel reduced from 659.7 ppm to 8.62 ppm (Jiang et al., 2016). However, the oxidants can not only oxidize sulfur compounds, but will also oxidize the hydrocarbon parts, which may deteriorates the quality of fuel oils. Furthermore, the post treatment of sulfoxides and sulfones mixture produced in the desulfurization process is still a tough problem. Extractive and reductive desulfurization (ERDS) has gained more and more attentions in the past few years due to its high desulfurization efficiency without deteriorating fuels (Khurana and Magoo, 2010). Previous works have proved that sodium borohydride ( $\text{NaBH}_4$ ) (Shu et al., 2014) can be used as a reductant for reductive desulfurization under the catalyst of nickel boride in-situ generated in ionic liquid (IL). Considering the high cost, as well as the unexplored ecosystem impacts, high viscosity and corrosion damages (halogen-containing ILs) IL is still limited in the industrial applications (Dharaskar et al., 2014).

In this research PEG is used as a green extraction agent due to its low viscosity (dynamic viscosity 58–85 mpa·s at 20 °C) (Kianpour and Azizian, 2014), non-toxicity (Zhang et al., 2016), corrosion inhibition and low cost (Karakoti et al., 2011) for ERDS process with nickel boride being as catalyst. This desulfurization method could be operated at ambient conditions, and thus more energy/cost saving and environment friendly in comparison with HDS. In this process  $\text{NaBH}_4$  can react with the crystal water in nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) and the trace water existing in PEG. The desulfurization efficiency in this work is 97% under the optimal conditions (95% under selected conditions), and a higher desulfurization efficiency of 99% can be obtained in a two-step desulfurization process.

## 2. Experimental

### 2.1. Materials

Simulated fuel with a sulfur content of 535 ppm was prepared by dissolving T, BT and DBT in n-octane.  $\text{NaBH}_4$  (96%, AR), nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , >98%, AR), were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). T, BT, DBT and n-octane(AR) were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). PEG-200, ethanol, ethylene glycol, glycerol and furfuryl alcohol were purchased from Aladdin Reagent Co. Ltd (Shanghai, China) Actual gasoline (76 ppmS) and diesel (85 ppmS) was supplied by Sinopec Shanghai Petrochemical Company.

### 2.2. Desulfurization process

A typical desulfurization experiment was carried out in a sealed two-neck flask at ambient conditions.  $\text{NaBH}_4$ , simulated or actual fuel and PEG (or other alcohol extracted solventS) were added into the two-neck flask with stirring.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  was then dripped into the mixture slowly.  $\text{NaBH}_4$  would react with  $\text{NiCl}_2$  and  $\text{H}_2\text{O}$  (crystal water in  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and trace water in PEG). After the reaction, the oil phase and PEG were separated by a separatory funnel. Sediment were separated from PEG by filtration and digested by hydrochloric acid. Gas phase was absorbed by sodium hydroxide solution. Desulfurization efficiency was calculated by the following formula (eq. (1)),

$$\text{Desulfurization efficiency (wt. \%)} = \frac{\text{TS}_1 - \text{TS}_2}{\text{TS}_1} \times 100\% \quad (1)$$

where  $\text{TS}_1$  is the total sulfur (TS) content in the original actual or simulated fuel and  $\text{TS}_2$  is the TS content in the fuel after desulfurization.

The after used PEG was mixed with an equal volume of water to obtain a PEG aqueous solution. The solution was first filtered by filter paper to remove the sediments, and then was distilled using rotary evaporator to remove  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ .

### 2.3. Analytical methods

The sulfur (S) content in simulated gasoline after desulfurization,  $\text{H}_2\text{S}$  generated from desulfurization process was determined by gas chromatograph-flame photometric detector (GC 7890B FPD, Agilent, USA) equipped with a HP-5 column (0.5 mm × 30 m). Injector temperature and detector temperature were 340 °C and 250 °C, respectively. Column temperature was programmed from 50 °C to 250 °C at 20 °C/min. The injection amount was 1 μL for all samples and the split ratio was 90:1. The S content in actual gasoline and diesel were determined by sulfur-nitrogen analyzer (Antek 9000, Antek). The components of simulated fuel after desulfurization were analyzed by gas chromatography/mass spectrometer (GC/MS, 7890A-5975C, Agilent, USA) equipped with a DB-5MS column (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas at a constant flow of 1 mL/min. Injector temperature was 300 °C and oven temperature was programmed from 20 °C to 200 °C at 20 °C/min. The injection amount was 1 μL for all samples and split ratio was 10:1. Mass spectra conditions were set as ionization voltage of 70 eV, and full scan model in m/z range of 20–400, with ion source and quadrupole temperatures of 230 °C and 150 °C.

## 3. Result and discussion

### 3.1. Effect of different alcohol extraction agent on desulfurization efficiency

The extractant in this experiment plays two important roles. On one hand, it can extract the sulfur compounds from oil phase. On the other hand, it directly takes part in the reaction of generating  $\text{H}^*$  with  $\text{NaBH}_4$  for sulfur compounds reduction. As shown in Fig. 1, different alcohol extractants have significant effects on the desulfurization efficiency. It can get a high removal rate of T about 95% whether added in alcohol extractant or not because T could be easily reduced by  $\text{NaBH}_4$ . BT and DBT were hardly removed in the absence of extractant. Among all of the alcohol extractant, PEG-200 and Furfuryl alcohol performed a better desulfurization performance for all of the sulfur compound (T, BT and DBT), and the total desulfurization efficiency were 95% and 87% respectively. The higher polarities of PEG and furfuryl alcohol makes T, BT and DBT can be extracted from oil phase easily. Another reason is that  $\text{NaBH}_4$  reacts with other alcohols so severely that most of the produced  $\text{H}^*$  run out of the reaction system. Moreover, because of the larger viscous of PEG, nickel boride produced in this process owns a finer particle size and higher specific surface area, which can perform a higher desulfurization efficiency (Shu et al., 2014).

### 3.2. Effect of various experiment conditions on desulfurization efficiency

#### 3.2.1. $\text{NaBH}_4$ /sulfur (B/S) molar ratio

$\text{NaBH}_4$  plays an important role in this desulfurization process. Firstly it reacts with  $\text{H}_2\text{O}$  to produce active hydrogen ( $\text{H}^*$ ) that can reduce sulfur compounds. Secondly it reacts with  $\text{Ni}_2\text{Cl}$  to generated nickel boride which play an important catalytic role in the desulfurization reaction. As shown in Fig. 2, desulfurization efficiency increases with the increasing ratio of B/S in the same reaction time, indicating the dosage of  $\text{NaBH}_4$  has a significant effect on desulfurization efficiency, and the desulfurization efficiency is about 97% at the B/S molar ratio = 15 in 60 min. More  $\text{NaBH}_4$  adds,

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