

Extraction and oxidative desulfurization of diesel fuel catalyzed by a Brønsted acidic ionic liquid at room temperature

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The Brønsted acidic ionic liquids 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO₄]) and *N*-butylpyridinium hydrogen sulfate ([C₄Py][HSO₄]) were used as extractant and catalyst for desulfurization of diesel. The results show that [BMIM][HSO₄] is better as extractant and catalyst than [C₄Py][HSO₄] during the desulfurization process. The sulfur removal of dibenzothiophene (DBT) in *n*-octane was 99.6% in 90 min under the conditions of $V_{\text{model oil}}/V_{\text{IL}} = 2:1$ and H₂O₂/DBT molar ratio at 5 (O/S = 5), at room temperature. The sulfur removal of four sulfur compounds by extraction and catalytic oxidation process followed the order of DBT > benzothiophene (BT) > thiophene (TS) > 4,6-dimethyldibenzothiophene (4,6-DMDBT). Moreover, the [BMIM][HSO₄] can be recycled for at least 6 times with a little decrease in the desulfurization activity. The sulfur removal of diesel fuel containing sulfur content of 97 ppm is 85.5%, which was much better than desulfurization performance by simple extraction with IL (11.0%). In this extraction and oxidative desulfurization process, DBT was oxidized to corresponding sulfone by H₂O₂ with Brønsted acidic IL [BMIM][HSO₄] which served as not only extractant but also catalyst.

Introduction

In the last decades, much attention has been paid to the deep desulfurization of fuels due to more stringent environmental regulations.¹ Although hydrosulfurization (HDS) is efficient in removing thiols, sulfides, and disulfides, it is difficult to reduce refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives to an ultra-low level. Owing to their steric hindrance, HDS usually requires severe operating conditions and large capital cost to achieve ultra-deep desulfurization of fuels. Therefore, the development of the alternative ultra-deep desulfurization processes, such as adsorption,² extraction,³ biodesulfurization,⁴ and oxidation,⁵ is desired. Among these methods, oxidative desulfurization (ODS) combined with extractive desulfurization is considered to be one of the most promising processes. Organic sulfur compounds, such as DBT and its derivatives, can be oxidized selectively to their corresponding sulfoxides and sulfones, and then removed in subsequent extraction process.⁵ However, extractants are usually flammable and volatile organic compounds, which result in additional safety and environmental problems.

The potentials and applications of room temperature ionic liquids (ILs) as “green” solvents for separations, organic synthesis, and catalysis have been extensively reviewed.⁶ The extraction of fuels using ILs to remove sulfur compounds has been reported

recently.^{7–11} However, the efficiencies of sulfur removal are rather low, only in the range of 10%–40%.

In order to increase the efficiencies of the sulfur removal, the extraction using ILs are combined with oxidative desulfurization process.^{12–14} In these processes, sulfur removal could reach more than 90.0%, with H₂O₂ as oxidant, ILs [BMIM][PF₆], [BMIM][BF₄], and Me₃NCH₂C₆H₅Cl·2ZnCl₂ served as extractant, and additional catalyst was added, such as CH₃COOH, Na₂MoO₄·2H₂O.

The oxidative desulfurization of fuel catalyzed by acidic ILs [HMIm][BF₄] and [Hnmp][BF₄] in the presence of H₂O₂ has been investigated by Lu *et al.*¹⁵ and Zhao *et al.*¹⁶ The sulfur removal also could reach more than 90.0%. But the experiment had to be carried out at high temperature or with large amount of ILs.

In this paper, Brønsted acidic ILs [BMIM][HSO₄] and [C₄Py][HSO₄] were used as catalyst and extractant for desulfurization of model diesel and diesel fuel, respectively. The aim of our study was to improve the efficiencies of desulfurization of diesel at room temperature.

Experimental

Materials

4,6-Dimethyldibenzothiophene (4,6-DMDBT), dibenzothiophene (DBT), and benzothiophene (BT) were purchased from Acros Organics, USA. All other reagents, including pyridine, 1-chlorobutane, ethyl acetate, dichloromethane, sulfuric acid (98%), thiophene (TS), *n*-octane, and H₂O₂ (30 wt%) were purchased from Beijing Chemical Company and were of analytical grade. *N*-Methylimidazole (purity, >99%) was purchased from

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Zhejiang Kaile Chemical Plant. Diesel fuel with 16% aromatics was kindly provided by the Research Institute of Petroleum Processing.

Preparation of ionic liquids

The ILs [BMIM][HSO₄] and [C₄Py][HSO₄] were prepared according to the published literature.^{17,18} Equimolar amounts of *N*-methylimidazole (1.0 mol) and 1-chlorobutane (1.0 mol) were added to a round-bottomed flask (500 mL) fitted with a reflux condenser and reacted at 70 °C for 24 h. The white precipitates were filtered off and washed three times with ethyl acetate to get [BMIM][Cl] which was monitored by copper(II) chloride in ethanol and no blue colour can be found.¹⁹ [BMIM][HSO₄] was obtained by a dropwise addition of one equivalent of concentrated sulfuric acid (98%, 11.5 g) to a cooled solution of [BMIM][Cl] (20 g) in anhydrous dichloromethane (CH₂Cl₂, 30 mL). The mixture was refluxed for 48 h and the by-product HCl formed in the reaction was carried out from the condenser under a stream of dry nitrogen and then dissolved in deionized water at 0 °C. When the formed HCl had been completely removed, CH₂Cl₂ was evaporated with a rotary evaporator. The product was dried under vacuum at 70 °C for 6 h and stored in a desiccator.

[C₄Py][HSO₄] was prepared according to a procedure similar to that used for [BMIM][HSO₄]. The water content in the [BMIM][HSO₄] and [C₄Py][HSO₄] was 0.04 wt% and 0.06 wt% by Karl Fischer titration. The content of chloride was determined by a chloride-selective electrode, and 0.019 and 0.021 mol kg⁻¹ of the impurity were observed in [BMIM][HSO₄] and [C₄Py][HSO₄], respectively. The structure of these ILs, as shown in Fig. 1, has been identified by ¹H NMR as follows. ¹H NMR, δ_H (600 MHz, CD₃CN): [BMIM][HSO₄]: 0.922 (t, 3H), 1.314 (m, 2H), 1.804 (m, 2H), 3.857 (s, 3H), 4.161 (t, 2H), 7.402 (m, 2H), 8.443 (s, 1H), 8.780 (s, 1H). [C₄Py][HSO₄]: 0.933 (t, 3H), 1.368 (m, 2H), 1.941 (m, 2H), 4.595 (t, 2H), 8.061 (t, 2H), 8.516 (m, 1H), 8.840 (d, 2H), 10.612 (s, 1H)



Fig. 1 Chemical structures of the Brønsted acidic ILs.

Oxidative and extractive desulfurization process

Model oil was prepared by dissolving 4,6-DMDBT, DBT, BT, and TS in *n*-octane, respectively, giving a corresponding sulfur content 500, 1000, 1000, and 1000 ppm. All the oxidative and extractive desulfurization experiments were conducted in a 50 mL flask containing 3 mL of IL and 6 mL of model oil using a magnetic stirrer with running speed 900 rpm at room temperature. During the experiment, the sample was periodically taken and analyzed by HPLC. The sulfur compound-IL extraction equilibrium was reached after 15 min when the sulfur content is constant. Then a certain amount of oxidant H₂O₂ (30%) was added to the mixture.

Analytical methods

HPLC was performed on an Agilent 1100 (HP1100, Agilent, USA) liquid chromatography equipped with an autosampler, a reversed-phase Zorbax SB-C18 column (4.6 mm × 250 mm; 5 μm), and a diode array detector. The mobile phase was 90% of methanol in water (v/v,%) with a flow rate of 1.0 mL min⁻¹. For the quantification of TS, the external standard method was used at 230 nm, and for the quantification of BT, DBT and 4,6-DMDBT, the external standard method was used at 280 nm.

The total sulfur content (by weight) in diesel fuel was measured in triplicate for each sample by combustion of samples and measurement of the released sulfur dioxide with a microcoulomb analyzer (RPA-200, JiangHuan Electroanalysis, China).

Regeneration of used ionic liquid

The oil phase was separated by decantation from the IL. An equal volume of water was added to the solution of the IL, and white precipitate was removed by filtration. The water and oxidant were evaporated from the IL phase at 100 °C for 3 h by rotary evaporation. The residue was washed with an equal volume of diethyl ether for three times to recover the IL for reuse.

Results and discussion

Influence of different desulfurization systems on DBT removal

Two kinds of desulfurization systems were investigated: extraction and extraction combined with catalytic oxidation. In extraction system, [BMIM][HSO₄] and [C₄Py][HSO₄] were used as extractant, the model oil was 1000 ppm S as DBT in *n*-octane, and the model oil/IL volume ratio was set at 2:1 ($V_{\text{model oil}}/V_{\text{IL}} = 2:1$) at room temperature. On the other hand, in the extraction combined with catalytic oxidation system, [BMIM][HSO₄] and [C₄Py][HSO₄] were used as extractant and catalyst, the model oil was 1000 ppm S as DBT in *n*-octane, the model oil/IL volume ratio was set at 2:1 ($V_{\text{model oil}}/V_{\text{IL}} = 2:1$), and O/S molar ratio was 5 (O/S = 5) at room temperature. As seen in Fig. 2, the data at the time 0 min reflected the abilities of [BMIM][HSO₄] and [C₄Py][HSO₄] to extract DBT from *n*-octane. The sulfur removal of DBT by [BMIM][HSO₄] and [C₄Py][HSO₄] was 17.7% and 28.1%, respectively. The two ILs have the same anion but different cations. It can be concluded that pyridinium cation has better extractive performance than imidazolium cation, which was also confirmed by our previous research.^{20,21}

With the addition of a certain amount of H₂O₂ (the molar ratio of H₂O₂/DBT was 5, O/S = 5), the sulfur removal of DBT increased sharply with the time increasing when the extraction combined with catalytic oxidation was carried out by [BMIM][HSO₄]. In contrast, the sulfur removal of DBT by [C₄Py][HSO₄] increased negligibly until 2 h. These results indicated that [BMIM][HSO₄] IL played a significant role in the desulfurization process. When [BMIM][HSO₄] served as extractant and catalyst, the equilibrium was reached after 90 min and the sulfur removal was up to 99.6%. However, for [C₄Py][HSO₄] the sulfur removal of DBT was less than 32.8% under the present conditions. It may be due to that the pyridinium cation was oxidized by H₂O₂.²² Fig. 2 also

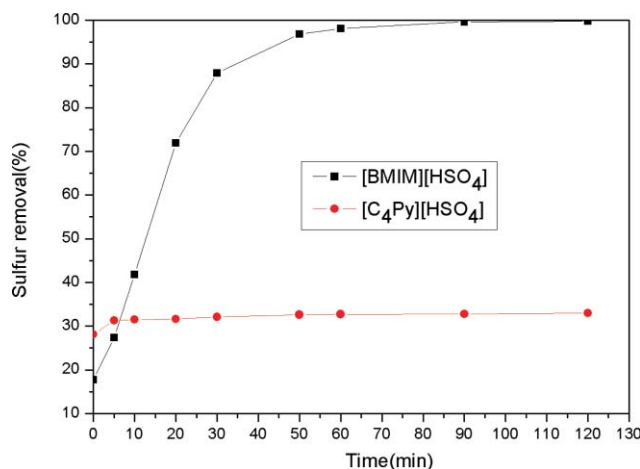


Fig. 2 Comparison of different desulfurization systems of model oil (DBT). Conditions: $V_{\text{model oil}}/V_{\text{IL}} = 2:1$, O/S = 5, room temperature.

shows that H_2O_2 play an important role in the desulfurization process using [BMIM][HSO_4]. Therefore, it was confirmed that [BMIM][HSO_4] acted as not only extractant but also catalyst in the process of extraction combined with catalytic oxidation.

Influence of different H_2O_2 /DBT molar ratio (O/S) on sulfur removal

In order to study the influence of the amount of oxidant on the sulfur removal, the extraction combined with catalytic oxidation of DBT by [BMIM][HSO_4] under different O/S molar ratio was carried out at room temperature. According to the stoichiometric reaction, 2 mol of H_2O_2 is consumed for every 1 mol of DBT to be oxidized the corresponding sulfones. As shown in Fig. 3, the sulfur removal was 84.6% when the O/S molar ratio was 2 in 90 min. With the increasing of O/S to be 3, 4, 5 and 6, the corresponding sulfur removal was up to 92.0%, 93.1%, 99.6% and 99.7% in 90 min, respectively, which was superior to the desulfurization systems of $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}/[\text{BMIM}][\text{PF}_6]$ ¹² and $\text{H}_2\text{O}_2/[\text{HMIm}][\text{BF}_4]$.¹⁵ It is notable that the O/S molar ratio has a strong effect on the sulfur removal of DBT. There was a competition between the decomposition of H_2O_2 and the DBT oxidation reaction. With the O/S molar ratio < 4, due to the

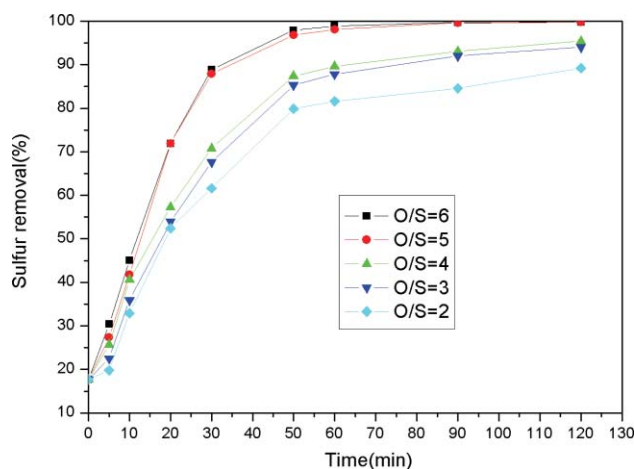


Fig. 3 Effect of different O/S molar ratio on sulfur removal (DBT). Conditions: $V_{\text{model oil}}/V_{\text{IL}} = 2:1$, room temperature.

decomposition of H_2O_2 , the H_2O_2 can not be used completely to oxidize DBT. However, with the O/S molar ratio > 5, there is enough H_2O_2 to oxidize DBT completely. The optimal O/S molar ratio was 5 in our study.

Influence of temperature on the sulfur removal

The extraction combined with catalytic oxidation of DBT by [BMIM][HSO_4] was carried out at different temperature 25, 40 and 60 °C in the time range of 0 to 120 min. Fig. 4 shows the influence of temperature on the sulfur removal of DBT. The model oil was 1000 ppm S as DBT in n-octane, O/S molar ratio was 5 (O/S = 5), and the model oil/IL volume ratio was set at 2:1 ($V_{\text{model oil}}/V_{\text{IL}} = 2:1$). It is presented in Fig. 4 that temperature played a key role in the desulfurization process using [BMIM][HSO_4], the influence of temperature was different at different time range. When the time was less than 5 min, the sulfur removal at different temperatures followed the order of 60 °C > 40 °C > 25 °C. From 5 to 15 min, the sulfur removal followed the order of 40 °C > 60 °C > 25 °C. After 15 min, the sulfur removal followed a new order of 25 °C > 40 °C > 60 °C. It is clear that the viscosity of IL reduces and the decomposition of H_2O_2 becomes quickly with the increasing temperature. When the time was less than 5 min, the model oil and IL mixed completely at high temperature and the decomposition of H_2O_2 was just beginning. When the time got to 10 min, due to the decomposition of H_2O_2 occurring quickly, the sulfur removal followed the order of 40 °C > 60 °C > 25 °C. After 15 min, due to the decomposition of H_2O_2 occurring more quickly, the sulfur removal followed a new order of 25 °C > 40 °C > 60 °C. When the reaction temperature increased from 25 °C to 60 °C, the sulfur removal of DBT decreased sharply from 99.6% to 64.6%. Therefore, the optimal reaction temperature was set at room temperature. Comparing with 90 °C and 60 °C by Lu *et al.*¹⁵ and Zhao *et al.*,¹⁶ respectively, 25 °C is beneficial for the industrial application with less energy cost.

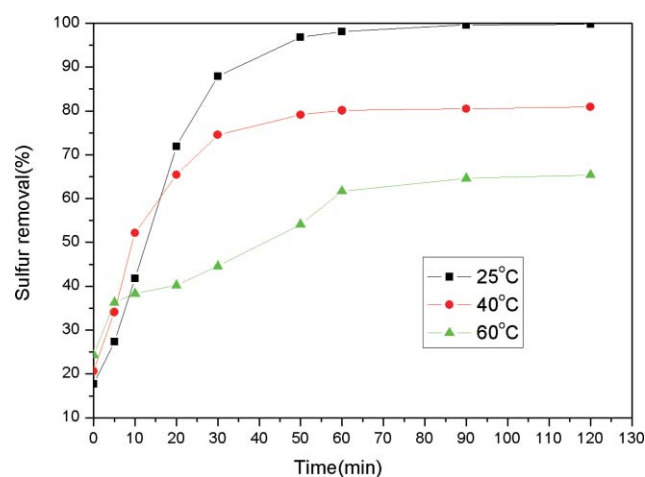


Fig. 4 Effect of different time and temperature on sulfur removal (DBT). Conditions: $V_{\text{model oil}}/V_{\text{IL}} = 2:1$, O/S = 5.

Influence of sulfur species on sulfur removal

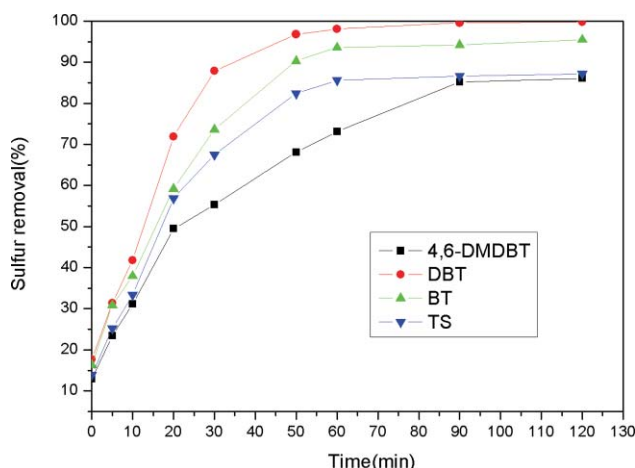
In order to investigate the desulfurization performance of [BMIM][HSO_4] on the different sulfur compounds, the

Table 1 Results of recycling of [BMIM][HSO₄] in desulfurization of model oil

Cycle	Sulfur removal (%)	Cycle	Sulfur removal (%)
1	99.8	4	99.2
2	99.6	5	99.0
3	98.9	6	98.5

Model oil: 1000 ppm S as DBT in n-octane, $V_{\text{model oil}}/V_{\text{IL}} = 2:1$, O/S = 5, mixing time 120 min, room temperature.

extraction combined with catalytic oxidation of four sulfur compounds such as TS, BT, DBT and 4,6-DMDBT was carried out under the same condition. As shown in Fig. 5, the sulfur removal of TS, BT, DBT and 4,6-DMDBT was 86.6%, 94.2%, 99.6%, and 85.2% after 90 min, respectively. It is obvious that the sulfur removal through extraction combined with catalytic oxidation process decreased in the order of DBT > BT > TS > 4,6-DMDBT. The relatively large differences in sulfur removal may be due to the difference of aromatic π -electron density of sulfur compounds. As calculated by Otsuki *et al.*,⁵ the electron density on the sulfur atoms is 5.758 for DBT, 5.739 for BT, 5.696 for TS, and 5.760 for 4,6-DMDBT. For sulfur compounds DBT, BT, and TS, the extractive performance grows with the increase of the aromatic π -electron density. But for 4,6-DMDBT, the methyl substitution at the 4 and 6 positions of DBT remarkably retards the extractive performance of [BMIM][HSO₄].

**Fig. 5** Effect of different sulfur compounds on sulfur removal. Conditions: $V_{\text{model oil}}/V_{\text{IL}} = 2:1$, O/S = 5, room temperature.

Recycling of the ionic liquid

For the industrial application of IL, the regeneration and subsequent recycling of IL are of vital importance. [BMIM][HSO₄] is a hydrophilic IL. Therefore, its regeneration was obtained through precipitating the sulfur compounds by a water dilution process. The data in Table 1 shows that the [BMIM][HSO₄] can be recycled up to 6 times without a significant decrease in the desulfurization performance.

Extraction combined with catalytic oxidation of diesel fuel

The extraction combined with catalytic oxidation using [BMIM][HSO₄] was also applied to the desulfurization of

Table 2 Sulfur removal of diesel fuel by [BMIM][HSO₄]

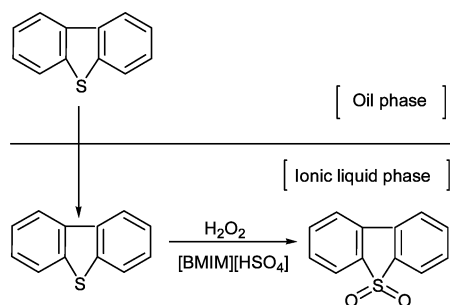
	Sulfur content (ppm)	Sulfur removal (%)
Diesel fuel	97	
Extracted fuel With [BMIM][HSO ₄]	86.3	11.0
Oxidized fuel ^a With [BMIM][HSO ₄]	13.8	85.8

^a With oxidant added to the extraction system. Condition: $V_{\text{model oil}}/V_{\text{IL}} = 1:1$, O/S=5, mixing time 120 min, room temperature.

diesel fuel containing sulfur content of 97 ppm. Table 2 shows the sulfur removal and sulfur content of the diesel fuel by [BMIM][HSO₄] IL. When in the extraction system, [BMIM][HSO₄] served as the extractant, the sulfur content varied from 97 ppm to 86.3 ppm and the sulfur removal was 11.0%. When in extraction combined with catalytic oxidation, [BMIM][HSO₄] served as extractant and catalyst, the sulfur content decreased greatly from 97 ppm to 13.8 ppm and the sulfur removal increased rapidly up to 85.8%. Although the results were not as fine as for treating model diesel because of the complex chemical composition of diesel fuel, the deep desulfurization of diesel fuel can be achieved through the extraction combined with catalytic oxidation process by [BMIM][HSO₄]. This process is simple, mild, and may be a complementary technology for the HDS process.

The process of extraction combined with catalytic oxidation in [BMIM][HSO₄]

As seen in Fig. 6, in the extraction combined with catalytic oxidation process, DBT was extracted into the IL phase, simultaneously was oxidized to sulfone, so a continuous decrease in the content of DBT in n-octane was observed during this process. As is well known, H₂O₂ is a strong oxidant in the acidic medium. In this process, DBT was oxidized to corresponding sulfone by H₂O₂ catalyzed by Brønsted acidic IL [BMIM][HSO₄] which acted as not only extractant but also catalyst.

**Fig. 6** The process of extraction and oxidation reaction of DBT in an oil-ionic liquid-H₂O₂ system.

Conclusions

In this paper, extraction and oxidative desulfurization of diesel catalyzed by a Brønsted acidic ionic liquid [BMIM][HSO₄] at room temperature was carried out. The sulfur removal of DBT-containing model diesel could reach 99.6% at room temperature after 90 min, which was remarkable superior to desulfurization by simple extraction with IL. Moreover, [BMIM][HSO₄] can

be recycled up to 6 times without a significant decrease for the desulfurization performance. The extraction combined with catalytic oxidation process using [BMIM][HSO₄] can be a complementary technology for the HDS process.

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