



Desulfurization of Fuel by [Bmim]CoCl₃ and Potassium Monopersulfate

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ABSTRACT

Functional ionic liquid [Bmim]CoCl₃ was prepared with potassium monopersulfate compound (PMS) to form extraction catalytic oxidative desulfurization system for benzothiophene (BT) removal. The best reaction conditions for removing BT were as follows: m (ionic liquid) = 2 g, m(PMS) = 1.5 g, C (initial sulphur) = 500 ppm, T = 40°C ~ 50°C. The desulfurization rate could be reached at 92.4 %. The ionic liquid still had higher activity after 5 cycles of reuse which exhibited that there was only a slight difference in the amount of the oxidant. It was proved that [Bmim]CoCl₃ ionic liquid combined with oxidant PMS has an excellent desulfurization performance.

INTRODUCTION

Over the past two decades, haze pollution events have taken place in many developing countries. Some Chinese cities are suffering from smog pollution in winter. The smog brings great harm to human health, especially causing two main types of diseases, i.e. respiratory disease and cardiovascular disease. There are many reasons for the formation of haze, of which the most important is the one caused by sulphur pollution. For example, cars that burn sulphur containing gasoline or diesel fuel emit sulphur dioxide, which forms sulphate, the main material of smog, under the reaction of nitrogen dioxide in the air (Xu et al. 2014). To reduce the air pollution caused by sulphur, the sulphur content in gasoline or diesel fuel is strictly controlled all over the world. In 2016, the Chinese government issued a national standard (GB 17930-2016 and GB 19147-2016) for gasoline and diesel with a sulphur content of less than 10 ppm, the same as the USA and European countries.

In petroleum, there are two kinds of sulphur containing compounds, i.e. aliphatic sulphur and aromatic sulphur. Aliphatic sulphur compounds have acceptable activity, which can be easily removed by hydrodesulfurization (HDS) method. The aromatic sulphur compounds have a stable structure, which are difficult to be treated (Chen et al. 2015). Thiophene sulphides have aromatic and steric hindrance, so they are more difficult to be removed than other sulphides. Extraction

catalytic oxidative desulfurization (ECODS) has become the most promising deep desulfurization technology due to its mild reaction conditions, simple experimental operation and excellent desulfurization effect, especially for aromatic sulphur compounds (Shakirullah et al. 2010). The desulfurization mechanism of ECODS is as follows: (1) the sulphur compounds in fuel are extracted by extractant (mostly ionic liquid), and (2) the catalyst and oxidant in the extractant cooperate for desulfurization. When the sulphur compounds are oxidized to sulfone organics, they are removed by polar solvent (Lv et al. 2013). For example, Jiang et al. (2014) selected [C₄mpip]FeCl₄/H₂O₂ system to perform a 73% sulphur removal from diesel. The dibenzothiophene (DBT) was treated by [Bmim] Cl/2ZnCl₂/H₂O₂ system with nearly 100% sulphur removal (Yu et al. 2011). Gao used [C₄min] HSO₄/H₂O₂ system to achieve 88.5% DBT removal (Gao et al. 2010). According to the analysis of literature, DBT as target pollutant was studied a lot and all the oxidant was H₂O₂.

Benzothiophene (BT), one of the thiophene sulphides, as target pollutant was studied. Compared with DBT, BT structure is relatively stable and difficult to be removed (Li et al. 2009). In our previous research (Xu et al. 2017), H₂O₂ was not a good oxidant because of instability characteristics and high price. In this study, potassium monopersulfate compound (PMS) was selected as the oxidant. Functional ionic liquid [Bmim]CoCl₃ was prepared with PMS to form ECODS for BT removal.

MATERIALS AND METHODS

Preparation of [Bmim]CoCl₃

[Bmim]CoCl₃ was prepared by mixing 1-n-butyl-3-methylimidazolium chloride ionic liquid ([Bmim]Cl) and cobalt chloride hexahydrate (CoCl₂·6H₂O) in the molar ratio of 1:1 at 110°C for 48 hours to form homogeneous phase and evaporation of water. [Bmim]CoCl₃ ionic liquid is viscous blue liquid and stored in a desiccator. All reagents were required in the experiment were of analytical grade and purchased from Shanghai Aladdin Reagent Co., Ltd.

Extraction Catalytic Oxidation Desulfurization Process

Ionic liquid [Bmim]CoCl₃ and model oil (6 g, sulphur content: 500 ppm) were added to a 40 mL flask in a certain ratio. A constant temperature water bath was used to control a certain reaction temperature, and stirred vigorously for 30 minutes so that the ionic liquid and the oil were in full contact until the extraction reached equilibrium. A certain amount of 20 wt% of PMS solution was added to the reaction vessel and stirred vigorously until the oxidative desulfurization reaction was complete. In the process of reaction, the upper liquid was taken regularly to analyse the sulphur content. The sulphur content was determined by an ultraviolet-visible spectrophotometer and calculated by the external standard method ($A=0.07418+0.05366BT$, $R^2=0.9998$). The desulfurization rate in the model oil is calculated by the following formula:

$$R(\%) = \left(1 - \frac{[S]_t}{[S]_0}\right) \times 100 \quad \dots(1)$$

Where, R is the desulfurization rate, [S]₀ is the initial concentration of sulphur in the model oil, [S]_t is the concentration of sulphur in the model oil at t time.

RESULTS AND DISCUSSION

Effect of [Bmim]CoCl₃ Ionic Liquid Dosage On Desulfurization Rate

Fig. 1 shows the curves of desulfurization rate with time under the different dosages of [Bmim]CoCl₃ ionic liquid dosages. The fixed reaction conditions are as follows: T = 50°C, m(simulated fuel) = 6 g, C(initial sulphur) = 500 ppm, m(PMS) = 1.5 g, t = 100 min.

From Fig. 1, the reaction can be divided into two stages. The first stage (-30 min~0 min) is the extraction process, in which the BT is extracted from the oil phase to the ionic liquid phase by the ionic liquid. As is apparent from Fig. 1, at this stage, the desulphurization rate increases with the increase of ionic liquid dosage. When the ionic liquid dosages are 0.5 g, 1 g, 2 g, 3 g and 6 g, the desulfurization rates are 2.8 %, 6.7 %, 14.7 %, 29.3 % and 40.3 %, respectively. The second stage (0 min~70 min) is the ECODS process. It can be seen from Fig.1 that when the dosage of [Bmim]CoCl₃ increases from 0.5 g to 2 g, the rate of desulfurization increases significantly. After 70 minutes, the desulfurization rate increases from 50.3% (0.5 g ionic liquid) to 92.4% (2 g ionic liquid). Especially in the initial stage of the reaction (0 min~15 min), the desulfurization rate increases significantly. After 15 minutes, the rate of increase in the desulfurization rate tends to be flat. Under the dosage of 2 g ionic liquid, from 15 minutes to 70 minutes, the desulfurization rate only increases by 15.1 % (77.3 % to 92.4 %). When the ionic liquid increases to 6 g continuously, the desulfurization rate increases rapidly at the initial stage of the second stage reaction, and the desulfurization rate reaches 86.1 % after 10 min reaction. The ionic liquid dosage increases from 2 g to 6 g, the desulfurization rate increases from 92.4 % to 93.7 % after

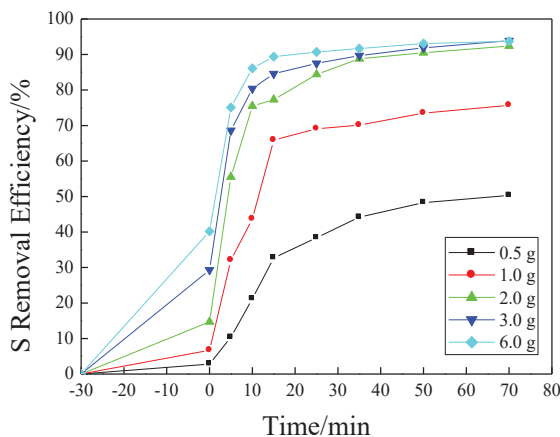


Fig. 1: Influence of the [Bmim]CoCl₃ dosage on S removal efficiency.

70 minutes. Therefore, considering the economic problems, the optimal dosage of [Bmim]/CoCl₃ ionic liquid is 2 g.

In the extraction stage, BT is extracted into the [Bmim] CoCl₃ ionic liquid phase firstly, and the extraction rate increases as the ionic liquid increases. After the addition of the oxidant PMS solution, cobalt ions catalyse the active component hydrogen ion in PMS to produce sulphate radicals which have strong oxidation ability to oxidize BT to oxidation products, such as BTO₂, and remove them. Therefore, with the increase of ionic liquid, the content of cobalt ions increases. The more sulphate radicals are formed to oxidize BT and the desulfurization rate increases. However, when the cobalt content of the system exceeds a certain value, the concentration of hydrogen ion does not increase, and the concentration of sulphate radicals does not increase significantly. Excess cobalt ions can be used as scavengers. Therefore, after the ionic liquid exceeds 2 g, the desulfurization rate increases less.

Effect of Oxidant PMS Dosage on Desulfurization Rate

Fig. 2 shows the desulfurization rate versus time for different oxidant PSM dosages. The fixed reaction conditions are as follows: T = 50°C, m([Bmim]CoCl₃ ionic liquid) = 6 g, C(initial sulphur) = 500 ppm, t = 100 min (including 30 minutes' extraction time). It can be seen from the figure that the desulfurization rate of the PMS solution increases greatly. When the dosage of the PMS solution is in the range of 0.1 g to 1.5 g, the desulfurization rate increases as the amount of PMS increases. After 15 min reaction, when the dosage of the PMS solution increases from 0.1 g to 1.5 g, the desulfurization rate increases from 33 % to 91.9 %

rapidly. When the dosage of PMS solution exceeds 1.5 g, the desulfurization rate shows a certain downward trend. The desulfurization rate is 77 % at 15 minutes, which is 14 % lower than the 1.5 g dosage.

Cause analysis: As an oxidant, PMS plays a vital role in the desulfurization process. As the amount of PMS increases, a large amount of sulphate radicals is produced, and the desulfurization rate is improved significantly. However, when the amount of PMS exceeds the optimum value, the strong acidity of hydrogen ion has a negative effect on the catalytic oxidation of cobalt ion. At the same time, hydrogen ion is also a scavenger for sulphate radicals, which is not conducive to reaction. Therefore, 1.5 g is the optimum dosage of the PMS solution.

Effect of Reaction Temperature on Desulfurization Rate

Fig. 3 shows the desulfurization rate as a function of time at different temperatures. The fixed reaction conditions are: m (ionic liquid) = 2 g, m(PMS) = 1.5 g, C (initial sulphur) = 500 ppm, t = 100 minutes (including 30 min of extraction time).

It can be seen from Fig. 3 that both high temperature and low temperature are not conducive to desulfurization. Low temperature (30°C) is more conducive to desulfurization than high temperature (60°C). The optimum temperature range of the reaction is from 40°C to 50°C, which is close to room temperature. During the extraction phase (-30 min ~ 0 min), BT diffuses from the oil phase into the ionic liquid. When the extraction temperature is 30°C, 40°C, 50°C and 60°C, the desulfurization rates are 15.9%, 15.2%, 14.6%, 14.1%, respectively. The extraction of the desulfurization

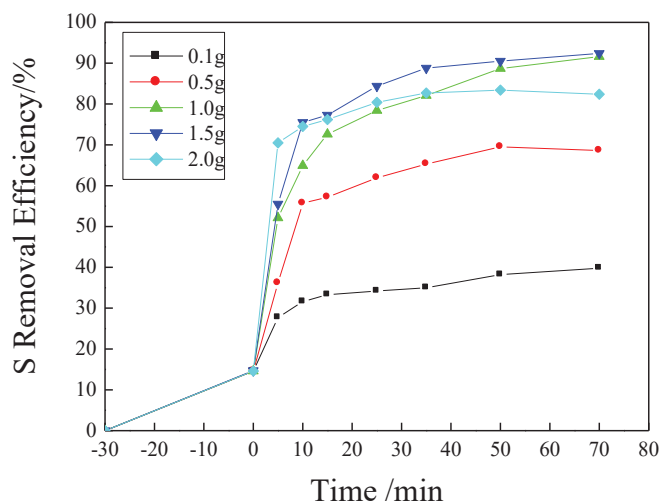


Fig. 2: Influence of the PMS dosage on S removal efficiency.

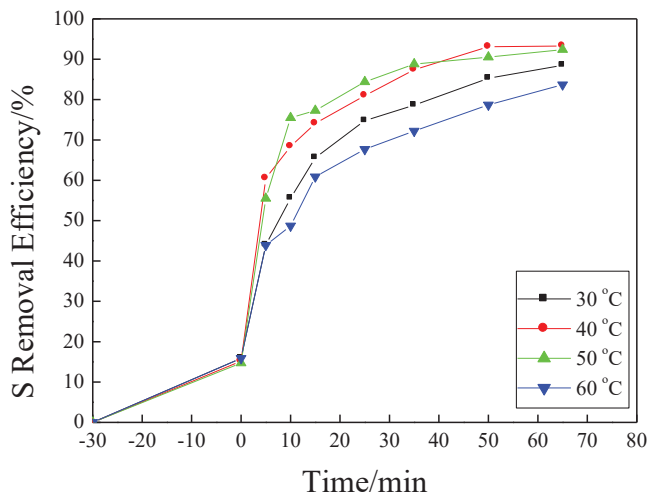


Fig. 3: Influence of temperature on S removal efficiency.

rate decreases slightly as the reaction temperature increases. In the ECODS phase (0 min ~ 70 min), the desulfurization rate at different reaction temperature is different after 15 min of reaction. When the reaction temperatures are 30°C, 40°C, 50°C and 60°C, the desulfurization rates are 65.7 %, 74.1 %, 84.9 % and 67.7 %, respectively.

Causes analysis: High temperature is not conducive to the catalytic oxidation process, PMS (decomposition temperature is 65°C) is unstable and easy to be decomposed at high temperature. However, high temperature helps to reduce the viscosity of the ionic liquid, which is beneficial to mix the ionic liquid and the oil phase. The ionic liquid [Bmim] CoCl₃ has a high viscosity at low temperature, which seriously hinders the mixing between the ionic liquid and the

oil phase. Therefore, 40°C to 50°C is the optimum reaction temperature.

Effect of Initial Concentration of BT on Desulfurization Rate

Fig. 4 shows the desulfurization rate versus time for different BT initial concentrations. The fixed reaction conditions are: m (ionic liquid) = 2 g, m(PMS) = 1.5 g, T = 50°C, t = 100 minutes (including 30 minutes' extraction time).

During the extraction phase (-30 min ~ 0 min), the initial sulphur content are 250 ppm, 500 ppm, 750 ppm, and 1000 ppm, the desulfurization rates are 18.3 %, 14.7 %, 11.5 %, and 8.7 %, respectively. In the ECODS phase (0 min ~ 70 min), after 70 min of reaction, the desulfurization rates of

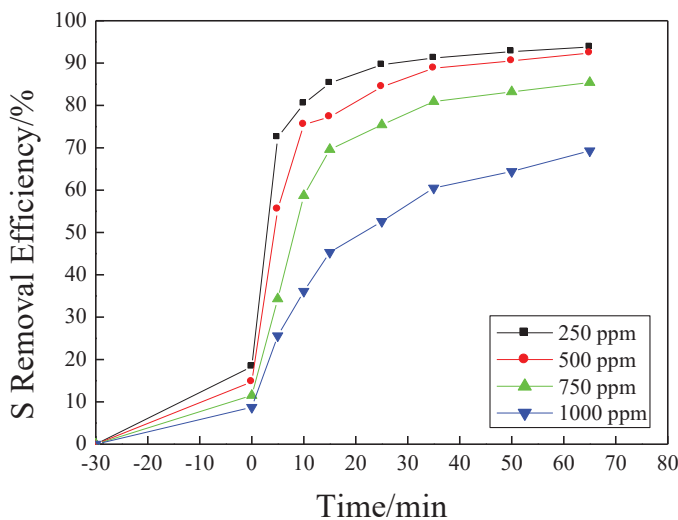


Fig. 4: Influence of initial S-content on S removal efficiency.

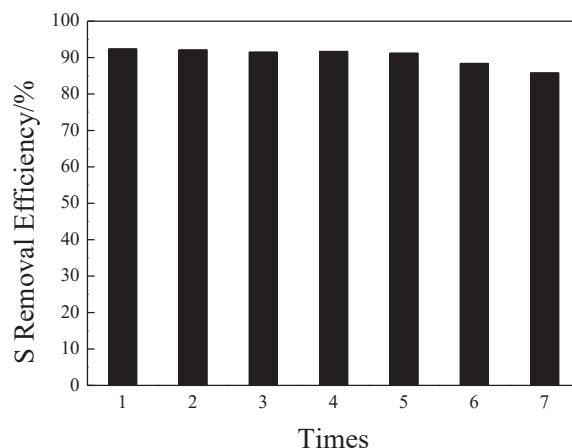


Fig. 5: Effect of recycling of used ionic liquid.

250 ppm, 500 ppm, 750 ppm, and 1000 ppm are 93.8 %, 92.4 %, 85.4 %, and 69.3 %, respectively. Therefore, in the case where the dosage of the ionic liquid and the PMS solution is constant, the desulfurization rate decreases as the initial sulphur content increases. However, in the entire reaction process, the overall removal of sulphur is increasing.

Recycling Performance of Ionic Liquid [Bmim]CoCl₃

The recycling of ionic liquids is an important indicator for the industrialization of the system in the future. Separation and drying of ionic liquids after one reaction, then new BT model oil and PMS solution were added under the determined optimal reaction conditions, we have tested the performance of cyclic desulfurization. Figs. 3-5 show the recycling performance of ionic liquids. It can be seen from the figures that after repeated use for 5 times, the ionic liquid still maintains a good desulfurization performance, and the desulfurization rate is maintained above 90 %. At the 7th time, the desulfurization rate decreased slightly (85.8 %). It is proved that [Bmim]CoCl₃ ionic liquid has good performance.

CONCLUSIONS

The best reaction conditions for removing BT were as follows: m(ionic liquid) = 2 g, m(PMS) = 1.5 g, C(initial sulphur) = 500 ppm, T = 40°C ~ 50 °C. The desulfurization rate could be reached at 92.4 %. The ionic liquid still had higher activity after 5 cycles of reuse which was exhibited that there was only a slight difference in the amount of oxidant. It was proved that [Bmim]CoCl₃ ionic liquid combines with oxidant PMS had excellent desulfurization performance once again.

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