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Extractive desulfurization and denitrogenation of fuels using functional acidic ionic liquids

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ABSTRACT

Due to the ineffectiveness in removing cyclic sulfur compounds (S-compounds) and nitrogen compounds (N-compounds) such as thiophene (TS), dibenzothiophene (DBT), carbazole, pyridine and their derivatives from fuel oils, the traditional hydrodesulfurization and hydrodenitrogenation processes are facing some challenges especially now in the wake of sterner regulation of S-/N-content in fuel oils. This work demonstrates that some acidic ionic liquids (ILs) are capable of extracting cyclic S-/N-compounds particularly the basic N-species from fuel oils. Both Lewis acidic ILs 1-butyl-3-methylimidazolium chloride/$ZnCl_2$ ([Bmim]Cl/$ZnCl_2$) and [Bmim]Cl/$2ZnCl_2$ as well as Brφnsted acidic ILs [Bmim]HSO_4 and [Hmim]HSO_4 are used to extract TS, DBT, carbazole and pyridine from their hexane (model gasoline) or octane (model diesel fuel) mixtures. Typically, 93.8% TS removal (S-content drops from 500 ppm to 31 ppm) and 95.9% DBT removal (S-content from 516 ppm to 21 ppm) by [Bmim]Cl/$ZnCl_2$ after 6-stage extraction are obtained at 25 °C, 1:1(w/w)IL:oil, 30 min; while 93.8% carbazole removal (N-content from 279 ppm to 17 ppm) and 97.8% pyridine removal (N-content from 495 ppm to 11 ppm) are realized after only one stage extraction and the N-content is undetectable after 2-stage extraction. [Bmim]Cl/$ZnCl_2$ is selected as a representative IL to undergo a series of parallel experiments to determine the influence of extraction time, temperature, IL:oil mass ratio and multi-stage extraction on S-/N-removal efficiency. The mutual solubility of [Bmim]Cl/$ZnCl_2$ in fuel oil as well as IL recycling is also performed.

1. Introduction

Sulfur compounds (S-compounds) in fuel oils give rise to SO_X emission during combustion, reduce the combustion efficiency of fuel oils, destroy three-way catalysts, and increase CO and particulates emission. To this end, more and more stringent regulations are being introduced to limit the S-content in fuel oils, e.g., the maximum S-content in all transportation fuels in many developed countries was set at 10 ppm in 2010 as opposed to the 150 ppm and 350 ppm limit in 2003 for gasoline and diesel fuel respectively [1,2]. Zero or ultra low S-content is desired in the future. Besides the S-compounds, the nitrogen compounds (N-compounds) in fuel oils must also be removed, because N-compounds are considered as strong inhibitors of the hydrodesulfurization (HDS) process. They can affect the stability of fuel oil and lead to NO_X emission. In fact, N-content limit for diesel fuel was reduced from >70 ppm in 2003 to <0.1 ppm in 2010 [3]. It is expected that regulation to further lower N-content will be introduced in the coming years.

HDS and hydrodenitrogenation (HDN) are widely used to catalytically remove S-/N-compounds. They, however, are ineffective in removing cyclic S-/N-compounds such as thiophene (TS), dibenzothiophene (DBT), carbazole, pyridine and their derivatives due to the steric hindrance encountered by these compounds on the surface of the catalyst. To lower the S-/N-content in fuel oils to an ultra low or zero level using the hydrogenation technology, harsher operating conditions (e.g. high temperature, high pressure, more active catalysts, etc.) are needed. To improve or complement HDS/HDN technology, some alternative techniques such as extraction [4–15], oxidation [16–20], adsorption [3,21–25] and bio-processing [26–28] have been investigated.

Recently, desulfurization with ionic liquids (ILs) has been intensively studied, e.g., imidazolium-based ILs, including [BMIM]BF_4 [29], [BMIM]PF_6 [29], [EMIM]$AlCl_4$ [29], [BMIM][SCN] [30], [BMIM]$AlCl_4$ [31] and [BMIM]DBP [4]. Pyridinium-based ILs, such

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as [BPy]BF_4 [13], [OPy]BF_4 [13], [EPy]BF_4 [14] and [BPy]NO_3 [14] were investigated to extract TS, DBT or their derivatives, and good extractive results were observed. Taking [OPy]BF_4 as a typical example, the S-content in DBT and *n*-dodecane mixture was reduced from 160 ppm to 57 ppm with 64.2% S-removal after one-stage extraction (25 °C, 1:1(w/w)IL:oil, 15 min). Recently, extraction with ILs has also been employed to remove neutral and basic N-compounds from fuel oils, such as $[BF_4]^-$, $[PF_6]^-$, chloride-based ILs, coupled with the conventional aromatic cations of imidazolium and pyridinium [8–10,32]. These ILs showed promising extractive capability for N-compounds from fuel oils; for example, in a single contact with a model oil containing pyridine, at RT and 1:2(w/w)IL:oil mass ratio, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF$_4$) lowered the N-content in fuel by 45% [10]. Besides the high S-/N-extractive capability, compared with traditional molecular solvents, ILs have some preferable properties such as non-volatility, non-flammability, high thermal/chemical stability, and good recyclability [33–37]. In addition, the extractive process has mild operating conditions, does not require catalyst or consume hydrogen, does not alter the structure of the fuel-containing compounds and the extracted compounds can be re-used as raw materials. Amid the prospect for ILs desulfurization/denitrogenation, there are some undesirable features, including the production of corrosive hydrogen fluoride (HF) from the decomposition of fluorinated anions, non-stability to moisture and air, etc. Denitrogenation with ILs has received less attention as opposed to its desulfurization counterpart.

By and large, N-containing compounds in middle distillate fuels are present as two classes of polyaromatic heterocycles, namely: neutral five-membered heterocycles (e.g. carbazole, pyrrole, indole, and their derivatives) and basic six-membered heterocycles (e.g. pyridine, acridine, quinoline, and their derivatives). In this work, some acidic ILs, i.e., Lewis acidic 1-butyl-3-methylimidazolium chloride/$ZnCl_2$([Bmim]Cl/$ZnCl_2$) and [Bmim]Cl/2$ZnCl_{2,}$ as well as Brφnsted acidic [Bmim]HSO_4 and [Hmim]$HSO_{4,}$ all fluorine-free and stable to moisture and air, are used to investigate factors affecting desulfurization and denitrogenation. TS and DBT are selected as representative S-compounds, while neutral carbazole and basic pyridine are selected as representative N-compounds. The structures of these ILs and representative S-/N-compounds are shown in Fig. 1. The mutual solubility, along with the influence of temperature, IL:oil mass ratio, multiple extractions and recycling of ILs are systematically investigated using the IL with the optimal performance [Bmim]Cl/$ZnCl_2$. This work demonstrates that these acidic ILs are capable of extracting S-/N-compounds especially the basic nitrogen species from fuel oils.

2. Experimental section

2.1. Chemicals and materials

The chemicals and suppliers are: N-methylimidazole (>99%), Shanghai SenHao Fine Chemical; chlorobutane ($\geqslant$99%), carbazole, TS(99%) and DBT(98%), J&K Chemical; hexane, *n*-octane, zinc chloride, pyridine and H_2SO_4(aqueous solution, 95–98 wt%), Beijing Chemical Plant. N-methylimidazole is further purified by distillation, while the other chemicals are used as received without further purification. [Bmim]Cl/$ZnCl_2$ [38], [Bmim]Cl/2$ZnCl_2$ [38], [Bmim]HSO_4 [39], [Hmim]HSO_4 [40] are synthesized according to the procedures as mentioned in the literature.

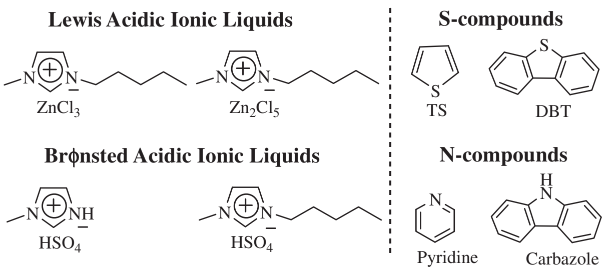

Fig. 1. Structures of the ILs and S-/N-compounds used in this study.

2.2. Composition of model oils

In the extractive desulfurization, model gasoline is prepared by dissolving a certain amount of TS in a solution of hexane (85 wt%) and toluene (15 wt%), while model diesel is prepared by dissolving a certain amount of DBT in *n*-octane; the S-content in both model oils is $\sim$500 ppm (here, ppm refers to weight ratio). In the extractive denitrogenation, the model oil containing the basic N-compound comprises *n*-octane (85 wt%) and toluene (15 wt%) and droplets of pyridine ($\sim$500 ppm),while the model oil containing the neutral nitrogen compound comprises *n*-octane (20 wt%), toluene (80 wt%) and carbazole ($\sim$300 ppm).

2.3. Desulfurization and denitrogenation procedure

In a typical experiment, the IL and model oil are placed in a 100 ml round-bottom flask, and the mixture is magnetically stirred at a fixed time and temperature. After appropriate mixing, the mixture is laid aside for $\sim$5 min for phase splitting and setting. The upper oil phase is then analyzed by a liquid chromatograph.

2.4. S-/N-content analysis

The analysis of TS, DBT, pyridine and carbazole content in fuel oil proceeded with the aid of HPLC (WUFENG LC-100, China, reversed phase ultimate™ XB-C18 column, 4.6 × 150 mm, 3.6 μm, UV detector) with external standard method. The selected wavelength is 230 nm for TS, 280 nm for DBT, 240 nm for pyridine, and 330 nm for carbazole. The mobile phase for the quantification of TS is 65% methanol in water (v/v,%) with a flow rate of 0.9 ml min^{-1}; 85% methanol in water (v/v,%) with a flow rate of 1.0 ml min^{-1} for DBT; 60% methanol in water (v/v,%) with a flow rate of 1.0 ml min^{-1} for pyridine; and 80% methanol in water (v/v,%) with a flow rate of 1.0 ml min^{-1} for carbazloe. Triplicate injections are performed for each sample.

3. Results and discussion

3.1. S-/N-removal performance by different ILs

The extractive desulfurization and denitrogenation performance results are shown in Figs. 2 and 3, respectively. [Bmim]Cl/$ZnCl_2$ exhibits the best S-extraction ability, e.g., the final S-content in gasoline is reduced from 495 ppm to 329 ppm (33.5% S-removal) after a single extraction while it is reduced from 501 ppm to 318 ppm (36.5% S-removal) in diesel fuel. Interestingly, all the acidic ILs in this study have proven to be good extractants for N-compounds from fuel oils. An interesting result is found, where N-content in the raffinate phase is very low after <5 min at 25 °C and 1:1(w/w)IL:oil, i.e., >97% N-extraction efficiency from the pyridine-containing fuel oil is realized for the ILs used. For the carbazole-containing fuel oil, the extraction efficiency is 93.2%, 90.1%, 71.2% and 24.2% for [Bmim]Cl/$ZnCl_2$, [Bmim]HSO_4, [Bmim]Cl/2$ZnCl_2$, and [Hmim]HSO_4, respectively; such different extractive capabilities for carbazole might be ascribed to their different anionic nature and length of alkyl side chain on cation, as observed in extractive removal of S-/N-compounds from fuel oils using ILs