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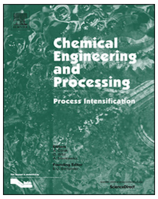

Intensification of water on the extraction of pyridine from *n*-hexane using ionic liquid

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ABSTRACT

One novel extraction process for denitrification of fuel based on ionic liquid was developed. Influence of water on this process was systematically investigated. The mechanism of this process was illustrated by density functional theory (DFT) calculations. The optimized extraction parameters were obtained by a series of experiments, such as mass ratio of ionic liquid and the initial N content. Meanwhile, [Bmim]BF_4 was recycled through rotary evaporation, and exhibited good recycling properties and extraction efficiency. Finally, a specific separation process and technology was proposed based on the experimental data.

1. Introduction

Nowadays, the large amount emission of vehicle exhaust is considered to be the main cause of haze [1]. Nitrogen compounds from fuel became one of the most harmful components during the exhaust emissions. Thus, more stringent environmental regulations were proposed such that the upper limit of nitrogen concentration in fuel was reduced from > 70 ppm N to less than 0.1 ppm N by 2011 [2,3]. A growing number of researchers have been attracted by deep denitrogenation of fuel and developed a series of techniques, such as hydrogenation, extraction, biological denitrification and etc [4–8].

According to the different materials, the methods can be divided into two categories: hydrogenation denitrogenation (HDN) and non-hydrogenation denitrogenation (non-HDN). The former is usually conducted over a series of transition metal oxide/sulfide/phosphide impregnated on supports γ-Al_2O_3, SiO_2, and zeolites [9–12] in the presence of molecular hydrogen, but this is obviously limited by large costs in operating and equipment, especially the presence of hydrogen. Furthermore, a HDN catalyst is easily deactivated by small amounts of aromatic nitrogen compounds present in the fuel, which is preferably adsorbed on the surfaces of the catalyst. In contrast, no molecular hydrogen was used in non-hydrogenation denitrogenation technology, which including solvent refining, extraction, adsorption, oxidization and combined denitrogenation. Liquid-liquid extraction (LLE) is an increasingly promising method in extracting nitrogen compounds at ambient and moderate condition because this type of extraction exhibits large capacity and easy accessibility [13–16]. Kodera [17] reported that nitrogen compounds in coal liquid can be extracted by methanol and water. Qi [18] found that 80% acetic acid can extract nitrogen compounds from catalytically cracked diesel oil and the extraction efficiency can achieve 78%. However, these methods do not have promotional value in the industry due to the high cost of recycling. Therefore, the development of extraction agent which has high N-removal efficient and is easy to recovery has become the hot spot.

In recent years with the appearance of the ionic liquids (ILs), researchers found that ILs as the extraction agent can remarkably improve the denitrogenation both in efficiency and regeneration [19–23]. Zhang [24] first reported that pyridine could be extracted by [Bmim]BF_4 from model oil with N-removal efficiency of 45%. Recently, with further research of ILs, more novel ILs is synthesis and using to extract nitrogen compounds. Xie et al. [25–27] did great effort on ILs extraction. They reported that chloride based ILs with varying cation classes (imidazolium, pyridinium) showed a high selectivity for N-compounds. An extraction of up to 50% of the N-compounds was obtained in one step whereas the sulfur concentration reduction was only 5%. Huh et al. [28] reported that imidazolium-based zinc-containing ionic liquids were highly effective for the denitrogenation of model oil containing quinoline, indole, or acridine in n-heptane. The zinc-containing IL can be successfully regenerated by employing diethyl ether as a back extractant. According to the research work of Asumana [29], for pyridine-

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containing fuel oil, the highest N-extraction efficiency was obtained using dicyanamide-based ionic liquids. Anugwom et al. [30] reported that liquid-liquid extraction by using 1-ethyl-3-methylimidazolium chloride was found to be a very promising method for the removal of N- and S-compounds. And the spent ionic liquid can be regenerated by using toluene as back extractant.

Although the extraction of nitrogen compounds from fuel with ILs has been sufficiently developed, there is scarcely literature taking the role of water into account. Most ILs would easily absorb water from air and in practice, however, it is difficult to remove the water in ILs. In many other applications, the influence of water on the properties of ILs has already been of interest [31,32] and the study of the influence of water on extraction of nitrogen compounds is necessary.

In this work, different imidazolium based ILs are using to extract pyridine from the model oil. Moreover, different experimental conditions with $[Bmim]BF_4$ were studied to probe the influence of water on the extraction, such as mass ratio of IL to water, extraction time, mass ratio of IL to model oil, and the initial N content. The regeneration of the IL was also investigated.

2. Experimental section

2.1. Materials

All imidazolium based ILs was purchased from Linzhou Keneng Material Technology CO., LTD. *N*-Hexane was purchased from Sinopharm Chemical Reagent Beijing CO., LTD, Pyridine was purchased from the Zhejiang Kaile Chemical Plant. Their Shorthand name, CAS registry numbers, and quality standard were listed in Table 1. The chemicals were used without further purification.

2.2. Preparation of the model oil

Due to the complexity of the real fuel, model oil was chosen to simplify the extraction process. Due to the nitrogen compounds in real oil was complex (such as: aliphatic amines, aniline, nitrile, pyridine, pyrrole, and their derivatives), pyridine was chosen as representative nitrogen compounds and *n*-hexane was selected as the typical solvent. In this study, the different component concentrations of the model oil were prepared in the same manner. A specific process was shown as below: 5.65 g of pyridine was placed in a volumetric flask and diluted to 1000 mL with *n*-hexane at 30 °C. The nitrogen concentration of the model oil was 1000 ppm N. (Formula 1) Different nitrogen concentration of model oil (i.e. 200 ppm, 400 ppm, 600 ppm, 800 ppm, and 1000 ppm) were prepared in the same method.

$$N\ (ppm) = \frac{m_{mass\ of\ N}}{V_{solvent}} \tag{1}$$

Table 1
Chemicals used in experiment.

Name	Shorthand name	CAS No.	Purity (wt. %)
1-Butyl-3-Methylimidazolium Tetrafluoroborate	$[Bmim]BF_4$	174501-65-6	> 99.0%
1-Butyl-3-Methylimidazolium Hexafluorophosphate	$[Bmim]PF_6$	174501-64-5	> 99.0%
1-Butyl-3-Methylimidazolium Chloride	[Bmim]Cl	79917-90-1	> 99.0%
1-Butyl-3-methylimidazolium Bromide	[Bmim]Br	85100-77-2	> 99.0%
1-Butyl-2,3-Dimethylimidazolium Tetrafluoroborate	$[BDmim]BF_4$	402846-78-0	> 99.0%
N-Ethylpyridinium Tetrafluoroborate	$[EPy]BF_4$	350-48-1	> 99.0%
Pyridine	–	203-809-9	> 99.0%
N-Hexane	–	203-523-4	> 99.0%

2.3. The extraction procedure

The extraction process was carried out as follows: a certain mass ratio of model oil, water and IL were mixed in a 50 mL erlenmeyer flask and then put this mixture into the constant temperature water bath with magnetic stirring for a certain period of time. The temperature for this study is 30 °C. After settling down, a sample from the upper layer was collected. N-removal efficiency can be determined by the nitrogen concentration of upper phase. The specific calculation formula is as follow:

$$N - removal\ efficiency = \frac{C_0 - C_f}{C_0} \times 100\% \tag{2}$$

The distribution coefficient (D) of pyridine between IL and model oil phases could be calculated as follows:

$$D = \frac{C_{IL}}{C_f} \tag{3}$$

where C_0 represent the nitrogen concentration of the original model oil, C_f represent the nitrogen concentration of the upper phase after extraction, and C_{IL} represent the nitrogen concentration of IL layer after extraction.

2.4. Analysis methods

Sulfur and Nitrogen analytical instrument was used to analyze the content of nitrogen under 1000 ppm, which was purchased from Keyuan Electronic Instrument Co., Ltd., Jiangsu, China. Sulfur and Nitrogen analytical instrument was performed with a quartz tube, a special pyrolysis furnace, and an integrated darkroom. Standard SH/T0704-2001 was used in N element analysis. For oxidation combustion method, high pressure oxygen was used as carrier gas with a flow rate of 150 ~ 200 mL/min at 1044 °C.

2.5. Regeneration of used ionic liquids

The oil and ionic liquids phases were separated by separating funnel The IL phase was moved into a rotary evaporator. Pyridine and water in ionic liquid phase were evaporated at 100 °C for 3 h. the standard and the regenerated IL were characterized using a Fourier transform infrared (FT-IR) spectrometer (Nicolet 380, Thermo Fisher Scientific, America) at room temperature.

3. Results and discussion

3.1. Selection of imidazolium based ILs

The extraction of model oil with a nitrogen content of 1000 ppm was studied using ILs. The N-removal efficiency of pyridine was calculated according to the experiment process described above. The extraction ability can be intuitively reflected by N-removal efficiency. Several ILs were used to investigate the influence of the substituents, such as $[Bmim]BF_4$, $[Bmim]PF_6$, [Bmim]Cl, [Bmim]Br, $[BDmim]BF_4$, $[EPy]BF_4$,and the optimum one was obtained.

In this research, the mass ratio of model oil to IL was maintained at 5:1. 4 g IL added into 20 g of model oil in an erlenmeyer flask. The experiment was carried out at 30 °C for 30 min. Table 2 shows the N-removal efficiency of pyridine using different ILs. ILs can separate pyridine from model oil to some extent, and different ILs exhibited different extraction abilities. For different anion, the extraction ability of pyridine follows the order below: $[Bmim]BF_4 > [Bmim]PF_6 > [Bmim]Cl > [Bmim]Br$. The N-removal efficiencies were 33.4%, 32.1%, 13.7% and11.4%. For different cation, the extraction efficiency follows the order below: $[Bmim]BF_4 > [BDmim]BF_4 > [EPy]BF_4$. The N-removal efficiencies were 33.4%, 10.6% and 5.3%. In conclusion, ILs can be used to separate pyridine from model oil. The highest efficiency