Removal of Basic Nitrogen Compounds from Fuel Oil with [Hnmp]H_2PO_4 Ionic Liquid

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doi: 10.15255/CABEQ.2016.955
Original scientific paper
Received: July 26, 2016
Accepted: March 7, 2017

Ionic liquid (IL) N-methyl pyrrolidone dihydrogen phosphate ([Hnmp]H_2PO_4) was synthesized and its structure was characterized with FT-IR spectroscopy and ^{1}H NMR. The denitrogenation performance of the ionic liquid was investigated using Fushun shale diesel oil that included 0.52 w% basic nitrogen as feedstock. Experiment results showed that under the operating conditions with temperature of 30 °C, 1:7 (w/w) IL: oil, reaction time of 20 min, and settling time of 2 h, the ionic liquid exhibited good denitrogenation performance achieving 86.27 % basic N-extraction efficiency and the yield of refined diesel oil can reach more than 90 %. In addition, the basic N-removal efficiency can still reach 54 % during four recycles of the ionic liquid.

Key words:
[Hnmp]H_2PO_4 ionic liquid, shale diesel oil, denitrogenation, basic nitrogen

Introduction

Nitrogen compounds (N-compounds) presented in fuel oils are mainly classified as basic N-compounds (such as pyridine and quinoline) and non-basic N-compounds (e.g. carbazole and indole), and they give rise to NO_X during combustion, which is one of the important factors causing acid rain and haze[1,2]. The presence of N-compounds can also affect deep removal of sulfur compounds, and are considered as strong inhibitors of the hydrodesulfurization process because of their preferable adsorption on the surface of the catalyst[3]. In addition, some basic N-compounds can cause hydrogenation catalyst to deactivate[4]. Removal of N-compounds, especially the basic N-compounds, from fuel oils has become an increasingly important research subject with the increasingly strict environmental regulations in recent years. Hydrodenitrogenation (HDN) technology[5] is widely used to remove N-compounds from fuel oils in the petroleum industry, but the technology is very costly due to high operating temperature, pressure, and hydrogen consumption. Several non-hydrodenitrogenation processes, including adsorption, solvent extraction, and oxidation have been proposed. Among these, denitrogenation based on solvent extraction has been most extensively studied because of its high extraction efficiency, facile operation, and low operating cost. Compared to the conventional organic extraction solvents, ionic liquids (ILs) seem to be more attractive due to their negligible volatilities (since high volatility of the solvent always results in a problem of fugitive emissions during the industrial processes), immiscibility with fuel oils, higher affinity to N-compounds and good recyclability[6–8]. Therefore, several ILs have been tried for removal of N-compounds from fuel oils by means of an extraction technology. The use of imidazolium-based ILs as extractants is predominant in the denitrogenation process. For example, imidazolium-based ILs with HSO_4^- anion or $H_2PO_4^-$ anion[9–11] achieved very high basic N-extraction efficiency of more than 90 %. Charles *et al.*[12] found that ILs with $N(CN)_2$ anion exhibited a better extraction effect for non-basic N-compounds than for basic N-compounds, e.g., the extraction efficiency of carbazole can reach 100 % with [BMI][$N(CN)_2$]. Zhang *et al.*[13] found that [Bmim][BF_4] can remove 45 % pyridine from dodecane model oil. [Bmim]Cl[14,15] has a very highly selective extraction for neutral N-compounds in the diesel oil, while a further study[16] found that the ionic liquid can remove 55 % of nitrogen from straight run gas oil containing 0.0105 w% nitrogen. Gabric *et al.*[17] selected five imidazolium-based ILs to extract thiophene, dibenzothiophene and pyridine from two model solutions, and found the extraction efficiency of pyridine was almost twice higher than that observed for thiophene and dibenzothiophene.

In view of the higher cost of imidazolium-based ILs, the objectives of this work were to synthesize N-methyl pyrrolidone dihydrogen phosphate ([Hnmp]H_2PO_4) ionic liquid using N-methyl pyrro-

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lidone (NMP) as feedstock, and for the first time investigate its performance for removing basic N-compounds. Meanwhile, considering that the study reported on denitrogenation with ILs was mainly confined to model oil, and that their denitrogenation effects for actual oil were rarely studied, Fushun shale diesel distillate with a large amount of basic N-compounds was selected as actual oil for investigation of N-removal performance of $[Hnmp]\cdot H_2PO_4$.

Experimental

Experiment reagent and apparatus

N-methyl pyrrolidone (99 %) was purchased from Nanjing Chemical Reagent Co. Ltd. (China). Phosphoric acid (85 %) was purchased from Shenyang Shenyi Fine Chemical Co. Ltd. (China). Ethyl acetate (≥99.5 %) was purchased from Tianjing Fuyu Fine Chemical Industry Co. Ltd. (China). 1-butyl-3-methylimidazolium hydrosulphates ($[C_4mim]HSO_4$, ≥99 %) was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. (China).

The experimental devices included: constant temperature magnetic heating stirrer DF-101S (Gongyi City Instrument Co., Ltd, China); electronic balance FA2104N (0.0001 g, Shanghai Jingke Scientific Instruments Co., Ltd., China); automatic potentiometric titrator ZD-2(A) (Shanghai Dapu Instruments Co., Ltd., China); rotary evaporators RE-52C (Shanghai Hualian Medical Apparatus Co. Ltd., China); vacuum oven ZK-82J (Shanghai Experimental Instrument Factory, China); Cary 600 Series FTIR Spectrometer (American Agilent Technologies); nuclear magnetic resonance spectrometer Varian Mercury-Plus 300BB (American Varian).

Synthesis of $[Hnmp]H_2PO_4$

The ionic liquid was prepared referring to the method described in the literature[18]. Phosphoric acid was dropped slowly into the equal molar NMP placed in a round-bottomed flask at room temperature and stirred continuously, then temperature was increased gradually to 80 °C. After three hours, the mixture became a light yellow liquid $[Hnmp]H_2PO_4$. Specific reaction equation is given as Fig. 1.

Table 1 – *Properties of diesel fraction from Fushun shale oil*

P_{20}/g mL^{-1}	Basic nitrogen/ μg g^{-1}	Pour point/ °C	v_{20}/mm^2 s^{-1}
0.8655	5223	2	4.47

Experimental feedstock

The shale oil used in the present study was obtained from Fushun, China, and it contained diesel distillate of about 40 %. The diesel distillate at the boiling range of 200 ~ 350 °C was obtained by fractionating the shale oil on a true-boiling-point distillation apparatus, and used as experiment feedstock. Its main properties are presented in Table 1.

As seen from Table 1, the content of basic nitrogen in Fushun shale diesel distillate was up to 0.52 w%, and denitrogenation prior to hydrogenation is quite necessary in order to make operating conditions moderate and reduce operating costs.

Denitrogenation experiment procedure and N-content analysis

In a typical experiment, the diesel oil and IL were placed at a mass ratio in a 50-mL beaker and magnetically stirred at a specified temperature. After the reaction continued for a specified time, the reaction mixture was settled and stratified, and the basic nitrogen content in upper oil (refined oil) phase was analyzed by adopting the perchloric acid-glacial acetic acid titration method (SH/T0162-92, China). Extraction efficiency (*E,* %) of N-compounds and the yield of refined oil (*Y*, %) are determined according to the equations (1) and (2), respectively.

$$E(\%) = (C_i - C_f)/C_i \cdot 100 \quad (1)$$

$$Y(\%) = m_f/m_i \cdot 100 \quad (2)$$

where C_i and C_f are the initial and final basic nitrogen contents in diesel oil; m_f and m_i are the mass of refined diesel oil and raw shale diesel oil.

Regeneration of IL

Recycle experiments were performed using carbon tetrachloride as a back extractant. Upon

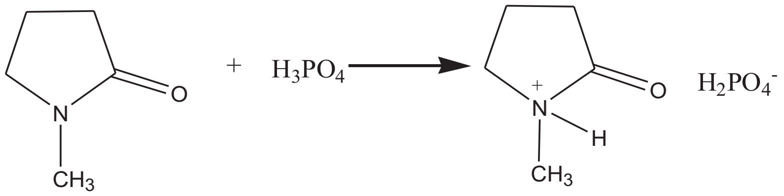

Fig. 1 – *Synthesis route of $[Hnmp]H_2PO_4$*

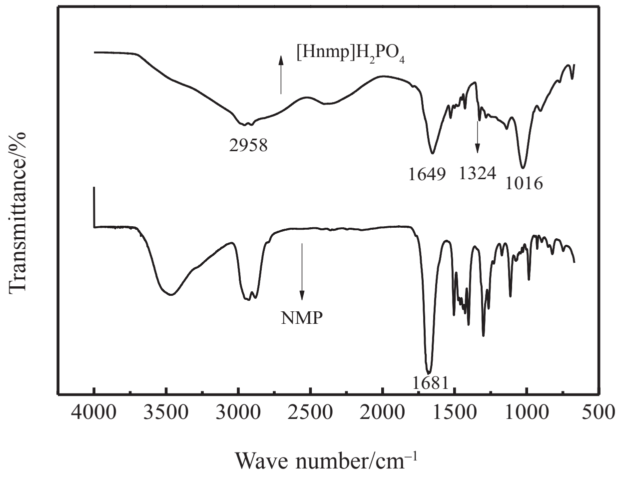

Fig. 2 – *FT-IR spectra of NMP and [Hnmp]H_2PO_4*

completion of the denitrogenation experiment, the oil phase was separated from the ionic liquid by a separating funnel. The IL layer was washed 3-5 times with the same quantity of carbon tetrachloride, and evaporated under vacuum to remove carbon tetrachloride. The regenerated IL was used for further extraction of fresh shale diesel oil under the same operating conditions to investigate its denitrogenation performance.

Results and discussion

Characterization of [Hnmp]H_2PO_4: FTIR

As can be seen in Fig. 2, the FTIR spectrum of ionic liquid is different from that of NMP. The broad peak near 2958 cm^{-1} was stretching vibration of protic NH^+ in ionic liquid. The C=O absorption peak centered at 1681 cm^{-1} shifted to a lower frequency at 1649 cm^{-1}, implying that the hydrogen bond between the molecules and $H_2PO_4^-$ anion had an effect on carbonyl. Absorption peaks centered 1324 cm^{-1}, 1016 cm^{-1} were generated by P=O, P–O group of H_2PO_4 anion, respectively.

Characterization of [Hnmp]H_2PO_4: ^{1}H NMR

^{1}H-NMR(D_2O, TMS), $\delta = 3.081$(2H, NCH_2^-),
$\delta = 2.045$(3H, NCH_3^-), $\delta = 2.011$(2H, $OCCH_2^-$),
$\delta = 1.619$(2H, $NCH_2CH_2^-$).

Investigation of the acidity of ionic liquids by IR spectroscopy

By using pyridine as IR spectroscopic probes[19], the acidity of the ionic liquid [Hnmp]H_2PO_4 was determined. Pyridine and [Hnmp]H_2PO_4 were mixed at 1:3 volume ratio, then detected by FT IR Spectroscopy with potassium bromide as the background at 20 °C, and the result is shown in Fig. 3. Obviously, the absorption peak of pure pyridine appeared at 1438 cm^{-1}, the peak disappeared after it reacted with [Hnmp]H_2PO_4, and a new peak appeared at 1504 cm^{-1}, which indicated the ionic liquid had bronsted acidity.

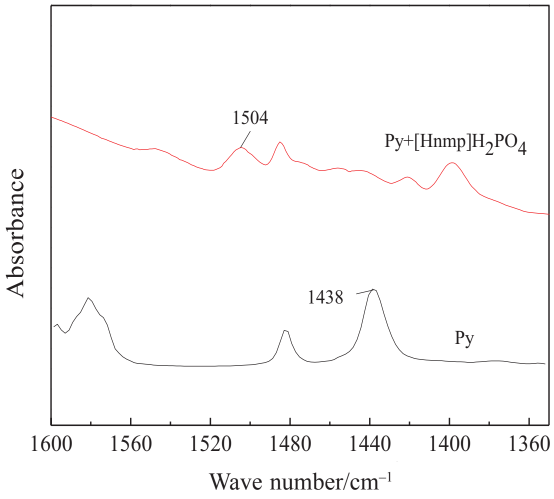

Fig. 3 – *Investigation of the acidity of [Hnmp]H_2PO_4 by FT-IR spectroscopy*

Denitrogenation with ionic liquid [Hnmp]H_2PO_4

Comparative study of N-removal performance

Comparison of denitrogenation performance between [Hnmp]H_2PO_4 and typical imidazolium-based IL [C_4mim]HSO_4 was investigated under the same operating conditions, and shale diesel oil was used as experiment feedstock. The results are presented in Fig. 4.

As can be seen from Fig. 4, [Hnmp]H_2PO_4 and [C_4mim]HSO_4 can remove basic N-compounds

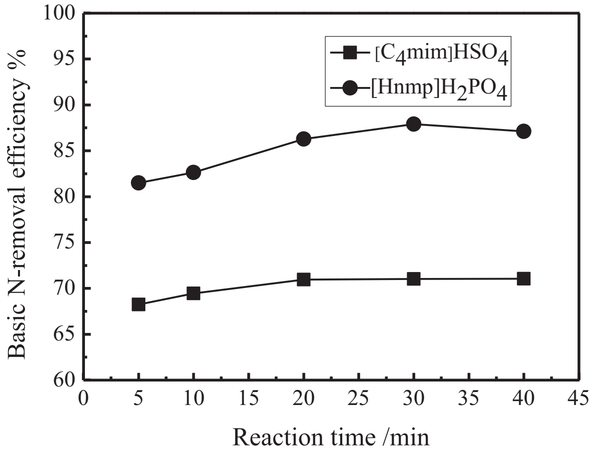

Fig. 4 – *Basic N-removal effect of two ionic liquids at different reaction times. Reaction conditions: IL/oil mass ratio = 1:7, temperature = 30 °C, settling time =2 h.*

from diesel oil, achieving 87.9 % and 71.03 % basic N-removal efficiencies, respectively. Both [C_4mim]HSO_4 and [Hnmp]H_2PO_4 showed bronsted acidity, and they were able to provide proton H^+, which attacked long pair electrons of the N atom in the basic N-compound in denitrogenation process and a complex reaction between the H^+ and N-compound occurred, thus N-compounds were removed from the diesel oil. Although the acidity of [C_4mim]HSO_4 was stronger than that of [Hnmp]H_2PO_4, the latter showed better basic N-removal performance. The viscosities of [C_4mim]HSO_4 and [Hnmp]H_2PO_4 at 30 °C were 577.98 $mm^2\ s^{-1}$ and 200.21 $mm^2\ s^{-1}$, respectively. During the process of denitrogenation experiment, [C_4mim]HSO_4 with a higher viscosity tended to stick on the wall of the bottle, resulting in insufficient contact with the diesel oil and a low denitrogenation efficiency.

As shown in Fig. 4, for IL [Hnmp]H_2PO_4, basic N-removal efficiency increased with the extension of reaction time, e.g., the basic N-extraction efficiency increased from 81.5 % at 5 min to 86.27 % at 20 min, because longer reaction time enabled a more efficient reaction between ionic liquid and N-compounds. Moreover, basic N-removal efficiency did not change basically after 20 min, which indicated that the extraction process had reached equilibrium in a shorter time because of the faster mass transfer and reaction between [Hnmp]H_2PO_4 and N-compounds. The reaction time was set at 20 min in the study to save operating time and increase efficiency.

In the following experiments, the effect of temperature, IL/oil mass ratio and settlement time on denitrogenation with [Hnmp]H_2PO_4 was investigated in detail.

Effect of temperature

Five sets of experiments at various temperatures were carried out to investigate the effect of reaction temperature on basic N-removal efficiency. The results are shown in Table 2.

From Table 2, it can be seen that the basic N-removal efficiency tended to decrease with increasing temperature under the experiment conditions. For example, basic N-extraction efficiency reduced from 86.27 % at 30 °C to 74.75 % at 70 °C. [Hnmp]H_2PO_4 removed basic N-compounds from diesel oil through complex extraction, the reaction was an exothermic process, and the increase in temperature was not conductive to the reaction in a positive direction. Accordingly, denitrogenation with the ionic liquid may be conducted at room temperature, thus consuming less energy, and making it more desirable for industrial applications.

Table 2 – *Effect of temperature on basic N-removal efficiency*

Temperature/°C	30	40	50	60	70
Basic N-removal efficiency/%	86.27	81.7	76.21	74.95	74.75

Reaction conditions: IL/oil mass ratio = 1:7, reaction time = 20 min, settling time = 2 h.

Effect of mass ratio of IL/oil

The IL/oil mass ratios considered were 1:15, 1:10, 1:7, 1:3, and 1:1, and the results are presented in Fig. 5. It can be seen that IL/oil mass ratio had a significant effect on N-removal efficiency. Removal efficiency of basic nitrogen increased from 59.06 % to 94.51 % when IL/oil mass ratio increased from 1:15 to 1:1, and the corresponding content of basic nitrogen reduced from 2138 μg g^{-1} to 287 μg g^{-1}. In addition, the yield of refined oil decreased with the increase in mass ratio of IL/oil. Since the yield of refined oil decreased markedly at IL: oil (w/w) > 1:7, the suitable IL/oil mass ratio was determined as 1:7 in this study.

Effect of settling time

It was necessary to separate the IL containing undesirable components (e.g. N-compounds) from the diesel oil by the settlement and stratification process to improve denitrification effect. The effect of settling time on the denitrogenation process is shown in Table 3. Obviously, when settling time extended from 0.5 h to 3 h, the basic N-extraction efficiency increased from 80.62 % to 86.25 %, and N-extraction efficiency remained nearly constant at settling time longer than 2 h. In addition, the yield of refined diesel oil decreased slightly with extended settling time. Therefore, 2 h can be regarded as the suitable time for the separation of IL and diesel oil.

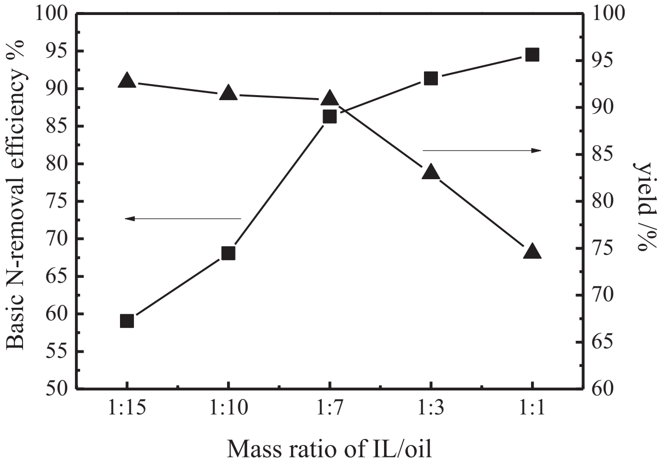

Fig. 5 – *Effect of mass ratio of IL/oil on denitrogenation process. Reaction conditions: reaction temperature = 30 °C, reaction time = 20 min, settling time = 2 h.*

Table 3 – *Effect of settling time on basic N-removal efficiency and refined oil yield*

Settling time/h	0.5	1.0	1.5	2.0	2.5	3.0
Basic N-removal efficiency/%	80.62	82.04	84.92	86.24	86.28	86.25
Yield of refined oil/%	91.82	91.47	91.05	90.79	90.62	90.58

Reaction conditions: temperature = 30 °C, IL/oil mass ratio = 1:7, reaction time = 20 min.

Table 4 – *Properties of refined diesel fraction*

P_{20}/g mL^{-1}	Basic nitrogen/ μg g^{-1}	Pour point /°C	v_{20}/mm^2 s^{-1}
0.8428	718	–1	4.35

Regeneration of IL

Fig. 6 shows the denitrogenation experiment results with regenerated [Hnmp]H_2PO_4. Obviously, regenerated IL [Hnmp]H_2PO_4 still presented a certain removal performance for basic N-compounds and about 54 % N-removal efficiency was reached after 4 recycles, which indicated that its denitrogenation performance was relatively stable. Considering the decrease in denitrogenation performance of [Hnmp]H_2PO_4 after regeneration, a more efficient regeneration method needs further study in the future.

Properties of refined diesel oil

The properties of the diesel oil obtained by refining with ionic liquid [Hnmp]H_2PO_4 are shown in Table 4. Compared with data in Table 1, density, viscosity and pouring point of refined oil had decreased while oil quality had improved after denitrogenation with ionic liquid.

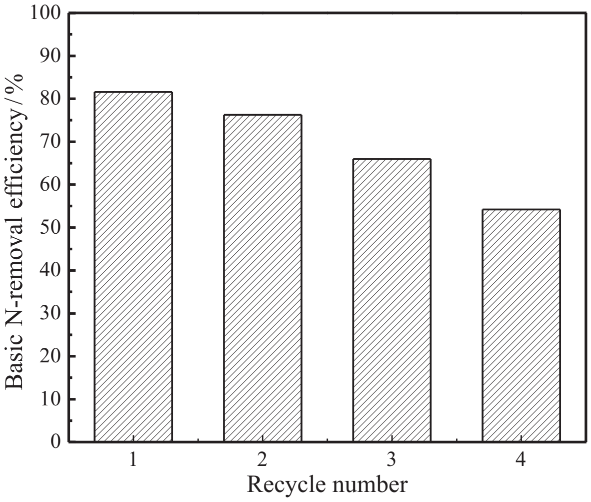

Fig. 6 – *Relation of basic N-extraction efficiency with recycle number. Reaction conditions: temperature = 30 °C, IL/oil mass ratio = 1:7, reaction time = 20 min, settling time = 2 h.*

Conclusion

The N-compounds in fuel oils need to be removed because of their inhibiting effects on the hydrodesulfurization process and environmental pollution caused by NO_x emissions. In this work, N-methyl pyrrolidone dihydrogen phosphate ([Hnmp]H_2PO_4) was synthesized, and its denitrogenation performance was investigated using Fushun shale diesel oil containing a large amount of basic N-compounds with about 0.52 w% of basic nitrogen as feed. Under the operating conditions, i.e., temperature of 30 °C, reaction time of 20 min, IL/oil mass ratio of 1:7, and settling time of 2 h, the basic N-removal efficiency was achieved at 86 % and its basic N-removal efficiency could still reach 54 % after the ionic liquid had been recycled 4 times. Compared with imidazolium-based IL [C_4mim]HSO_4, the denitrogenation performance of [Hnmp]H_2PO_4 is competitive. This work may present a new approach to fuel oil denitrogenation.

ACKNOWLEDGMENTS

The authors thank Fushun Research Institute of Petroleum and Petrochemicals, SINOPEC, for supporting the ionic liquids characterization in this work.

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