Fuel Processing Technology 130 (2015) 38–45

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Synthesis of ionic liquids and their use for extracting nitrogen compounds from gas oil feeds towards diesel fuel production

Georgina C. Laredo [a,*], Natalya V. Likhanova [a], Irina V. Lijanova [b], Bernardo Rodriguez-Heredia [b], J. Jesús Castillo [a], Patricia Perez-Romo [a]

[a] *Programa de Investigación y Posgrado, Instituto Mexicano del Petróleo, Lázaro Cárdenas 152, México 07730 D.F., Mexico*
[b] *Centro de Investigacion e Innovacion Tecnologica, Instituto Politecnico Nacional, Cecati s/n. Sta. Catarina, Azcapotzalco Mexico 02250 D.F., Mexico*

ARTICLE INFO

Article history:
Received 23 April 2014
Received in revised form 15 August 2014
Accepted 20 August 2014
Available online 12 October 2014

Keywords:
Extraction
Nitrogen
Diesel
Denitrogenation
Ionic liquids

ABSTRACT

Seventeen ionic liquids (ILs), containing imidazole (7) and quaternary ammonium groups (10), were tested in the removal of nitrogen compounds present in the gas oil feed for diesel fuel production. A model mixture composed by quinoline, indole, and carbazole in hexadecane/toluene was used to run experiments with a Feed/IL ratio of 20/1 and 30 °C. In general, the synthesized ILs presented higher removals of indole and carbazole than of quinoline. Additionally, when the carbon number of the carboxylate counterpart of the quaternary ammonium ILs increased, the carbazole removal increased. Further experiments using model mixtures that contained also benzothiophene and benzothiophene and aniline, showed that none of these added compounds affected the ILs solubility for indole and carbazole under the same experimental conditions.

Experiments carried out in a batch setup using straight run gas oil (SRGO) proved that only triethylmethylammonium butyrate and triethylmethylammonium acetate of all the ILs selected, presented good nitrogen removal capabilities and adequate chemical stabilities at the experimental conditions used. Therefore, they were chosen for a dynamic study that showed that a 30% organic nitrogen extraction could be attained when 200 and 170 mL per gram of material had passed before a regeneration process was required.

1. Introduction

The production of ultra low sulfur diesel (ULSD) is very important due to current air pollution problems. Consequently, many stringent environmental regulations for this nonrenewable fuel have been established worldwide in spite of the sustained decrement in the crude oil quality. Nitrogen compounds (N-compounds) present in the straight run gas oil (SRGO), coker gas oil (CGO) and light cycle oil (LCO), which are used as feedstocks for diesel fuel production have been identified as strong inhibitors of the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions [1–7]. It has been proved that the withdrawal of these N-compounds from the feedstocks reduces the severity of the HDS process, facilitating the complying with the new regulations [4–7].

The N-compounds are frequently classified in two groups: basic (e.g. pyridines, quinolines) and neutral (e.g. indoles, carbazoles) [8,9]. While the basic N-compounds exert an inhibiting effect by being adsorbed onto the Lewis and Brönsted acidic sites of the HDS catalysts, the neutral N-compounds tend to form gums by polymerization, which leads to pore and intraparticular plugging of these catalysts [10–13]. As stated by Laredo et al. [14], indoles and carbazoles derivatives represent 75 wt.% of the total N-content (300–400 wppm), and the concentration of the quinoline derivatives is around 25 wt.% in SRGO. Concentrations of total and neutral N-compounds in LCO and CGO are higher than those of SRGO [14–17].

A quite often used alternative for increasing the HDS performance is the selective adsorption of these inhibitory N-compounds by solid adsorbent materials [4]. However, until now, such a suitable, highly adsorptive, highly selective and low price material has not been found yet.

Several selective N-compound removals have been described by using ionic liquids (ILs) [18–26]. Table 1 shows the names and abbreviations of the discussed ILs found in the literature, while Table 2 shows data regarding the extraction efficiency as a percentage of nitrogen compounds removal (NR, %).

Zhang et al. [18] removed N-compounds such as pyridine (PY) and piperidine (PIP) in the presence of dibenzothiophene (DBT) from dodecane as solvent, using [MeBuIm][BF_4]. As it was shown, at low concentrations, the N- and S-containing compounds were extracted from fuels without mutual hindrance.

By means of an extraction procedure ([MeBuIm][Cl]), Xie et al. [19] attained 55% of nitrogen reduction using SRGO containing 13,240 wppm of sulfur (S) and 105 wppm of nitrogen (N). The removal

---

* Corresponding author. Tel.: +52 55 91758382.
E-mail addresses: glaredo@imp.mx (G.C. Laredo), nvictoro@imp.mx (N.V. Likhanova), irinalijanova@yahoo.com.mx (I.V. Lijanova), herediaber@hotmail.com (B. Rodriguez-Heredia), jcastill@imp.mx (J.J. Castillo), pperezr@imp.mx (P. Perez-Romo).

http://dx.doi.org/10.1016/j.fuproc.2014.08.025
0378-3820/

Table 1
Names and abbreviations used for the ionic liquids from the literature.

Ionic liquid	Abbreviation	Ref
1-Buthyl-3-methylimidazolium tetrafluoroborate	[MeBuIm][BF$_4$]	[18]
1-Butyl-3-methylimidazolium chloride	[MeBuIm][Cl]	[19]
1-Octyl-3-methylimidazolium tetrafluoroborate	[MeOcIm][BF$_4$]	[20]
1-Octyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)-imide	[MeOcIm][NTf2]	[20]
1-Ethyl-3-methylimidazolium ethylsulfate	[MeEtIm][EtSO4],	[20]
1-Butyl-3-methylpyridinum dicyanamide	[MeBuPy][N(CN)$_2$]	[21]
1-Butyl-3-methylimidazolium dicyanamide	[MeBuIm][N(CN)$_2$]	[22]
1-Ethyl-3-methylimidazolium dicyanamide	[MeEtIm][N(CN)$_2$]	[22]
Tetrahedral ethyldimethylsulfonium dicyanamide	[EtMe$_2$S][N(CN)$_2$]	[22]
Cyclic ethylated tetrahydrothiophenium dicyanamide	[S2][N(CN)$_2$]	[22]
1-Buthyl-3-methylimidazolium trichlorobromoferrate	[MeBuIm][BrFeCl$_3$]	[24]
1-Buthyl-3-methylimidazolium tetrachloroferrate	[MeBuIm][ClFeCl$_3$]	[24]
1-Ocyl-3-methylimidazolium tetrachloroferrate	[MeOcIm][ClFeCl$_3$]	[24]
1-Buthyl-2,3-dimethylimidazolium tetrachloroferrate	[Me$_2$OcIm][ClFeCl$_3$]	[24]
1-Octylpyridinium bromide	[BuPy][Br]	[24]
1-Ethyl-3-methylimidazolium ethyl sulfate	[MeEtIm][EtSO$_4$]	[25]
1-Pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[MePenIm][Tf$_2$N]	[25]
1-Hexyl-3,5-dimethylpyridinium bis(trifluoromethylsulfonyl)imide	[MeHexPy][Tf$_2$N]	[25]
1-Benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[MeBzIm][Tf$_2$N]	[25]
1-Heptyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide	[MeHepIm][Tf$_2$N]	[25]
1-Decyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide	[MeDecIm][Tf$_2$N]	[25]
1-Methylimidazolium phosphate	[MeIm][H$_2$PO$_4$]	[26]
1-Buthyl-3-methylimidazolium phosphate	[MeBuIm][H$_2$PO$_4$]	[26]
1-Methyl-3-(3-sulfopropyl)-imidazolium phosphate	[MeSProIm][H$_2$PO$_4$]	[26]

of the S compounds was 7%, therefore, a N/S selectivity higher than 60 was achieved in this experiment.

Alonso et al. [20] studied five ternary systems (i.e. IL, pyridine and n-hexane) involved in the gasoline and diesel desulfurization using a non random two-liquid (NRTL) equation. With this data, the ability of some ILs such as [MeOcIm][BF4], [MeOcIm][NTf2], and [MeEtIm][EtSO4], was tested for carrying out simultaneous desulfurization and denitrogenation of fuel oil.

After carrying out experiments with model and real refinery streams, Hansmeier et al. [21] confirmed that N-compounds were extracted more efficiently (>99%) than S-compounds from model mixtures using 42 ILs and sulfolane. Additionally, both S- and N-compounds can be removed from real refinery streams, albeit with a lower efficiency than with model feeds.

Asumana et al. [22] found that four dicyanamide-based ILs with different cationic characteristics, e.g. [MeBuIm][N(CN)2], [MeEtIm][N(CN)2], [S2][N(CN)2], and [EtMe2S][N(CN)2] were capable of extracting effectively the N-compounds from a model fuel, being carbazole more efficiently extracted than pyridine. After five regenerations of the ILs, the nitrogen removal efficiency remained constant.

By a quantum-chemical-based COSMO-RS (Conductor-like-Screening Model for Real Solvents) model, Anantharaj and Banerjee [23] predicted the hydrodesulfurization and hydrodenitrogenation capabilities of several imidazolium and pyridinium ILs. I-Ethyl-1-methylpyrrolidinium (MeEtPyrr), 1-ethyl-3-methylpiperidinium (MeEtPy), and 4-ethyl-4-methylmorpholinium (MeEtMor) based ILs showed higher selectivity and capacity for the simultaneous removal of acidic heterocyclic sulfur and basic and neutral heterocyclic N-compounds from simulated diesel oil.

Ceron et al. [24] proved that halogenated ILs are an excellent alternative for the selective extraction of nitrogen containing compounds from real fuels since these ILs are relatively inexpensive, and can be regenerated and recycled. Table 2 shows several ILs that presented removals higher than 80% when extracting N-compounds from SRGO. It is interesting to observe that some ILs with a cation/anion ratio of 1/1.5 (mol/mol) presented better extraction capabilities than the stoichiometric salts (1/1).

Five imidazolium-based ILs and one pyridinium-based IL were selected for the extraction of thiophene (TH), dibenzothiophene (DBT), and pyridine (PY) from two model solutions by Gabric et al. [25]. The extraction efficiency of PY was almost two times higher than the observed ones for TH, and DBT. The increase in the mass ratio of the ionic liquid/model fuel solution and multistage extraction promoted the desulfurization and denitrogenation capabilities of the examined ILs. All the selected ILs can be reused and regenerated by means of vacuum evaporation.

Wang et al. [26] synthesized and tested three dihydrogen-phosphate-based (H_2PO_4) ionic liquids (ILs) with different cations, i.e., 1-methylimidazolium (MeIm) 1-butyl-3-methylimidazolium (MeNuIm), 1-methyl-3-(3-sulfopropyl)-imidazolium (MeSProIm) to determine their properties on the denitrification from simulated oil composed of quinoline and n-heptane. Experimental results show that the mechanism of denitrification not only comes from the liquid–liquid extraction, but also from the acidity of the ILs. With the increase in acidity, the ILs showed a high selectivity to quinoline. When ILs such as [MeBuIm][H$_2$PO$_4$] and [MeSPrImo][H$_2$PO$_4$] were used at IL/oil and IL/H_2O mass ratios of 1/10 and 2/1, respectively, the denitrification rate reached more than 99%. These ILs can be recycled six times without significant decrease in activity.

The objectives of this work were to synthesize some new imidazole and quaternary- ammonium-derived ILs, which were selected by considering the results of a previous work [27]. The choice of the model mixtures and experimental conditions was based on the hypothesis that N-compounds exert a powerful inhibiting effect on the HDS of middle distillates [10–13], where non-basic-nitrogen compounds are present in higher concentrations than the basic ones [14–17]. Thus, in order to study the removal efficiency of N-compounds by type using ILs, simple model mixtures conformed by aniline (A), quinoline (Q), indole (I) and carbazole (Cz) as N-compounds and benzothiphene (BT) as S-compound, in a 1/1 heptane/toluene mixture, were prepared. It was also considered that the amount of IL would have to be kept at a minimum just enough to remove the N-compounds to facilitate the HDS process and to avoid that most of other SRGO components such as sulfur and aromatic compounds were extracted. The preparation and test of some of the ILs with metallic salts such as $AlCl_3$ and $FeCl_3$ (Lewis acidity) [24] are not presented in this paper. In spite of their well-known good S- and N-compound removal capabilities [27], this type of ILs is frequently moisture sensitive and tend to form hydrochloric acid in the presence of water, making very difficult their use in continuous systems.