

Extractive and oxidative-extractive desulfurization of fuels with ionic liquids



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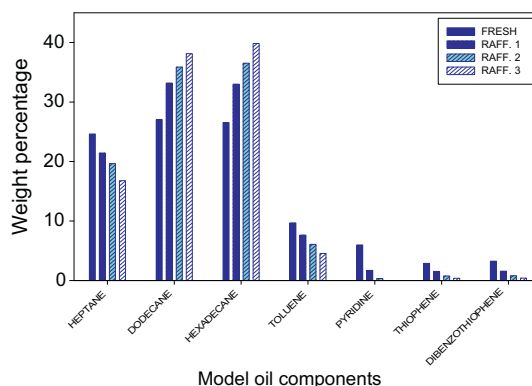
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HIGHLIGHTS

- A fuel nature influences the strategy for its desulfurization by ionic liquids (ILs).
- For gasoline desulfurization, extraction with the IL $[\text{C}_2\text{mim}][\text{OAc}]$ is preferred.
- Oxidative desulfurization works better for fuels with heavy sulfur compounds.
- The IL $[\text{C}_2\text{mim}][\text{NTf}_2]$ is proposed for the oxidative desulfurization of diesel fuel.

GRAPHICAL ABSTRACT

Three-stage EDS of synthetic gasoline, at 298.15 K, with $[\text{C}_2\text{mim}][\text{OAc}]$.



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ABSTRACT

Concerns about the pollution associated to the sulfur content of fuels have stimulated the search for new alternative technologies to the classical hydrodesulfurization process. The use of ionic liquids to remove sulfur compounds from hydrocarbons by solvent extraction is the object of ongoing research. Most of the publications in this front, however, present two serious drawbacks: they are not based on rigorous thermodynamic data, and they do not consider the effect of the ionic liquid on the different fuel constituents. In the present work, a comparative study of the extractive desulfurization and the oxidative-extractive desulfurization of fuels was carried out. In particular, the sulfur extraction ability of four ionic liquids (1-hexyl-2,4-dimethylpyridinium bis(trifluoromethylsulfonyl)imide ($[\text{C}_6^4\text{mppy}][\text{NTf}_2]$), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_2\text{mim}][\text{NTf}_2]$), 1-ethyl-3-methylimidazolium diethylphosphate ($[\text{C}_2\text{mim}][\text{Et}_2\text{PO}_4]$), and 1-ethyl-3-methylimidazolium acetate ($[\text{C}_2\text{mim}][\text{OAc}]$) was tested in real and synthetic fuels (gasoline and diesel). The selection of the ionic liquids was based on previously determined liquid–liquid equilibrium data. In the case of the oxidative desulfurization, an optimization of the oxidation and extraction conditions was done, taking into account catalyst type, ratio of catalyst and oxidant, temperature, mixing and settling times, etc. On the basis of the results, $[\text{C}_2\text{mim}][\text{OAc}]$ is suggested for the desulfurization of gasoline in an extractive process, whereas $[\text{C}_2\text{mim}][\text{NTf}_2]$ is preferred for the oxidative desulfurization of diesel.

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1. Introduction

Over the last years, worldwide environmental policies have gradually decreased the allowed limits of sulfur content in automotive fuels, in order to reduce atmospheric pollution and derived effects such as acid rain [1,2]. The classical hydrodesulfurization (HDS) process uses high pressure and temperature, and has a limited capacity to efficiently eliminate the refractory sulfur compounds in the fuel. In order to meet the more restrictive regulations, new alternative techniques to obtain ultralow sulfur fuels have been sought [3–5]. Among them, extractive desulfurization (EDS) is probably the most studied technique, where a solvent is put in contact with the fuel to remove the sulfur compounds by liquid–liquid extraction. Besides traditional volatile organic solvents, the use of ionic liquids to extract sulfur from gasoline and diesel has been the object of active research in recent times due to their interesting properties. Ionic liquids are salts (hence entirely composed by ions) with a low melting temperature (usually a threshold of 373.15 K is considered). Many ionic liquids are thermally and chemically stable, and they are in liquid state over a wide range of temperatures. As a result of their ionic character, they have a practically negligible vapor pressure under common process operating conditions, thus being easily recoverable from molecular volatile compounds and avoiding losses to the atmosphere (with the subsequent polluting effects). Moreover, a judicious selection of their constituent ions can tune the properties of the ionic liquids to a considerable extent, thus allowing the ‘design’ of a specific ionic liquid to meet the requirements for a particular target.

The use of ionic liquids for the selective extraction of sulfur compounds from fuels was reported for the first time in 2001 by Wassercheid and co-workers [6]. Since then, the desulfurization ability of many ionic liquids has been tested. The first studies focused on ionic liquids containing the $[\text{PF}_6]^-$ and $[\text{BF}_4]^-$ anions [7,8]. However, these ionic liquids are prone to hydrolyze even in the presence of humidity, generating dangerous hydrolysis products [9,10]. Thus, the use of other ionic liquids incorporating anions such as alkylsulfates, thiocyanate or bis(trifluoromethylsulfonyl)imide became more intense, also because of their lower viscosities [11–17]. Some works with acetate and dialkylphosphate ionic liquids were also published [18–20]. Regarding the selection of cations, a trend to use pyridinium cations acquired relevance in the last years, since Holbrey et al. [21] established the following ranking of ionic liquids for desulfurization depending on the cation core: alkylpyridinium \geq pyridinium \approx imidazolium \approx pyrrolidinium. Recently, several studies with ionic liquids based on morpholinium and piperidinium cations have also been published [22,23].

Regarding the type of experiments carried out, many research articles are based on the ability of ionic liquids to extract sulfur compounds (mainly thiophene and/or dibenzothiophene) from their mixtures with only a hydrocarbon [24,25]. Other studies focus on the liquid–liquid equilibrium of systems composed by an ionic liquid, a sulfur-containing compound, and an aliphatic hydrocarbon [14,15,22,26,27]. The high selectivities obtained in some of these systems [15,16,23] render the extraction with ionic liquids a promising alternative in desulfurization processes. However, few studies are found in the literature [15,28,29] that focus on the desulfurization-related equilibria while including other compounds such as aromatic hydrocarbons or nitrogen-containing compounds. In desulfurization research, little attention is usually paid to other parallel and relevant processes such as denitrogenation of the fuel or its dearomatization, which directly affect the properties of the fuel. In this vein, few works use synthetic fuels and analyze the behavior of all the compounds during the desulfurization process [8,30]. For instance, Hansmeier et al. [31] have tested pyridinium and imidazolium ionic liquids with

tricyanomethanide and dicyanamide anions for the desulfurization of model fuels consisting of several sulfur- and nitrogen-containing compounds. They concluded that these ionic liquids have a higher removal ability than sulfolane, a commercial extraction solvent used for extraction of aromatic hydrocarbons from petroleum fractions. Moreover, they showed that nitrogen-containing compounds are more efficiently extracted than sulfur components. These and other authors [15,30,32] also checked the efficiency of their proposed desulfurization process with real fuels.

One way to improve the solubility of the sulfur containing compounds in the ionic liquid is to oxidize these components and then they can be more easily extracted. This is the basis of the oxidative desulfurization (ODS). The oxidizing systems used for ODS with ionic liquids are very varied. The main oxidant used is hydrogen peroxide, with only a few works using others, such as sodium hypochlorite, dioxygen, or ozone [33–35]. Conversely, numerous catalysts have been explored, ranging from traditional organic acids, such as acetic or formic acid, to polyoxometalates (POMs) [36–38], or to other metal-based solid compounds [39,40]. For example, V_2O_5 was used by Xu et al. [39] with imidazolium ionic liquids comprising the $[\text{PF}_6]^-$ and $[\text{BF}_4]^-$ anions. Liu et al. [40] used Na_2WO_4 as catalyst, which apparently formed a complex with the ionic liquid, leading to a POM-based ODS system. Recently, acidic ionic liquids have led to very good results in desulfurization of fuels [41–44], without the need of addition of an external catalyst to the medium, since the intrinsic acidic character of the ionic liquids allows them to act as both catalysts and solvents. Nonetheless, some of these ionic liquids, for instance those with chloroaluminate anions, are extremely sensitive to moisture and must be handled either in vacuum or under inert atmosphere [45]; which is quite an unrealistic operating condition in a scaled-up industrial process for desulfurization of fuels. Other acidic ionic liquids, such as those with the hydrogensulfate and hydrogenphosphate anions, lose their protons in aqueous solutions to form acidic by-products. Moreover, corrosive and harmful acids are used for their synthesis.

In the last years we have carried out an exhaustive research work on liquid–liquid equilibria of ternary systems composed of a hydrocarbon (aliphatic or aromatic), a sulfur- or nitrogen-containing compound, and an ionic liquid [46–48]. Two classical thermodynamic parameters for the evaluation of the performance of extracting solvents were calculated from the liquid–liquid equilibrium data: the solute distribution ratio, or simply solubility (related to the amount of solvent needed to carry out the extraction); and the selectivity (related to the separation power of the solvent to achieve the target separation). To support and complete the knowledge obtained through the thermodynamic liquid–liquid equilibria in our previous studies, the desulfurization of simulated gasoline and diesel fuels was carried out in this work. With that aim, four ionic liquids were used: 1-hexyl-2,4-dimethylpyridinium bis(trifluoromethylsulfonyl)imide ($[\text{C}_6^{\text{H}}\text{mppy}][\text{NTf}_2]$), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_2\text{mim}][\text{NTf}_2]$), 1-ethyl-3-methylimidazolium diethylphosphate ($[\text{C}_2\text{mim}][\text{Et}_2\text{PO}_4]$), and 1-ethyl-3-methylimidazolium acetate ($[\text{C}_2\text{mim}][\text{OAc}]$). Their suitability as solvents in the EDS and ODS processes is evaluated. In the case of ODS, an optimization of the different oxidation parameters (type of catalyst, ratio of catalyst and oxidant, temperature, and extraction time) was also developed. The possibility of using nanofluids composed of metal oxide nanoparticles in ionic liquid was tested with the aim of studying the catalytic behavior of the nanostructures. The evolution of the sulfur-containing compounds, as well as of the other components of synthetic fuels, was monitored along several extraction stages. Finally, EDS and ODS with the ionic liquids were applied to real fuels, and the evolution of the total sulfur content was measured.

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