Deep Desulfurization of Oil Refinery Streams by Extraction with Ionic Liquids

A. Jess, J. Eßer
Department of Chemical Engineering, University Bayreuth
Universitätsstraße 30, D – 95448 Bayreuth, Germany

S-compounds in transportation fuels and fuel oil lead to SO_x-emissions that cause air pollution and acid rain. Mineral oil products like diesel oil, gasoline and fuel oils are subject to increasing regulatory pressure to reduce the residual concentration of sulfur compounds. In 2010 practically all transportation fuels need to meet a sulfur limit of <10 ppm S in order to minimize direct SO_2-emissions and enable the application of novel catalyst technologies like DeNOx-storage catalysts and advanced particulate filters for diesel engines.

State of the art in desulfurization technology is heterogeneously catalyzed hydrodesulfurization (HDS). Typical reaction conditions of HDS are a hydrogen pressure of 30 to 100 bar at 350 °C. This technology however is limited to ultra-low sulfur specifications due to the decreasing hydrogenation activity of different sulfur species in fuels. While paraffinic S-compounds (**1** to **3** in Fig. 1) are readily converted into H_2S and the corresponding alkanes, cyclic and especially sterically hindered aromatic S-compounds like dibenzothiophene (DBT)-derivatives (**6** to **8** in Fig.1) are less reactive for HDS.[1-3] The rate to convert 4-methyl-DBT (**7**) or 4,6-dimethyl-DBT(**8**) decreases by factors of about two and ten respectively compared to DBT (**6**).[4-5]

In the case of gasoline a S-limit of <10 ppm can only be met by deep HDS of all gasoline streams including naphtha from fluid catalytic cracking (FCC), which is nowadays the main source for S in gasoline but also contributes significantly to the total octane number of the product. The desulfurization of FCC-naphtha is easily achieved, because thiophene-derivatives (**4** in Fig. 1) are relative reactive for HDS. But hydrotreating also leads to olefin saturation and therefore to a loss in octane number. Alternative processes without the need for high pressure and hydrogen are therefore of high interest for refiners.

This paper proposes the use of Ionic Liquids (ILs) as extracting agent in liquid-liquid extraction as an alternative or supplemental technology for the desulfurization of refinery streams.

Early experiments on the selective extraction of S-compounds from model diesel oil (mixture of *n*-dodecane with DBT-derivatives) using chloroaluminate ILs like $[BMIM][AlCl_4]$ showed promising results.[6-7] Nevertheless, the use of chlorometallate ILs is not desired for technical large scale applications due to their very limited hydrolysis stability and in some cases toxicity. Further screening experiments showed that tetrafluoroborate or hexafluorophosphate ILs are also suitable for the extraction of model-sulfur compounds. Although ILs of this type are significantly more hydrolysis stable, their use as a large scale extracting agent is not optimal because of the relatively high price of the starting material. Additionally the formation of hydrolysis products - especially HF - is observed at elevated temperatures and in the presence of water.

To avoid these stability and corrosion problems the present work concentrated on completely halogen-free ILs for the extraction of S- and N-compounds. Very promising ILs are 1-*n*-butyl-3-methylimidazolium octylsulfate ($[BMIM] [OcSO_4]$) (**9**), 1-ethyl-3-methyl-imidazolium ethylsulfate $[EMIM][EtSO_4]$ (**10**), and 1,3-dimethylimidazolium dimethylphosphate ($[MMIM] [Me_2PO_4]$) (**11**) (Fig. 2).

The available data suggest that the use of ionic liquids as an extracting agent for sulfur and nitrogen compounds from various refinery streams following the basic concept shown in Fig. 3 is feasible.[8] However for a final dimensioning of the process more data are still needed.

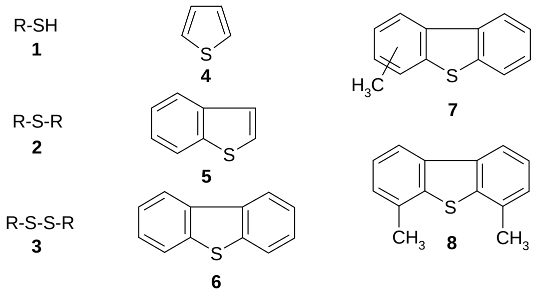

Fig.1:Typical S-compounds in transportation fuels

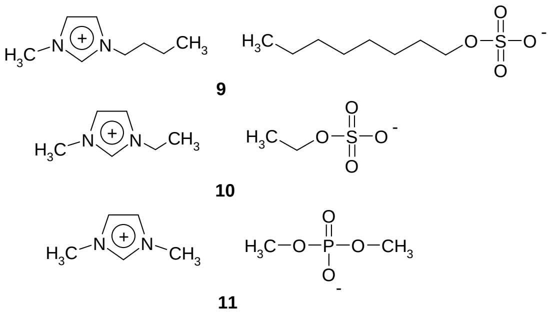

Fig. 2: Halogen-free ILs suitable for extractive desulfurization

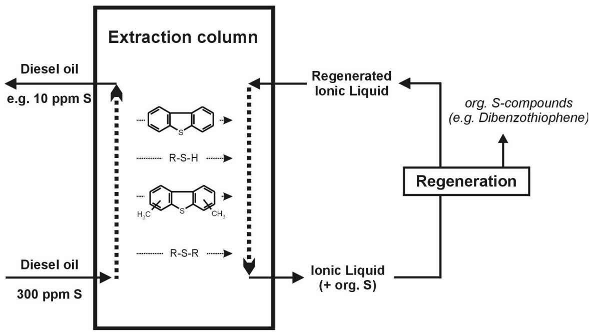

Fig.3 : Concept of deep desulfurization of refinery streams by Extraction with ILs

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