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Ionic liquid based deep oxidative desulfurization of liquid fuel

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Abstract

Increase in refractory sulfur compounds accompanied by the depleting oil reserve coupled with the stringent regulation on sulfur content of diesel fuel have rendered the current liquid fuel desulfurization technology inefficient. Consequently, alternative desulfurization technologies have been subject of investigations in recent years. Extractive and oxidative desulfurization technologies (EDS/ODS) appeared to be some of the most promising alternatives partly due to their broadness and compatibility with each other. The advent of ionic liquids (ILs) as extraction solvents have made this even more so. Therefore, investigation into ionic liquid-based deep oxidative desulfurization of diesel fuel was carried out in this work.

At first, a total of nine ionic liquids were screened. These ionic liquids were categorized as hydrophobic pyrrolidinium-based ILs containing cation with non-aromatic ring, hydrophobic and hydrophilic phosphonium-based ILs containing cations with no ring. Studies carried out in this phase of the work included physical properties measurement, solid-liquid equilibria, oxidant stability and liquid-liquid equilibria. The investigations carried out revealed the hydrophobic pyrrolidinium and hydrophilic phosphonium-based ILs as the most suitable ILs for further studies.

In the second part of the work, the suitable ILs were subjected to investigations involving EDS. A modest desulfurization efficiency of up to 69% dibenzothiophene (DBT) removal was achieved at mild operating conditions. The obtained result was better than most of the imidazolium-based ILs reported in the literature, suggesting that π- π interaction may not be solely responsible for the modest efficiencies obtained using ILs containing cations with aromatic ring. A study of the possible predominant interactions in EDS revealed that addition of a modifier with similar structure as the sulfur compounds can improve the efficiency to up to 81% DBT removal. Addition of an oxidation step using an electrophilic oxidant improved the extraction efficiencies of the pure ILs to almost complete removal of the sulfur compounds from simulated fuel. Upon application of the optimum operating conditions, IL (tetrabutylphosphonium methanesulfonate) and process (post-oxidation extractive desulfurization), the sulfur content of a commercial diesel fuel was reduced from 275.0 ppm down to 15.6 ppm, which is within the acceptable range of an ultra-low sulfur diesel fuel.