Deep desulfurization of diesel fuel using ionic liquids: current status and future challenges

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Deep desulfurization of diesel fuel has attracted the attention of a growing number of scientists and engineers due to the stringent regulations imposed on the presence of sulfur in fuel (10 ppm). To bring down the concentration of sulfur compounds to less than 10 ppm is very challenging and demands newer technologies. Novel processes are being proposed for this purpose. It is observed that ionic liquids as class of green solvents can play a major role in the deep desulfurization of diesel fuel. For this reason, this review focuses on the current status in application of ionic liquids for achieving ultra-low-sulfur diesel (ULSD). To get a comprehensive perspective about the topic, other techniques of desulfurization are also discussed in brief in the introduction. Here we propose that the appropriate removal method should be selected according to different systems. To achieve deep desulfurization using ionic liquids, a better understanding regarding the regeneration of ionic liquids is vitally important.

1. Introduction

Production of ultra-low-sulfur diesel (ULSD) has become a major task of refineries all over the world. The presence of sulfur compounds in diesel fuel has shown an adverse impact on the environment and hence it is getting ample attention from the media and scientific community.[1–2] It is because sulfur-bearing compounds are converted to SO_x during the combustion of car engines. This conversion not only results in acid rain, but also high contents of sulfuric oxides in exhaust fumes lowers the efficiency of catalytic converters in cars. Sulfuric oxides also poison catalysts in catalytic converters used for reducing CO and NO_x emissions and this severely affects environment.[3]

Therefore governments all over the world are implementing stringent standards for the production of ULSD from petrochemical industries. The EU legislation set the upper limit of sulfur content in diesel fuel to 10 ppm and in 2006 the US Environmental Protection Agency (EPA) reduced the limit for sulfur content of diesel fuel to 15 ppm.[4–5] It is also important

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to note that deep desulfurization is not only used for producing clean fuels to meet the new legislation standards, but also for producing sulfur-free hydrogen used in fuel-cell devices, in which the hydrogen can be produced potentially through reforming fuel oils. Fuel cell devices should run with zero sulfur content because sulfur can irreversibly poison the precious metal catalysts and electrodes used.[6,7]

The hydrodesulfurization (HDS) process has been used for the past several years to eliminate sulfur compounds for industrial purposes (Scheme 1). The HDS process uses Co–Mo/Al$_2$O$_3$, Ni–Mo/Al$_2$O$_3$ or Ni–W/Al$_2$O$_3$ catalysts for the conversion of organic sulfur to H$_2$S. The shortcomings of this method are: (i) it is operated at very high temperatures (300–400 °C) and pressures (20–100 atm of H$_2$), (ii) octane/cetane number is reduced due to hydrogenation side reactions, and (iii) it is efficient for the removal of thiols, sulfides and thiophenes, but less effective for removing refractory sulfur compounds such as benzothiophene, dibenzothiophene, and their alkyl derivatives.[8,9]
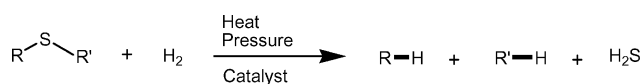
Scheme 1 Hydrodesulfurization (HDS) process used for removal of sulfur compounds.

Fig. 1 shows structures of the refractory sulfur compounds that are present in the petroleum streams. Total removal of such compounds is vital to meet the current stringent regulations. Their lower reactivity to the HDS process is mainly attributed to the steric hindrance. It has been estimated that removal of such compounds by the HDS process to the desired levels would demand improvement of the catalytic activity (300–400%), increase in process severity (50–100% increase in H$_2$ pressure), finding new catalyst combinations and synergies with non-catalytic processes and designing new reactor configurations.[10–11] This brings about a number of problems including high investment and operating cost, reduction of the catalyst cycle length, and an increase in consumption of hydrogen. Additionally, it is important to note that most easily accessible sweet (low sulfur) crude reservoirs have been tapped and increasing demand has led to extraction of lesser quality crudes (*e.g.* oil sands with 5% sulfur).[9]

For these reasons, alternate desulfurization processes are absolutely necessary for producing clean fuels. Possible strategies to realize deep desulfurization currently include oxidative desulfurization, bio-desulfurization, reactive adsorption, non-destructive adsorption, N-adsorption, extraction, and miscellaneous processes. In order to make the review comprehensive but to maintain the length, herein all such processes are summed up in short. A major emphasis is given to state-of-the-art desulfurization technologies using ionic liquids with comments on future challenges and outlook.

1.1 Oxidative processes

Sulfur removal by oxidative process aims to promote a reaction in the opposite direction to HDS, *i.e.* by forming oxidized sulfur species. Several oxidative desulfurization technologies exist. The general process consists of three parts: peroxide supply, sulfone generation and sulfone separation. The initial part comprises the peroxide storage and handling facilities. In the second phase, the fuel is mixed with the oxidant and catalyst and the oxidation of sulfur to sulfone occurs in this section. The oxidation reaction causes physical-chemical properties of the sulfur compounds to change significantly. This change helps in the final step of the process for the separation of oxidation products from the diesel stream. Sulfones are polar molecules so they are easily separated by way of adsorption on a solid adsorbent such as Al$_2$O$_3$ or by solvent extraction using extracting agents like acetonitrile.

Early attempts of oxidative desulfurization involved the use of nitric oxide/acid type oxidants like HNO$_3$ or NO/NO$_2$ gases.[12,13] However, in 1990, Tam *et al.* pointed that the approach involving nitric acids or nitric oxides leads to the formation of a relatively high amount of residues.[14] After the 1990s, the sulfur specification in diesel became very stringent, and reports started to appear in the scientific literature that use hydro peroxides like H$_2$O$_2$, TBHP with a catalyst or *in situ* produced per-acids (*e.g.*, H$_2$O$_2$ and formic acids) as an oxidant. These oxidants can efficiently convert organic sulfur to sulfones without forming a substantial amount of residual product (Scheme 2).
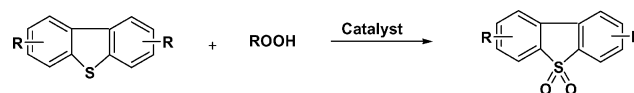
Scheme 2 A typical reaction showing oxidative desulfurization (ODS).

The advantages of the oxidative desulfurization process can be summarized as follows: it does not use hydrogen to produce ultra-low-sulfur diesel (ULSD), it requires mild operating
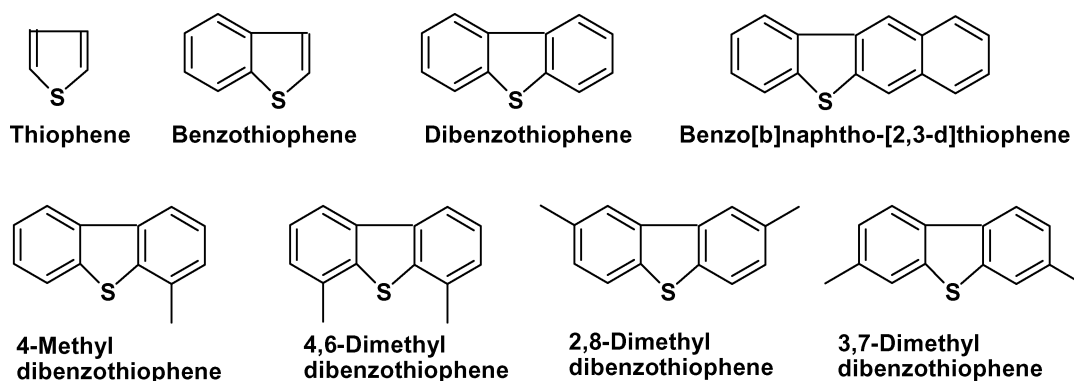
Fig. 1 Structures of refractory sulfur compounds.

conditions, it is complementary chemistry to hydrodesulfurization, and it uses conventional reaction and separation refinery equipment. However, the waste management of sulfone compounds and regeneration of extractant or adsorbent requires special attention.[15]

1.2 Bio-desulfurization

A 'green' approach is to use a biological system to do the oxidation chemistry of sulfur species. The reaction proceeds in the presence of water and oxygen at ambient temperature and pressure. Recent studies focus on organisms that use a sulfur-selective oxidative pathway to remove sulfur from organic sulfur compounds and are capable of desulfurizing dibenzothiophene (DBT) and sterically hindered DBT compounds.[16] A number of bacteria that use the sulfur-selective oxidative desulfurization pathway have been isolated.[17,18] This pathway involves a sequential oxidation of the sulfur moiety and cleavage of the carbon–sulfur bonds. This system consists of two monooxygenases, Dsz and DszC, which sequentially oxidize DBT to DBT sulfone and 2-hydroxybiphenyl-2-sulfinic acid. An NADH-flavin mononucleotide oxidoreductase (DszD) supplies the two monooxygenases with reduced flavin and a desulfinase (DszB) which converts 2-hydroxybiphenyl-2-sulfinic acid to the desulfurized end product 2-hydroxybiphenyl.[19,20] A schematic of biological oxidation of dibenzothiophene is shown in Scheme 3.
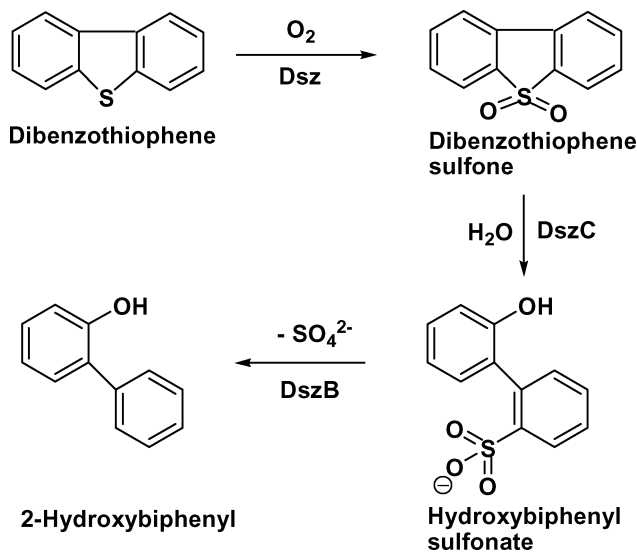
Scheme 3 Schematic of biological oxidation by bacteria.

The current literature suggests that bacteria converting dibenzothiophene and alkyl sulfides are well investigated, whereas fewer bacteria are found for benzothiophene, and furthermore only a few bacteria have been detected for thiophene. In general, the reports on bio-desulfurization do not show very deep desulfurization, down to 10–100 ppm of sulfur. It may be due to the higher bacterial activity in the higher concentration range.[13] In that sense, the probability of achieving 10 ppm sulfur level by biodesulfurization might be not so high. Another important feature to consider in the bio-system is the competitive reactions caused by other bacteria.

1.3 Reactive adsorption

Reactive adsorption using transition metals is another method to remove sulfur species. The adsorbent is supported on base oxides. They react with sulfur-containing molecules in the presence of hydrogen at temperature of 200–400 °C. Sulfur species are converted into hydrocarbons and H_2S, and H_2S is subsequently adsorbed by the sorbent component. The process in general involves two types of processes: a continuously regenerative adsorbent and the other fixed bed configuration. ConocoPhillip's S-Zorb work on diesel comes under the first class.[21] However some important issues would appear with this process such as the process requiring full evaporation of the diesel feed for a proper contact with moving catalyst particles and the reaction conditions appear to approach those of regular HDS. For fixed bed reactive adsorption, the work of Japanese oil/energy Company can be a good example.[22] Their focus was on stringent desulfurization of kerosene for fuel cell application. Types of adsorbents reported are ZnO promoted with transition metals like Ni or Cu. Similar to HDS, they apply hydrogen at mild conditions to convert sulfur species to H_2S, which is subsequently adsorbed by the ZnO support. Ni–ZnO is thought to remain working well because ZnO, through its fast uptake of H_2S, reduces the H_2S partial pressure to such low levels that part of the Ni remains unsulfided, thus still acting as catalytic desulfurization sites, as illustrated in Fig. 2. After completion of the ZnO to ZnS conversion, the adsorbent can be regenerated. This is a simpler process compared to the continuously regenerative adsorbent, but it will require already low-S feeds, to ensure sufficient on-stream times, and it may suffer from the same reactivity limitations.
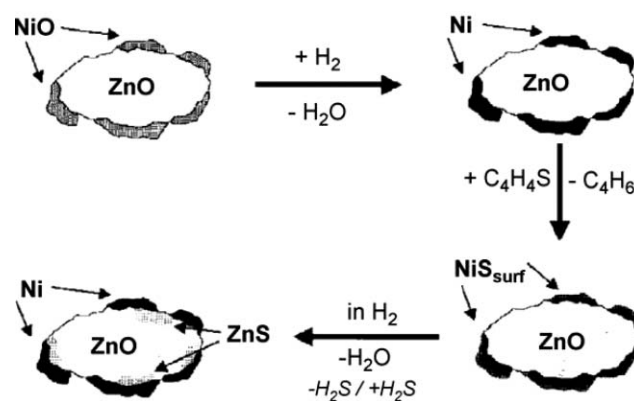

Fig. 2 Schematic illustration of reactive adsorption (adapted from reference 15).

A major challenge for separating sulfur compounds from fuels is to find an adsorbent that selectively adsorbs the sulfur compounds, but does not adsorb (or only weakly adsorb) the co-existing aromatic hydrocarbons and olefins. This is because the thiophenic sulfur compounds and pure aromatic and olefinic compounds have some common features due to the presence of one or more double bonds to which metal species can interact.[23]

1.4 Non-destructive adsorption

Here the sulfur molecules are adsorbed as such without conversion. Song *et al.* in their patented investigation employed mild

adsorption conditions (*e.g.*, 80 °C) for the selective removal of sulfur.[24] They worked on the desulfurization of kerosene for producing a fuel cell grade fuel and used several types of adsorbents, *i.e.* transition metal chlorides on support, activated Ni adsorbent (*e.g.*, Ni–SiO$_2$), metal ions in zeolite (*e.g.*, CeY, Ni–Y), NiAl layered double hydroxides, NiZnAl layered double hydroxides, Ni/SiO$_2$/Al$_2$O$_3$ and even HDS catalyst like sulfided CoMo/alumina. In a recent article, they reviewed the interesting differences in the adsorption selectivity between different adsorbents.[25] The same group has reported an interesting approach to remove refractory sulfur species, *viz*. applying high surface-area active carbon containing a high amount of oxygen atoms. Such a carbon seems to be selective in removing the more refractory sulfur species.[26]

The largest issue of this approach is still a low uptake capacity of sulfur. Another important issue in the adsorption approach is the waste treatment of organic sulfur molecules released at the end of the process.

1.5 N adsorption

The N adsorption is coupled with the HDS process. As basic N-compounds like quinolines and acridines strongly inhibit the HDS reaction, the denitrogenation of refinery streams is also of interest.[27] The SK Corporation in South Korea claims that they can remove nitrogen compounds very efficiently by which the production of 10 ppm sulfur diesel becomes relatively easy with HDS.[28] Macaud *et al.* reported the use of tetranitrofluorenone (TENF) on polymer (*e.g.*, polystyrene) as an efficient adsorbent for removing nitrogen compounds.[29] However, in this type of adsorption, it is important to know how deeply the adsorbent needs to denitrogenize the feed in order to make the production of <10 ppm sulfur effluent in the subsequent process of HDS that much easier. Another problem is with the spent, N-loaded, adsorbent, which seriously complicates matters. Further obstacles are that if [N] becomes very low, the HDS catalyst might start to deeply hydrogenate the feed, which is often undesirable because of the consequent high hydrogen consumption.[30]

1.6 Extraction

Extraction of organic sulfur compounds from diesel fuel by extractants such as acetonitrile, pyrrolidones, DMF and DMSO is another method of desulfurization. However, it is observed that selective extraction of aromatic sulfur compounds from diesel is not simple, owing to the similar polarity of aromatic sulfur and aromatic hydrocarbon molecules. The experimental findings on extraction indeed demonstrate a poor removal of sulfur compounds from the feed (~50% at most) with a high amount of co-extraction of aromatic hydrocarbon molecules, leading to a major loss in feed volume.

A better approach to effectively remove sulfur in extraction is to first oxidize sulfur compounds prior to extraction, due to which the polarity of sulfur compounds becomes substantially higher, and thus the partition coefficient of the sulfur molecules in the polar solvent is much increased. In 1990, Tam and co-workers have reported that oxidation prior to extraction leads to an increased sulfur removal with better volume retention of

the hydrocarbon feed.[14] The extent of co-extraction of the feed is, however, still regarded as high (*e.g.*, 10–20%).

1.7 Membranes

Fuel oil desulfurization by membrane process is a newly emerging technology, which may offer a number of potential advantages over conventional sulfur removal processes.[31] One such example is the desulfurization using pervaporation (PV) process. Pervaporation compared to traditional separation technology such as distillation, molecular sieves or extraction has many advantages: (i) high separation efficiency, (ii) low energy consumption, (iii) simple operation and so on.[32] With the aim for higher sulfur enrichment factor at constant flux or both, the research for development of new membrane materials and modification of present membrane materials is under way. For example, Lin *et al.* improved the PEG membrane performance by cross-linking modification successfully.[33–35] Their PV experimental results showed that the sulfur enrichment factor and flux of cross-linked PEG membranes come to 3.05 and 1.63 kg m^{-2} h for typical FCC (fluid catalytic cracked) gasoline feed with sulfur content of 1227 μg g^{-1}. Similarly, Qi *et al.* prepared cross-linking PDMS (polydimethylsiloxane) with cross-linking agent ethyl orthosilicate and catalyst dibutyltin dilaurate to remove thiophene from hydrocarbon.[36,37] The current research using membranes is in its infancy and is mainly focused on the process introduction, technology scale-up, membrane materials, optimization of operating parameters, *etc.* Therefore, it is difficult to predict its future role.

1.8 Miscellaneous

Alternative approaches have also been proposed for the removal of sulfur from fuel. An attempt has been made to precipitate the sulfur compounds by adding a chemical agent, TENF (2,4,5,7-tetranitrofluorenone). TENF forms an insoluble charge transfer complexes when reacting with sulfur compounds.[38] However, the desulfurization ratio is very low (12%) and the complexation efficiency is not high. Shiraishi *et al.* reported the use of Chloramine T (sodium *N*-chloro-*p*-toluenesulfonamide) for reacting aromatic sulfur species in diesel.[39] The sulfur species reacts with Chloramine T (sodium *N*-chloro-*p*-toluenesulfonamide) to produce *N*-tosylsulfimides (RS N-Ts) in the presence of methanol, which can be precipitated when water is added to the methanol phase. A drawback of the precipitation method is a side reaction of chlorination of aromatics and the consumption of expensive chemicals and the treatment of organic sulfur waste. In some cases, application of an energy source in the form of microwaves or X-rays is also reported along with the catalyst to decompose sulfur compounds. However, the process economy and practicality of this method could be important issues.

2. Removal of sulfur compounds by extractive processes using ionic liquids

Successful accomplishment of ULSD at ambient temperature and pressure and without the need for hydrogen is a difficult task to perform considering the present need and status of the crude oil reserves. The works (2001 onward) on deep desulfurization using ionic liquids (ILs) have shown that the ILs have the

potential to play a major role in achieving ULSD. They have several advantages over polar organic solvents, such as that they can be used over a wider temperature range and are compatible with oxidizing and reducing agents. More general advantages are that ILs have no measurable vapor pressure, they are thermally stable, and they tolerate moisture.[40] The first attempt of deep desulfurization using ILs was made by the groups of Wasserscheid and Jess in 2001, which was followed by several publications and patents on this topic.[41,42] The following sections describe, in detail, the current status of deep desulfurization of diesel fuel using ILs.

2.1 Imidazolium-based ionic liquids

Firstly, S. Zhang and C. Zhang used imidazolium ILs, such as 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM$^+$BF$_4^-$), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM$^+$PF$_6^-$) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM$^+$BF$_4^-$) for selective removal of sulfur-containing compounds from transportation fuels at room temperature.[43] They found that structure and size of the cation and anion of an IL can affect the absorption process. For most model aromatic compounds selected, the ILs BMIM$^+$PF$_6^-$ and BMIM$^+$BF$_4^-$ have shown higher absorption capacities than EMIM$^+$BF$_4^-$. Further observation reveals that absorption is favored for molecules with a higher density of aromatic π electrons. For example, thiophene with a five-membered ring had a stronger interaction with the ILs than the nonaromatic isobutylthiol. They also treated ILs with actual fuel and found about 30 wt% of sulfur was preferentially removed with little change in the content of the aromatics.

Recently, dibenzothiophene (DBT) was extracted from a model diesel fuel at room temperature using six types of halogen-free ILs: l-butyl-3-ethylimidazolium ethyl sulfate (BEIMEt$^+$SO$_4^-$), l-ethyl-3-ethylimidazolium ethyl sulfate, (EEIMEt$^+$SO$_4^-$), l-ethyl-3-methylimidazolium ethyl sulfate (EMIMET$^+$SO$_4^-$), l-ethyl-3-methylimidazolium methyl sulfate (EMIMMe$^+$SO$_4^-$), l-butyl-3-methylimidazolium methyl sulfate (BMIMMe$^+$SO$_4^-$), and 1,3-dimethylimidazolium methyl sulfate (MMIMMe$^+$SO$_4^-$).[44] A linear increase in the extraction yield of DBT was observed with an increase in the length of alkyl chains, i.e. IL BEIMEt$^+$SO$_4^-$ having the longest alkyl chain, showed the highest extraction yield. They also reported a good selectivity for DBT over diphenylsulfide and diphenyldisulfide. With further studies on the effect of co-solvent, they noticed that a change in the type of solvent did not make an appreciable difference, and DBT was efficiently removed regardless of whether tetralin, benzene, or n-dodecane was used as the solvent. They also mentioned that an increase in mass ratio of the IL to the model fuel (1.0) increased the extraction yield up to 70% after one round of extraction. After five rounds of extraction the sulfur content could be decreased considerably, for example, from 1000 to 350 ppm.

Alonso and co-workers used the IL 1-methyl-3-octylimidazolium tetrafluoroborate (C8MIM$^+$BF$_4^-$) for the extraction of thiophene and dibenzothiophene from model fuel and observed nearly 80% extraction in three stages.[45,46] A combination of imidazolium cation and alkylphosphate anion was also used for the extractive desulfurization using

model fuel.[47–49] Reference 50 gives an overview on the extractive desulfurization using different neutral types of ILs, particularly on the most promising water-stable and less costly 1-n-butyl-3-methylimidazolium octylsulfate (BMIM$^+$OcSO$_4^-$) and 1-ethyl-3-methyl-imidazolium ethylsulfate (EMIM$^+$EtSO$_4^-$) type. A poor extraction of alkylthiols and sulfides was reported compared to thiophene and benzothiophene and hence the formation of π–π interaction was assumed to be the main driving force for extraction. Interestingly, they indicated that extraction of 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) proceeded almost as efficiently as that of DBT. Moreover, nitrogen compounds are also found to be efficiently extracted. However, the problems of extraction using ILs are the limited extraction efficiency of sulfur compounds and cross-solubility of hydrocarbons. With respect to the extraction efficiency, the same group has, for instance, proposed a 10 step extraction to reduce sulfur content from 300 toward <10 ppm.[51]

2.2 Pyridinium-based ionic liquids

The solubility of the IL in the fuel is an important factor to consider in choosing an extractant, because the variation of diesel composition and quality can be influenced by the cross-solubility of the ILs and diesel. Solubility of ILs in diesel can contaminate the fuel and further lead to a NO$_x$ pollution, as well as increase the cost of recycling ILs. Gao and co-workers explored a new class of pyridinium ILs for the extraction of sulfur compounds.[52] They observed that pyridinium-based ILs, viz. N-butylpyridinium tetrafluoroborate (BPy$^+$BF$_4^-$), N-hexylpyridinium tetrafluoroborate (HPy$^+$BF$_4^-$), and N-octylpyridinium tetrafluoroborate (OPy$^+$BF$_4^-$) have negligible solubility in the fuel. By analyzing the IL-saturated diesel sample using HPLC, they did not find any IL peak. On the other hand, diesel has a certain solubility in pyridinium-based ILs (0.5 wt%). The group further studied selective removal of aromatic heterocyclic sulfur compounds from a model diesel fuel at room temperature. Their results suggest that the structure and size of the cation greatly affect the extractive performance of ILs. The extractive performance using pyridinium-based ILs followed the order (BPy$^+$BF$_4^-$) < (HPy$^+$BF$_4^-$) < (OPy$^+$BF$_4^-$) and for the ILs the sulfur removal selectivity of sulfur compounds followed the order thiophene < benzothiophene < dibenzothiophene under the same conditions. These results indicate that extraction is favored for those aromatic heterocyclic sulfur compounds having higher density aromatic π-electrons. A possible π–π interaction between aromatic sulfur compounds and the pyridinium rings of ILs was suggested as extraction mechanism. The effects of cation and anion sizes on the interaction of absorbed thiophene and ILs have been also confirmed by Su et al.[53] Molecules with highly polarizable π-electron density preferably insert into the molecular structure of the ILs. Holbrey et al. indicated formation of liquid-clathrate due to the interaction between the ILs and aromatics through π–π interaction.[54]

Holbrey and co-workers also studied extraction of DBT from dodecane using ILs with varying cation classes (imidazolium, pyridinium, pyrrolidinium, and quinolinium) and with a range of anions.[55] Partition ratios for DBT to ILs ranged from 0.8 to 9, and showed clear variation with cation class. They

ranked extraction performance by cation: methylpyridinium ≥ pyridinium ≈ imidazolium ≈ pyrrolidinium and also observed that ILs with ethanoate and thiocyanate anions gave the best extraction performance with each cation. These two anions with the pyridinium cations showed highest extraction performance with 81–83% of the DBT removed in one contact.

2.3 Lewis and Brønsted acidic ionic liquids or redox ionic liquids

Overall efficiency of sulfur removal with neutral ILs was very low, so focus was shifted in using acidic or task specific ILs.[41,56] Wasserscheid et al., in their first set of experiments, investigated desulfurization of model diesel oil by dissolving 500 ppm DBT in n-dodecane.[41] Based on the initial idea to extract sulfur compounds by chemical interaction, they studied the extraction process using Lewis and Brønsted-acidic ILs. As Lewis-acidic ILs, an acidic mixture of 1-n-butyl-3-methylimidazolium (BMIM$^+$Cl$^-$) with AlCl$_3$ (molar ratio [cation]Cl/AlCl$_3$ = 0.35/0.65) and a 1:1 (mol/mol) mixture of two trialkylammonium methanesulfonate salts (HN(C$_6$H$_{11}$)Et$_2$$^+CH_3SO_3$$^-$ and HNBu$_3$$^+CH_3SO_3$$^-$) was tested as Brønsted-acidic IL. A neutral IL, 1-n-butyl-3-methylimidazolium octylsulfate (BMIM$^+$octylsulfate$^-$), was used for comparison. All ILs formed a biphasic system with model oil at room temperature. They also tested these ILs with 'real' predesulfurized diesel oil (without additives, sulfur content 375 ppm) and have observed that the Lewis-acidic IL, BMIM$^+$Cl/AlCl$_3$ showed much higher efficiency in sulfur extraction from real diesel in comparison to Brønsted-acidic and neutral IL. This indicates that Lewis acid–base interactions enhance the extraction power of the IL here. However, it is reported that more extraction steps are necessary in the case of 'real' diesel oil to reach future technical sulfur content specifications (<10 ppm).

Fe^3-containing ILs or redox ILs, prepared from the reaction of anhydrous FeCl$_3$ and 3-butyl-1-methyl-imidazolium chloride (BMIM$^+$Cl$^-$), were used as effective extractants for desulfurization of a model oil containing DBT.[57] The amount of DBT extracted increased with an increasing molar ratio of FeCl$_3$/BMIM$^+$Cl$^-$ and was completely extracted from model oil at FeCl$_3$/BMIM$^+$Cl$^-$ molar ratios of 2 and higher. These results can be attributed to increased Lewis-acidity of the resulting IL at higher molar ratios of FeCl$_3$/BMIM$^+$Cl$^-$.[58] However, FeCl$_3$ and BMIM$^+$Cl$^-$ alone exhibited lower extraction ability than Fe-containing ILs, suggesting the importance of mixture. For comparison, the performances of Fe-containing ILs were tested with the ILs prepared from BMIM$^+$Cl$^-$ and CuCl or AlCl$_3$ (CuCl/BMIM$^+$Cl$^-$, and AlCl$_3$/BMIM$^+$Cl$^-$). The results showed that the extraction abilities of these ILs were significantly lower than that of the corresponding FeCl$_3$-based IL (FeCl$_3$/BMIM$^+$Cl$^-$) which was attributed to the high affinity of FeCl$_3$ to DBT. The authors further applied these Fe-containing ILs (FeCl$_3$/BMIM$^+$Cl$^-$) to the desulfurization of commercial diesel oil containing sulfur content of 1180 ppm and reported complete removal of sulfur compounds.[57]

Superiority of the Lewis acidic ILs over neutral ILs can be also confirmed by the observations of Gao and co-workers.[59] They performed multistage desulfurization (three times) of model

diesel oil (dibenzothiophene, 160 ppm) using ILs, BMIM$^+$PF$_6$$^-$, BMIM$^+BF_4$$^-$, and BMIM$^+$FeCl$_4$$^-$, and observed a decrease in sulfur content from 160 ppm to 89.1, 82.9, 27.3 ppm, respectively. It was suggested that Lewis acid–base interaction and Fe^{3+} can form π-complexation bonding with aromatic sulfur compound and thus enhances the extraction of sulfur species.

3. Removal of sulfur compounds by oxidative processes using ionic liquids

Although ILs have numerous advantages over conventional solvents, the Nernst partition coefficient favors extraction of most aromatic components of the fuel oil and this can be a limitation of the extractive method.[60] Hence the efficiency of sulfur removal using various kinds of ILs as an extractant is low. Moreover some problems in the regeneration of the Lewis-acidic IL TMAC-AlCl$_3$ and BMIM-AlCl$_4$ were also reported.[61,62] Therefore, researchers turned towards addition of an oxidant in the IL to achieve better efficiency and enhancement in the selectivity.[63–65]

3.1 Chemical oxidation

The first example of a combination of chemical oxidation and solvent extraction using ILs for deep desulfurization was reported by Lo et al.[66] In the one pot operation, both an environmentally benign oxidation system (H$_2$O$_2$ and AcOH) and extraction solvent (ILs) were employed. Tetradecane doped with DBT was used as model light oil for the investigation of sulfur removal. The ILs, BMIM$^+$PF$_6$$^-$ and BMIM$^+$BF$_4$$^-$, which are immiscible with light oils, were selected as solvents for the liquid–liquid extraction system. DBT was extracted from the model light oils and oxidized in the ionic-liquid phase, as is shown in Fig. 3. In this process, IL is not only acting as an extractant but also as the catalyst. One of its catalytic roles is to decompose hydrogen peroxide to form hydroxyl radicals. Cooper et al.[67] observed that a coordination compound could be generated between hydrogen peroxide and an amide, such as urea; then the hydrogen peroxide on the coordination compound decomposes to produce hydroxyl radicals that are strong oxidizing agents. Likewise in the present case, DBT in the IL phase was oxidized to sulfone by hydroxyl radicals. Fig. 3 shows that sulfone does not exist in the oil phase because of the high polarity of IL. DBT sulfone was detected in the IL phase. Within 6 h of
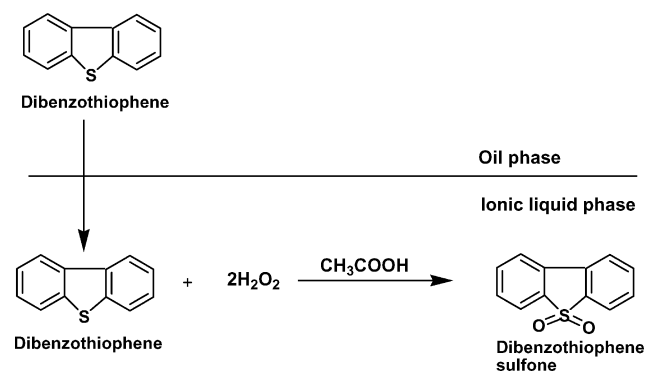

Fig. 3 Oxidation of DBT using H$_2$O$_2$ and AcOH in an oil–ionic liquid system.

oxidation the DBT content had decreased from 758 to 7.8 ppm, indicating 99% extraction of DBT from the model light oil while mere extraction of DBT using IL BMIM$^+$PF$_6^-$ has shown only 47% extraction. These experimental findings demonstrate that a combination of chemical oxidation and solvent extraction in a water-immiscible IL has the potential to completely remove sulfur compounds from light oil in one step. The authors also applied this oxidation/extraction system to actual light oil containing a sulfur content of 8040 ppm. After 10 h, in the BMIM$^+$PF$_6^-$ extraction/oxidation system, the decrease of sulfur content was observed from 8040 to 1300 ppm.

Zhao and coworkers employed Brønsted-acidic and quaternary ammonium coordinated ILs along with the benign oxidant H$_2$O$_2$ and investigated sulfur removal from model and actual fuels.[68–72] While using N-methylpyrrolidonium tetrafluoroborate (Hnmp$^+$BF$_4^-$) as an extractant and catalyst for oxidative desulfurization of model oil containing DBT in n-octane in presence of H$_2$O$_2$, they observed Nernst partition coefficient of 0.64 mg(S) kg(IL)$^{-1}$/mg(S) kg(oil)$^{-1}$. It is reported that the O (oxidant)/S (sulfur) mole ratio has a strong influence on the reaction rate. The conversion of DBT increased from 91.3% at O/S = 2 to 100% at O/S = 3 in 60 min. Further, the reaction rate was found to increase with increasing temperature. The IL Hnmp$^+$BF$_4^-$ can be recycled 7 times without decrease in activity of desulfurization. Their results with the actual diesel fuel reveal that 99.4% sulfur-containing compounds which are present in the actual diesel fuel can be removed. In a similar fashion, Lu and co-workers employed IL HMIM$^+$BF$_4^-$ as an extractant and catalyst along with H$_2$O$_2$ and reported that sulfur removal decreases in the order dibenzothiophene > benzothiophene > thiophene in the temperature range of 70 to 90 °C.[73]

Very recently oxidative desulfurization using task-specific ionic liquids was studied.[74] These ILs are reported to be less viscous containing N-bis(trifluoromethanesulfonyl) imidate anion with the alkoxy or carboxylate group attached to the imidazolium cation moiety. The extraction experiments were performed on a model fuel mixture, consisting of an n-octane (1.0 g) solution containing 1000 ppm of S derived from dibenzothiophene, using 1 mL of the IL in the presence of H$_2$O$_2$. It is observed that the oxidative desulfurization and extraction abilities of the DBT by task-specific ILs increase with temperature up to 75 °C (<10 ppm in 1 h). Above this temperature, the oxidation/extraction process is less effective due to the extended decomposition of the H$_2$O$_2$ in IL. The carboxylic group attached to the imidazolium ring is found to increase both the solubility of H$_2$O$_2$ and DBT in the ionic phase and increases the oxidation stability and power of the peroxide, possibly due to the formation of a peracetic acid-like intermediate. Significantly, it is found that the reaction is sensitive to the electron-rich sulfur compound moieties (i.e., it is much more effective for electron-rich DBT than for thiophene) and the order of reactivity in the oxidation/extraction process with task-specific carboxylate IL (dibenzothiophene > benzothiophene > 2,5-dimethylthiophene > thiophene) is the opposite of that observed in the catalytic HDS process, in which the more sterically demanding substrates are reluctant to undergo the reduction reaction. The performance of the system when tested with the real diesel sample up to 80% reduction in the S-containing compounds was observed.

An ammonium type IL, Me$_3$NCH$_2$C$_6$H$_5$Cl·xZnCl$_2$ (BTMAC$^+$·xZnCl$_2^-$, x = 1–3) prepared from cheap starting materials of Me$_3$NCH$_2$C$_6$H$_5$Cl and ZnCl$_2$ and used as an extractant in oxidative desulfurization of DBT at room temperature.[75] In the presence of H$_2$O$_2$ and AcOH, DBT was extracted from oil phase and oxidized to its corresponding sulfone. It was observed that the IL BTMAC$^+$2ZnCl$_2^-$ is stable to moisture and exhibits remarkable extraction desulfurization for DBT in n-octane. The desulfurization yield of DBT can reach 94% at 30 min and 99% at 50 min. This was attributed to the π-complexing interaction of DBT and Zn(II). Their further observation reveals that the extraction ability increases with the increase of Lewis-acidity and the decrease of viscosity of IL. The kinetics of oxidative desulfurization of DBT by H$_2$O$_2$ and AcOH was found to be of first-order with an apparent rate constant of 0.0842 min^{-1} and half-time of 8.23 min.

A systematic comparison between the extractive and oxidative desulfurization methods using redox ILs based on FeCl$_3$ was made by Li et al.[76] The group studied removal of DBT, benzothiophene (BT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) from a model oil. The sulfur removal from the DBT-containing model oil in BMIMCl/FeCl$_3$ could reach 99.2% at 30 °C in 10 min while only 66% of DBT was reported to be removed using extractive desulfurization. The S-removal through the oxidative desulfurization process decreased in the order DBT > 4,6-DMDBT > BT. The authors reported a Fenton-like chemistry mechanism, as Fe^{3+} exists in the presence of H$_2$O$_2$ and believed that Fe^{3+} hydroperoxo intermediate is formed via hydrolysis, as shown in eqn (1).

$$Fe^{3+} + H_2O_2 \rightarrow [Fe^{III}OOH]^{2+} + H^+ \qquad (1)$$

This intermediate might be able to react with organic substrates or break up into smaller active species and produces reactive OOH$^•$ or OH$^•$ radicals, which are strong oxidizing agents. Later, the oxidizing agent attacks the sulfur-bearing species thereby causing deep desulfurization.

3.2 Catalytic oxidation

In the previous section, we have shown that desulfurization using oxidizing agent is far more effective than mere extraction with IL. More than 95% of sulfur removal could be achieved using a chemically oxidizing method, in one step. The application of catalysts in selective oxidation with peroxides may offer an efficient procedure that could be compatible with different functional groups and leads to good yields and selectivities. Further, as a new desulfurization process, there is still much room for the development of more efficient oxidative methods from both industrial and green chemistry perspectives.[77–78] The group of Li and co-workers proposed to use peroxotungsten and peroxomolybdenum complexes such as [WO(O2)$_2$·Phen·H$_2$O] and [MoO(O2)$_2$·Phen] (Phen = 1,10-phenanthroline) as catalyst.[79] In their preliminary work, they immobilized such catalysts in ILs, 1-butyl-3-methylimidazolium tetrafluoroborate (Bmim$^+$BF$_4^-$), 1-n-octyl-3-methylimidazolium tetrafluoroborate (Omim$^+$BF$_4^-$), 1-butyl-3-methyl-imidazolium hexafluorophosphate (Bmim$^+$PF$_6^-$), and 1-n-octyl-3-methylimidazolium hexafluorophosphate (Omim$^+$PF$_6^-$) for extraction and catalytic oxidation of DBT containing model fuel. Their results with

the model oil demonstrates that when only IL was used as an extractant about 12.2–22.0% and after the addition of 30 wt % H_2O_2 in IL, about 30.0–63.0% sulfur removal was obtained *via* chemical oxidation. While H_2O_2 and catalyst were introduced together, the removal of sulfur increased sharply. In the case of the system containing H_2O_2 (O/S = 10/1), catalyst $[WO(O2)_2 \cdot Phen \cdot H_2O]$ and IL, Bmim$^+$BF$_4^-$, extraction and catalytic oxidation increased the sulfur removal to 98.6% at 70 °C for 3 h. However, the oxidative desulfurization systems containing $[WO(O2)_2 \cdot Phen \cdot H_2O]$ and H_2O_2 only led to 50.3% sulfur removal in the absence of IL. In a parallel investigation using a series of peroxyphosphomolybdates and decatungstates for the removal of DBT, 4,6-DMDBT and BT from model oil, they found the catalysts having short alkyl chains have higher catalytic activity than the longer alkyl chains.[80,81]

Owing to the high consumption of H_2O_2 (O/S = 10/1) and complicated synthesis of catalyst, in their further work, they used commercially available molybdic compounds such as $Na_2MoO_4 \cdot 2H_2O$, H_2MoO_4, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $H_3PMo_{12}O_{40} \cdot 13H_2O$, $(NH_4)_3PMo_{12}O_{40} \cdot 7H_2O$ and $Na_3PMo_{12}O_{40} \cdot 7H_2O$ as catalysts.[82] The precatalyst of a molybdic compound was oxidized with H_2O_2 to form a peroxomolybdic compound, which was soluble in IL and dissolved in oil. The sulfur-containing compounds, such as BT, DBT and 4,6-DMDBT in model oil were extracted into the IL phase and oxidized to their corresponding sulfones by peroxomolybdic compound. In a typical experiment containing model oil DBT, H_2O_2, $Na_2MoO_4 \cdot 2H_2O$ and IL, Bmim$^+$BF$_4^-$, extraction and catalytic oxidation increased the sulfur removal to 99.0% at 70 °C for 3 h. The desulfurization system could be recycled five times with very little decrease in activity.

In their extended work with another commercially available catalyst, $H_3PW_{12}O_{40} \cdot 14H_2O$, they combined the catalyst with H_2O_2 and IL Bmim$^+$BF$_4^-$ and achieved 98.2% removal of DBT from model oil at 30 °C for 1 h.[83] Further completely removed DBT, 4,6-DMDBT, and BT at 70 °C in 3 h. These experiments demonstrate that a combination of catalytic oxidation and extraction in IL can deeply remove DBT from oil. The results also highlight a remarkable advantage of this process over the desulfurization by mere solvent extraction with IL or catalytic oxidation without IL.

4. Regeneration of ionic liquids

Successful regeneration and subsequent recycling of IL after the extraction of S-compounds is of vital importance from industrial point of view. The method may vary with type of IL used and efficiency of extraction. Several options were explored for the regeneration of S-loaded IL. S. Zhang and C. Zhang performed regeneration of hydrophobic IL BMIM$^+$PF$_6^-$ by direct distillation after saturated absorption of thiophene.[43] They reported that the IL can be fully regenerated after heating at 110 °C for 3 h under nitrogen and the absorbed thiophene recovered from distillation corresponds to the amount absorbed. For the hydrophilic IL EMIM$^+$BF$_4^-$ the absorbed thiophene was released into a separated phase upon addition of water. Water was further vaporized from the IL phase under a nitrogen flow at 110 °C for about 3 h and the IL EMIM$^+$BF$_4^-$ was nearly quantitatively recovered. NMR analyses indicated that the

ILs, BMIM$^+$PF$_6^-$ and EMIM$^+$BF$_4^-$, maintained their original structures after the regeneration.[43] Very recently, Seeberger and Jess also reported on the efficient regeneration of IL by the addition of water (50 mass%) in the IL/water mixture. They noticed a complete displacement of the sulfur species, thereby forming S-free IL/water–mixture and S-rich oil phase. Further, water separation by evaporation was performed before the IL can be re-used for extraction.[84]

However, the regeneration of S-loaded ILs from real diesel oil extraction was observed to be difficult owing to the higher boiling point of DBT or alkylated DBTs (200 °C). Only about 20% of these S-compounds could be removed from a S-loaded IL (model system: 500 ppm S as DBT in IL, BMIM$^+$OcSO$_4^-$) by stripping with air at 120 °C for about three days. Therefore additional re-extraction step was used, followed by distillation separation of the re-extraction medium and the high boiling sulfur compounds. The most promising re-extraction mediums are low boiling hydrocarbons like pentane or hexane. As these solvents can be easily recovered and separated from the higher boiling sulfur compounds by evaporation. The organic sulfur would then be converted into elemental sulfur by the common Claus-process. The group of Wassercheid and Jess studied the influence of the hydrocarbon used as re-extraction agent on the partition coefficient of DBT and observed short chain hydrocarbons are suitable for IL-regeneration by re-extraction.[41,51]

After the chemical oxidation of sulfur compounds, Lo and co-workers examined the possibility of recycling the ILs. At the end of each run they washed with water the oxidation products and extracted substrates of the ILs. Then the IL phase was filtered to remove the precipitates, the volatiles were evaporated, and the residue extracted with diethyl ether. The ^{1}H NMR spectroscopy confirmed that the purity of IL, BMIM$^+$PF$_6^-$ and BMIM$^+$BF$_4^-$, was retained. After the reaction, the IL phase was recycled and used as the catalyst and extractant for the next reaction. So the system was re-charged with the oxidizing agent (H_2O_2 and AcOH) and the same desulfurization yields were observed for four cycles of operation.[66] For the chemical oxidation using Brønsted-acidic IL, Zhao *et al.* reported that the IL can be recycled 7 times without a significant decrease in activity.[68]

An alternative process for the recycling of ILs involves application of supercritical carbon dioxide, scCO$_2$. Although the solvating power of scCO$_2$ is generally lower compared with organic solvents, extraction with scCO$_2$ has significance to separation of sulfur compounds from ILs. On decompression of the fluid solution in scCO$_2$, the solvating power of the expanding CO$_2$ decreases rapidly, and the dissolved sulfur compounds and co-extracted hydrocarbons nucleate and can be separated from CO$_2$. The design and feasibility assessment of super-critical re-extraction requires the partition coefficient values of sulfur compounds between ILs and scCO$_2$. Planeta *et al.* used open tubular capillary-column chromatography to measure the partition coefficients of several sulfur compounds between 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM$^+$Tf$_2$N$^-$) and scCO$_2$, with HMIM$^+$Tf$_2$N$^-$ serving as the stationary liquid and scCO$_2$ as the mobile phase (carrier fluid). They observed a gradual decrease of the amount of HMIM$^+$Tf$_2$N$^-$ in the column during the retention measure-ments. The probable reason for the decrease was a higher

solubility of HMIM$^+$Tf$_2$N$^-$ in scCO$_2$. Their results indicate that, for the re-extraction of sulfur compounds from IL with scCO$_2$ to be feasible, competitive in a large-scale process an IL would have to be found with significantly (~10 times) higher values of partition coefficients. They summarized that the role of cohesive energy density of the IL and thermal effects associated with expansion and compression of scCO$_2$ may present a hindrance to a large-scale re-extraction of sulfur compounds from ILs with scCO$_2$.[85]

5. Challenges and outlook

This review focuses on the new approaches for the deep desulfurization of diesel oil, especially with regard to those sulfur compounds that are very difficult to remove by common hydrodesulfurization techniques. Traces of such sulfur compounds could easily be removed using ILs as catalyst and extractants. The application of very mild process conditions (low pressure and temperature) is an additional advantage of this new approach in comparison to the traditional HDS. The co-miscibility of the ILs and feeds, selectivity and specificity of the extracting phase for polyaromatic sulfur compounds over hydrocarbons and polyaromatic hydrocarbons require special attention.

In the extractive process, the ILs EMIM$^+$BF$_4^-$, BMIM$^+$PF$_6^-$ and BMIM$^+$BF$_4^-$ showed remarkable selectivity for the absorption of aromatic S-containing molecules from the model fuel. The preferential absorption of thiophene and dibenzothiophene over other aromatic hydrocarbons suggests that compounds with higher aromatic π-electron density in C5 rings are favorably absorbed. The cation and anion structure and size in the ionic liquids are important parameters affecting the absorption capacity for aromatic compounds. These ILs are moisture insensitive at low temperature, thermally stable under the distillation conditions, and readily regenerated for reuse after the distillation. The absorbed aromatic S-containing compounds were quantitatively recovered during the regeneration. However, it requires several extraction stages to completely remove the sulfur compounds.

Very recently a new approach for the desulfurization was proposed by using supported ionic liquid phase (SILP) materials and a comparison of extraction was made between biphasic and SILP phase. The SILP materials were prepared by dispersing the ionic liquid as a thin film on highly porous silica, which exhibited a significantly higher extraction performance owing to their larger surface areas, reducing the sulfur content to less than 100 ppm in one stage. Multistage extraction with these SILP materials reduced the sulfur level to 50 ppm in the second stage. The SILP technology offers very efficient utilization of ionic liquids and circumvents mass transport limitations. However, leaching of the small quantity of ionic liquid from the support should be avoided and hence clever engineering of the ionic liquid loading and solid support is required.[86]

It was observed that Lewis-acidic ILs, for example FeCl$_3$/BMIM$^+$Cl$^-$, can play a major role in the desulfurization process. They may bring down the sulfur content to the levels of prescribed standards. However, chlorine plays a major role in the most pressing environmental problems which we face today; depletion of the ozone layer, global warming and acid rain. The pollution caused by its widespread use has been linked to a variety of serious health effects; poisonings have occurred in the chlorine industry since its inception and chlorine compounds have accumulated in the body fat of animals and humans. Therefore an equally competent, organo Cl-free ILs is particularly promising as the use of Cl in desulfurization is probably unlikely to be accepted by refiners.

The Brønsted IL Hnmp$^+$BF$_4^-$ can be used as a catalyst and extractant for the oxidative desulfurization of diesel fuel and has shown that DBT in n-octane can be effectively removed with an IL–H$_2$O$_2$ system. The extraction of real diesel oil is much more complicated due to its complex chemical composition, including many different sulfur compounds and other impurities like organic nitrogen and oxygen compounds. Nevertheless, the results of experiments with real predesulfurized diesel oils are also promising although more extraction steps are necessary in the case of "real" diesel oil to reach future technical sulfur content specifications. However, some sulfones that have alkyl substituents, such as 4,6-DBTO2, can not be extracted by the IL completely because of steric hindrance. Hence, much more data are still needed with respect to the extraction of S-compounds from "real" diesel oils.

The use of commercially available molybdenum catalysts to oxidize sulfur compounds with hydrogen peroxide for deep desulfurization under moderate conditions has shown very good results. In this method, the S-removal of DBT-containing model oil in IL, BMIM$^+$BF$_4^-$, could reach 99.0% at 70 °C for 3 h, which was the remarkable advantage of this process over the desulfurization by mere solvent extraction with IL or catalytic oxidation without IL. Moreover, the catalysts hardly dissolved in oil. The catalytic oxidation system containing Na$_2$MoO$_4$·2H$_2$O, H$_2$O$_2$ and BMIM$^+$BF$_4^-$ could be recycled five times without a significant decrease in activity and oxidized sulfur could be reclaimed by centrifugation. However, studies with the "real" diesel oil are yet to perform.

In the extraction process of a refinery stream with ILs, regeneration and recycling of the S-loaded IL will be essential, and several suggestions for separation of sulfur from ILs have appeared in the literature. Depending on the properties of the IL employed, a hydrophilic, moisture-insensitive IL can be dissolved in water, with sulfur compounds separating or precipitating. As most ILs have negligible vapor pressure, water can be removed by evaporation under a stream of nitrogen at 110 °C. This procedure requires a large amount of heat for water evaporation, and would be difficult to integrate in a continuous process on a multi-ton scale. Some efficient techniques for separating water and ILs need further investigation. From a hydrophobic or moisture-sensitive IL, sulfur compounds can be removed by distillation. The distillation again requires heat, and it is only feasible with low-boiling sulfur compounds (e.g., thiophene). With high-boiling sulfur compounds such as DBT or 4,6-DMDBT, distillation is less effective. The possibility of using re-extraction with scCO$_2$ needs detailed investigation about the applicability of the process on a multi-ton scale considering the large scale usage of energy. Electrochemical approaches to hydrodesulfurization recovering the hydrocarbon-portion of the molecules may also be considered. The worldwide chemical industry is working hard toward the efficient production of ILs, which will develop a simple, safe, reproducible and

environmentally benign post-treatment to the traditional HDS for ultra-deep desulfurization.

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